

CO₂ desorption from activated DEA using membrane contactor with vacuum regeneration technology

Nidia Intan Listiyana, Yeni Rahmawati*, Siti Nurkhamidah, Hafan Rofiq Syahnur, and Yusuf Zaelana

Chemical Engineering Department, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember Surabaya, Kampus ITS Keputih, Sukolilo, Surabaya

Abstract Carbondioxide (CO₂) content in natural gas must be removed because it inhibits liquefaction process of natural gas. CO₂ gas separation technology using membrane contactor has been developed, however solvent regeneration using membrane contactors are still rare because it requires a larger energy. The regeneration process by using membrane vacuum technology was put forward to reduce the regeneration energy consumption. In this work, arginine, piperazine (PZ), and potassium carbonate (K₂CO₃) as activators were added into diethanolamine (DEA) solution to form aqueous solutions of activated DEA. The experiment of CO₂ desorption from activated DEA was carried out in hollow fibre membrane contactor (HFMC). The solvent with rich CO₂ at 30-70°C was flowed in the lumen of the hydrophobic polypropylene HFMC, and the shell side was maintained at a reduced pressure by a vacuum pump at 20 kPa. The effect of solvent temperature and activators were investigated to get CO₂ desorption flux and regeneration efficiency. Experimental result shows that increasing of solvent temperature could enhance CO₂ desorption flux and regeneration efficiency. Instead of that, the activated DEA also give better result compared with non-activated DEA. Among three activators, K₂CO₃ give the best result for desorption flux and regeneration efficiency.

1 Introduction

Natural gas is the third largest natural resource in the world after coal and petroleum. Natural gas processing industry is an important sector in supplying energy or fuel. Compare to traditional coal, combustion of natural gas only produce half of CO₂ and 33% compared to oil. The high potential of natural gas resources increasing efforts to develop more effective and efficient processing in terms of operations, economics, and environment.

In natural gas processing processes where the main component is a hydrocarbon must be separated from impurity components such as CO₂, H₂S, N₂, and water vapor as they may affect the quality and processing of natural gas further. CO₂ as an impurity in natural gas can cause corrosion of piping and equipment, otherwise CO₂ is able to decrease the heating value of natural gas [15]. In the process of Liquefied Natural Gas (LNG) processing, CO₂ content must be removed to prevent icing during natural gas liquefaction process, because the process runs at very low temperatures of -161 °C while the freezing point of CO₂ around -78.4°C [14].

Contacting membrane technology is an improvement of CO₂ removal technology combining gas absorption process with solvent and membrane technology in order

to set the pattern of flow rate for avoiding flooding, loading, foaming, and entrainment that usually occurs in conventional absorption technology. The advantages of membrane contactors compared to conventional absorption technology are high surface area per unit contactor volume, independent control of gas and liquid flow rates without any operational problems, small size device, known gas-liquid interfacial area, modular and being easy to scale up or down. [9].

Feron et al. [3] conducted a study in CO₂ gas separation process using a conventional hybrid membrane contactors for absorption and regeneration column for the desorption process with amine solvents. They compared the performance of the membrane absorber and packed column absorber. The results showed that performance CO₂ absorption in membrane absorber was same compared to conventional absorber column, but the size of absorber can be reduced ten-times using a membrane absorber. Hollow fiber gas-liquid membrane contactor as CO₂ absorber has been comprehensively studied by several researchers. Those experimental and theoretical result have been reported [2, 8, 12, 16].

Research and study about membrane technology for CO₂ removal is increasing. However, it is important to

* Corresponding author: yeni_18des@yahoo.com

notice that there are only a few research on CO₂ desorption through membrane contactors. The solvent regeneration operation unit requires greater energy, it was estimated that the energy requirement for CO₂ desorption reaches 15-30% of coal burning power plant production [1]. Therefore, it is necessary to do a lot of research on CO₂ desorption through membrane contactors with low operating costs and capital costs.

CO₂ desorption using membrane contactor can be done by vacuum or sweep gas method. Kosaraju et al. [9] conducted a study using polypropylene membrane contactor by combining CO₂ absorption and desorption process. They performed a process of CO₂ absorption and desorption on two continuously separated membrane contactor modules for 55 days using novel solvent and helium gas as stripping gas. The result showed that the performance of the membrane contactor was stable and the PP membrane material was not wetted by the solvent.

Mansourizadeh and Ismail [13] also conducted a similar study using a polivinildenefluorid membrane material (PVDF) with two separate modules for absorption and desorption using water as solvent and N₂ as stripping gas. The results showed that the temperature of the solvent also affects the CO₂ desorption efficiency, which higher by increasing the temperature of the solvent. While increasing the flow rate of solvent could decrease desorption flux.

CO₂ desorption for solvent regeneration using membrane contactor vacuum was performed by Fang et al. [1]. MEA with a lot of CO₂ content was flowing to the membrane lumen and membrane shell was pressed by vacuum pump. Low temperature steam flowed in shell side of membrane module which acts as sweep gas improve desorption performance in order to avoid liquid loss. The results showed that CO₂ desorption using membrane vacuum technology represented good performance and reduce energy consumption because it was operated at low temperatures.

Proper choice of solvent plays an important role in determining the performance of gas liquid membrane contactor for CO₂ regeneration. Various solvent such as pure water, aqueous solution of NaOH, KOH, alkanolamines and ammonia have been studied experimentally. Many studies of CO₂ absorption-desorption with membrane contactors still use a single solvent without any mix of activators, such as Khaisri et al. [7], Lv, et al. [10], and Fang, et al. [1] who use MEA as a solvent. Then Mansourizadeh and Ismail [13], Karoor and Sirkar [6], used water, and several other studies using NaOH, MDEA (methildiethanolamine), or DEA [16]. Some amines have some advantages, such as primary and secondary group amines whose reaction rate are faster than the tertiary amine group, but the tertiary amine group has a higher absorption capacity than the primary and secondary amines [11].

Recently, the blended alkanolamines or addition of activator have been presented by several researches in order to improve the performance of CO₂ separation. Yeon, et al. [18] conducted CO₂ separation using membrane contactor for absorption and stripper column for solvent regeneration by mixing PZ and triethanolamine (TEA) as solvent. The results showed

that TEA with low absorption capacity could be increased by addition of PZ. TEA is a tertiary amine with high volatility can prevent hollow fiber membrane from wetting phenomenon. Then Hedayat, et al. [4] conducted a study for the absorption of CO₂ and H₂S gases from natural gas using membrane contactors by comparing MDEA solvents mixed with MEA and MDEA with DEA. The results showed that the addition of MEA into the MDEA improved the efficiency of CO₂ separation, while the addition of DEA did not give significant results. Rahim, et al. [15] used four different amino acid salt (AAS) solvents and compared with aqueous solutions of MEA and NaOH. The results showed that AAS improved the performance of CO₂ absorption-desorption when compared with MEA.

In this work, arginine, PZ, and K₂CO₃ as activators were added into diethanolamine (DEA) solution to form aqueous solutions of activated DEA. The activated mechanism were presented to explain the activation phenomenon. The experiment of CO₂ desorption was carried out in polypropylene hollow fiber membrane contactor (HFMC). The use of such amine solvent mixture is expected to increase CO₂ regeneration efficiency and reduce the cost of solvent usage so that it is more economical.

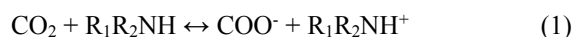
2 Theory

2.1. Characteristic of Activators

Three activators, arginine, PZ, and K₂CO₃ were chosen to form the three DEA-activated aqueous solutions : DEA-Arginine-H₂O, DEA-PZ-H₂O, and DEA-K₂CO₃-H₂O. Arginine is a primary amino acid that can form alkaline amino acids salt. This amino acid salt is predicted as one of the proper substances in CO₂ absorption because it has functional groups that are identical with alkanolamines. While PZ has a special molecular structure, the cyclic structure of a symmetrical diamino. PZ is an efficient and highly successful activator used for high CO₂ separation capacity in industrial processes. Then K₂CO₃ is alkaline salt which has a high CO₂ loading capacity and low heat of reaction. Therefore, it's to be a good activator for CO₂ absorption.

2.2 Reaction Mechanism

The mass transfer of CO₂ gas to the liquid phase is influenced by the diffusivity of the CO₂ into the solvent. If the pore is hydrophobic and membrane is not wetted, then it is assumed that the pore membrane is only fully filled by gas. Diffusion begins in the bulk gas phase by the diffusion of the boundary layer and the chemical reactions on the fluid-membrane surface. The reaction between a CO₂ and DEA is as follows :



Where R₁R₂NH is the primary or the secondary amine. The formation of carbamate proceeds as follows :

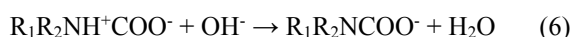
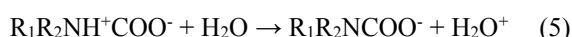
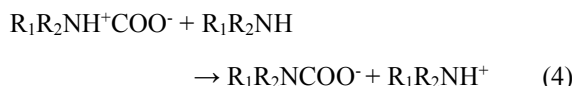
- Formation of zwitterion (intermediate reaction)



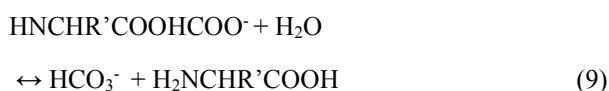
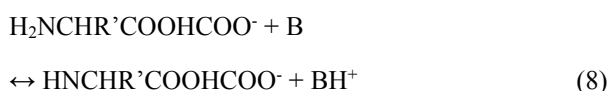
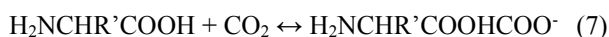
- Removal of the proton by a base B



Where the base B, could be the amine itself, water molecules, or hydroxyl ions that reacted with DEA solution. The corresponding reactions are as follows :



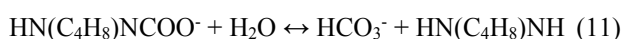
If there is an activator, the reaction that occurred not only CO₂-DEA but also CO₂-activator take place in the system. Here is the reaction between DEA-Arginine-H₂O with CO₂ :



For the system DEA-PZ-H₂O, will give different reactions which will directly form carbamic ions without going through intermediate reactions, as follows :



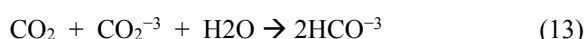
Then the carbamate will convert CO₂ into bicarbonate ion and PZ will regenerate as Eq. (11)



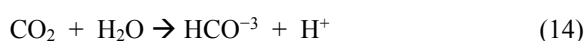
The overall reaction for the absorption of CO₂ using DEA-K₂CO₃-H₂O is described by reaction below :



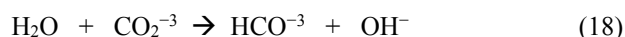
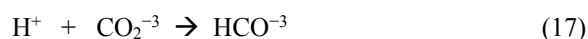
Since potassium carbonate and bicarbonate are strong electrolytes, it can be assumed that the metal is present only in the form of K⁺ ions and Eq. (12) can be represented as :



Reaction (13) proceeds according to the following sequence of elementary steps :



Reactions (14) and (15) are both followed by subsequent instantaneous reactions as follows :



The reaction sequence (14), (16) and (17) are known as the acidic mechanism. The contribution of the acidic mechanism to the overall rate is negligible unless the pH of the liquid solution is very low. Almost all cases of industrial absorption is held at high pH (generally, pH > 8) and as such the acidic mechanism can be neglected. Therefore, reaction (15) is the rate controlling step for absorption of CO₂ into potassium carbonate solution as reactions (16) and (18) are instantaneous reactions.

2.3. Data Analysis

In this study, CO₂ desorption flux (J_{CO₂}) and CO₂ loading (α) were used to analyze the CO₂ desorption performance. They can be expressed by the following equations :

$$J_{\text{CO}_2} = \frac{(C_{in} - C_{out}) \times Q_l}{A} \quad (19)$$

$$\alpha = \frac{\text{mole}(\text{CO}_2)}{\text{mole}(\text{solvent})} = \left[\frac{(V_{\text{gas}} - V_{\text{HCl}})(P)(273\text{K})}{(101325\text{Pa})(T)(22,4\text{L/mole})} \right] \frac{1}{C_1 V_1} \quad (20)$$

C_{in} and C_{out} are the liquid phase inlet and outlet CO₂ concentration. Q_l is volumetric flow rate of solvent. A represent the liquid-gas contact area in the membrane module.

CO₂ concentration in the aqueous solution which written in Eq.20 was determined by the apparatus adapted from Chittick CO₂ analyzer apparatus [15]. From Eq.20, V_{gas} is volume of displaced solution in the manometer tube (mL), V_{HCl} is volume of titrant (mL), P is pressure (Pa), T is room temperature (K), C₁ is solution concentration (mol/L), and V₁ is sample volume (mL).

Regeneration efficiency was calculated to evaluate the regeneration performance of rich solvent by using membrane vacuum regeneration technology in this study. Regeneration efficiency is defined by the ratio of amount of CO₂-rich solution, which can be calculated by the following equation :

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (21)$$

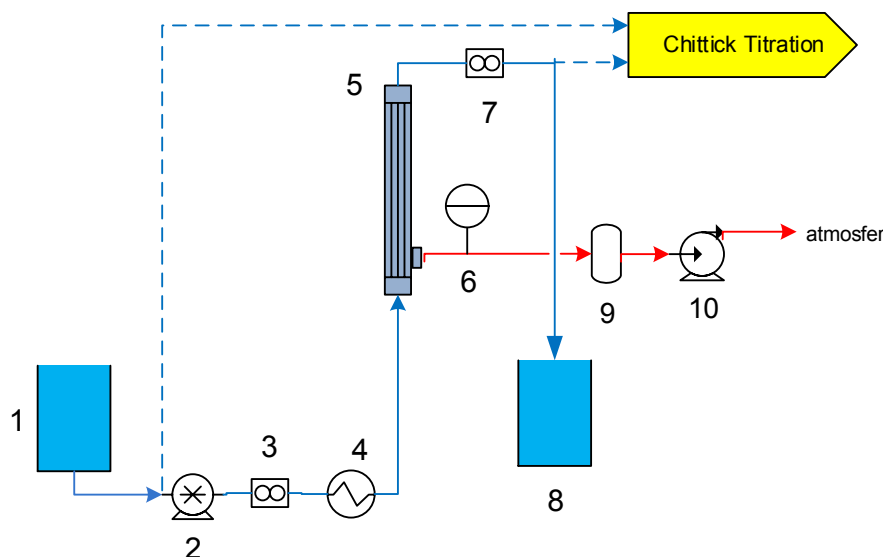


Fig. 1. Experimental setup for CO₂ desorption. 1. Rich solvent tank; 2. Liquid pump; 3. Rich solvent flow meter; 4. Heater; 5. Membrane contactor; 6. Pressure gauge; 7. Lean solvent flow meter; 8. Lean solvent tank; 9. Buffering tube; 10. Vacuum pump

3 Experimental

3.1. Material

In this experiment, the material of membrane is a hydrophobic polypropylene membrane from GDP Filter Indonesia membrane industry with its characteristics shown in Table 1.

Table 1. Specification of polypropylene hollow fiber membrane

Parameter	Specification
Inside Diameter (mm)	0,35
Outside Diameter (mm)	0,5
Pore Diameter (µm)	0,2
Fiber Length (mm)	100
Number of fibers	3302
Membrane porosity (%)	65
Membrane tortuosity	2,3669
Membrane area (m ²)	0,0413

Solvent used is diethanolamine (DEA) were obtained from PT. Pertamina, Balikpapan, Indonesia. CO₂ gas cylinder with 40% volume and 60% volume N₂ balance purchased from PT. Aneka Gas, Sidoarjo, Indonesia. PZ was purchased from Shenzen Lodi Chemical Co.Ttd. While Arginine and K₂CO₃ were purchased from Sigma Aldrich Chemical Co. Ltd. In this study, concentration of solvent used was 30% volume with 1% vol. activator and 69% vol. H₂O.

3.2. Experimental Procedure

The experimental set-up for CO₂ desorption was shown in Fig.1. The solvent containing CO₂ gas from the absorber was prepared with CO₂ loading 0,22 mole/mole and was added into the tank (1), then flows into coil heater water bath (3) by diaphragm pump (2) before entering the desorber (4). This aim of heating was to reduce the solubility of CO₂ in the solvent so CO₂ can easily released from the solvent. The temperature range in this study was 30-70°C. After pre-heating, CO₂-rich solution continuously pumped into tube side of the hollow fiber membrane contactor with flow rate 100 mL/min. Liquid flow rate was controlled by liquid flow meter. During the regeneration operation, shell side of the module membrane contactor was kept at 20 kPa absolute by vacuum pump (8) that controlled with pressure gauge (5). Buffering tube (7) used to capture water vapor from output gas desorber before entering vacuum pump. The dissolved CO₂ in the solvent in the tube section diffused outward through the membrane pores which was driven by the vacuum pressure. Finally, CO₂ gas enriched and could be collected from the vacuum pump. The solvent exit desorber is called lean solvent (6) then analyzed with chittic titration.

4 Result and Discussion

4.1. Effect of Temperature on Desorption Flux

The effect of rich absorbent temperature on CO₂ desorption flux was shown in Fig.2.

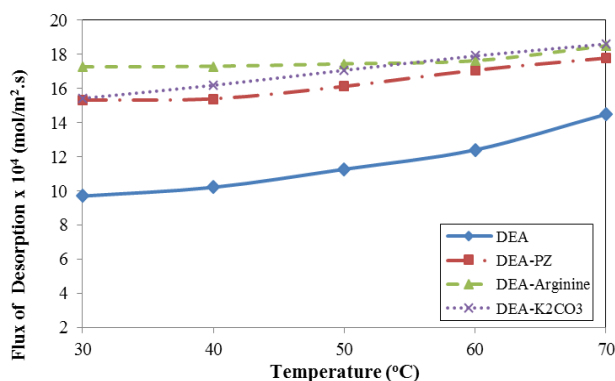


Fig.2 Effect of liquid temperature on CO₂ desorption flux ($Q_1 = 100$ mL/min ; $P = 20$ kPa ; $C_{DEA} = 30\%$ vol. ; $C_{activator} = 1\%$ vol. ; α – rich solvent = 0,22 mol/mol)

It is shown that desorption flux increased when temperature of rich absorbent was increased. This phenomenon due to the solubility of CO₂ decreases very rapidly with the increasing of temperature. The increasing of absorbent's temperature increased the CO₂ equilibrium partial pressure; thus also increased the driving force of CO₂ desorption. Moreover, the reversible reaction equilibrium constant and CO₂ diffusivity in DEA solution increased with the solution temperature, which leads to the improvement of desorption performance as well. The effect of temperature on these factor was studied by several researchers through experiments and mathematical modeling also which reported the similar result [2, 5, 13, 15, 17,]. However, the membrane stability must be considered against high temperature operation due to susceptibility to chemical and thermal effect.

4.2. Effect of Temperature on CO₂ Loading of Lean Absorbent

The effect of the rich absorbent temperature on CO₂ loading was shown by Fig.3.

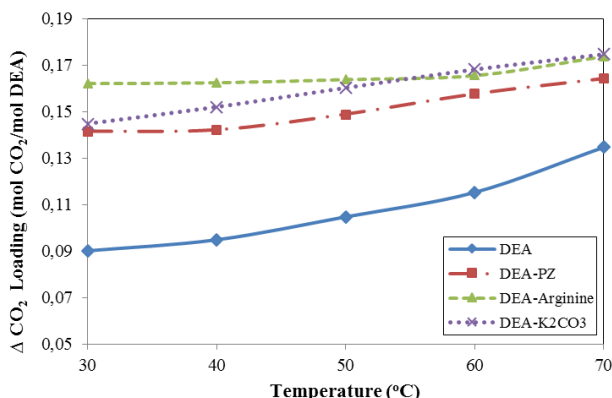


Fig.3 Effect of liquid temperature on CO₂ loading ($Q_1 = 100$ mL/min ; $P = 20$ kPa ; $C_{DEA} = 30\%$ vol. ; $C_{activator} = 1\%$ vol. ; α – rich solvent = 0,22 mol/mol)

It is shown for each type of absorbent with the same CO₂ loading of rich amine value of 0.22 mol CO₂/mol DEA, CO₂ loading of lean absorbent decrease with increasing absorbent temperature. In other words, the

higher the temperature of the solvent, the more the amount of CO₂ released from the solvent and cause the amount of CO₂ contained in the lean amine solvent decreases. The parameter α is the content of CO₂ dissolved in the solution from both physical and chemical absorption. It is expressed as moles of CO₂ per mole of amine.

4.3. Effect of Activator on Desorption Efficiency

Value of desorption efficiency expresses the performance of CO₂ regeneration process. It is shown in Fig.4.

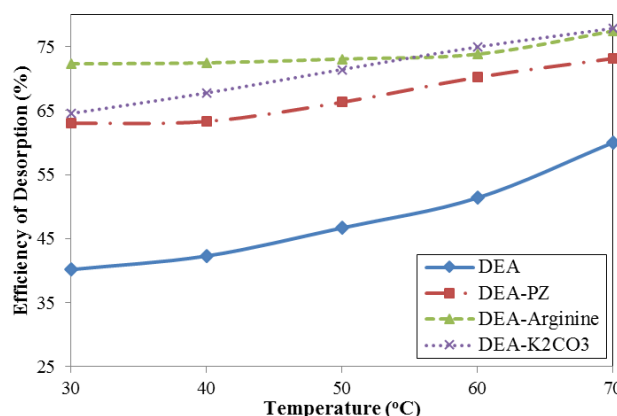


Fig.4 Effect of liquid temperature on efficiency of desorption ($Q_1 = 100$ mL/min ; $P = 20$ kPa ; $C_{DEA} = 30\%$ vol. ; $C_{activator} = 1\%$ vol. ; α – rich solvent = 0,22 mol/mol)

At constant liquid flow rate of 100 mL/min and pressure of 20 kPa, efficiency increased with the increase of liquid temperature for any given absorbent. It was caused by the chemical reaction kinetics and CO₂ diffusion coefficient. At higher temperatures, the dissolved CO₂ concentration in the solvent moved to the low-concentration side and increased CO₂ mass transfer driving force. Many researchers had conducted research about the effects of temperature on desorption through experiments and mathematical modeling which reported similar results [2, 13, 15, 17].

The experimental results showed that the DEA-K₂CO₃ solvent was the best desorption efficiency. The K₂CO₃ solution has an ionic structure, and bicarbonate and carbonate ions were formed by reacting with the CO₂ in the solution. Therefore, bicarbonate and carbamate ions in reaction was unstable which caused the flux of desorption increase and the partial CO₂ equilibrium pressure higher.

5. Conclusion

Desorption of CO₂ from activated DEA using membrane contactor with vacuum regeneration technology was achieved in polypropylene hollow fiber membrane contactor using membrane vacuum regeneration technology. Arginine, PZ, and K₂CO₃ as activators were added into DEA solution to form aqueous solutions of activated DEA. The three activator

was compared at any temperature operation and 20 kPa pressure vacuum in order to determine the effect of temperature and chemical structures of absorbent on vacuum regeneration performance.

The experimental results showed that the increasing of solvent temperature could enhance the CO₂ desorption flux and reduce CO₂ loading from rich solvent. Among three solvent in this study, the best solvent for desorption of CO₂ is DEA-K₂CO₃ with a ratio of separation efficiency 1.3 times higher than that of unactivated solvent. Flux of desorption with DEA unactivated at 70°C was 14.49 x 10⁻⁴ mol/m².min, while DEA-K₂CO₃ was 18.62 x 10⁻⁴ mol/m².min. Therefore, the best performance for CO₂ desorption in this study is using K₂CO₃ as activator with efficiency of 77.83%.

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