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Effect of Activated Alkanolamine for CO_2 Absorption using Hollow Fiber Membrane Contactor

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Abstract. Hollow Fiber Membrane Contactor (HFMC) technology has been widely developed as an alternative technology to separate CO_2 gas. HFMC technology combines gas absorption process with absorbent and membrane technology. Membrane contactor technology has advantages than conventional technology such as larger gas-liquid contact area, smaller equipment, modularity, and gas-liquid flow rates adjusted independently. In this research, the CO_2 absorption experiments was conducted for absorption process at 30°C temperature and various gas flow rate from 200 - 600 mL/min, feed gas of CO_2 20%vol. flowed into shell side and the absorbents flowed in tube side of membrane contactor. Piperazine (PZ) and monosodium glutamate (MSG) as activators with 1%w/w concentration, added into methyldiethanolamine (MDEA) 30% w/w solution to form aqueous solutions of activated MDEA. The membrane material used in this experiment was hydrophobic polypropylene membrane. The effect of liquid flow rate and various activators used to get CO_2 absorption flux and CO_2 removal in HFMC. The results showed that the best of CO_2 absorption process using activated alkanolamine was MDEA-PZ, where the highest flux value was 5.5×10^{-4} mole/m^2.s and CO_2 removal reached 96.9% at a gas flow rate of 600mL/min.

1. Introduction

Indonesia is a developing country with high population, the world's fourth most populous nation. With a large population, there are many jobs will be needed to support Indonesia's economic growth. The industry has been the fastest growing sector of the Indonesian economy since the late sixties. As the industry grows in Indonesia, it turns out give a bad impact on the environment. Waste gas from industry can cause air pollution. The content in industrial waste gas is CO_2, SOx, NOx, CO, and hydrocarbon with percentage composition as follows: 30% of CO_2 gas, 27% of CO gas, 25% of hydrocarbon gas, 10% of NOx gas, 9% of SOx gas, and 8% of particulate dust.

In recent years, CO_2 has attracted attentions because of increasing the emission of CO_2 as a determining greenhouse gas into the atmosphere. Fossil fuels, including petroleum, coal and natural gas are all non-renewable resources and contain high percentages of carbon. They are still the major sources of energy throughout the world. The emission of CO_2 into the atmosphere causing as the main reason for climate change effects including global warming, changes in sea levels, extreme hot summers and cold winters, and agricultural problems [1].

Several technologies has been developed to remove CO_2 from the gas streams, such as physical and chemical absorption with liquids especially aqueous amines solutions, solid adsorption, cryogenic distillation, membrane technology, and most recently membrane contactors [2]. However, in conventional absorption using packed column, CO_2 absorption is not efficient enough due to the flow rate of gas and absorbent has not yet separately each other so that can generate entrainment, flooding, loading and foaming [3]. On the other hand, cryogenic distillation needs a very huge installation and a very expensive operational cost. While adsorption process has a poor affectivities in CO_2 separation by using solid adsorbent [2].

In the recent time, conventional column absorption still becomes the best equipment despite needs great energy and big installation of equipment that depends on the other operational units. These shortages encourage some experiments towards the new contactor technology was expected to resolve the above problems.

Membrane contactor is a new method in contacting absorbent to CO_2 by using hollow fiber membrane contactor. This method has several advantages including wider liquid gas contact space, smaller tool, its modular characteristic which is easy to scale up , and the flow rate of gas and liquid which independently easy to be arranged; thus it can solve the operational issue [4]. Research on removing CO_2 by membrane contactors from natural gas has been carried out since 1980. Qi and Cussler [5] fabricated the first membrane for gas absorption process to remove CO_2 from a gas stream.

Typical membranes nowadays are prepared from polyethylene (PE), polypropylene (PP), polyvinyldenefluoride (PVDF), polytetrafluorethylene (PTFE) and polysulfone (PS) in gas-liquid contacting process. Currently hydrophobic membranes are widely used due to a larger contact area than the hydrophilic membranes. Among these, PTFE together with amine-based solutions are of high hydrophobicity, good mechanical properties and chemical stability [6]. Proper choice of absorbent plays an important role in determining the performance of gas liquid membrane contactor for CO_2 absorption. Various absorbent such as pure water, aqueous solution of NaOH, KOH, alkanolamines and ammonia have been studied experimentally. In this work PP membrane was used because it is more affordable and already have tested high temperature stability up to 100^0 C. Besides, the PP membrane already has tested for wetting phenomenon using alkanolamines solvents.

Many studies of CO_2 absorption-desorption with membrane contactors still use a single solvent without any mix of activators, such as Fang, et al. [7], Khaisri et al. [8] and Lv, et al. [9] who used MEA as a solvent. Then Mansourizadeh and Ismail [10], Karoor and Sirkar [11], Rahmawati et al. [12] used water, and several other studies using NaOH, MDEA, or DEA.

Recently, the blended alkanolamines or addition of activators have been done by a number of researches in order to improve the performance of CO_2 absorption. One of the previous studies, Yeon, et al. [13] was absorption using membrane contactor for absorber and desorber columns for regeneration of absorbents by mixing PZ and triethanolamine (TEA) as absorbents. The results showed that TEA with low absorption capacity can be increased by adding piperazine. TEA is a tertiary amine with high volatility that can help hollow fiber membranes to be maintained from the phenomenon of wetting.

In this work, PZ and mono sodium glutamate (MSG) as activators used into methyldiethanolamine (MDEA) solution to form aqueous solutions of activated MDEA. The activated mechanism were presented to explain the activation phenomenon. The experiment of CO_2 absorption was carried out in polypropylene hollow fiber membrane contactor (HFMC). The use of such amine solvent mixture going to increase CO_2 separation efficiency and reduce the cost of solvent usage so that it is more economical.

2. Materials and Methods

2.1. Materials

In this experiment, the material of membrane is a hydrophobic polypropylene membrane purchased 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)	300
Number of fibers	6500
Membrane porosity (%)	65
Membrane area (m^2)	1.3943

Absorbent used was MDEA, CO_2 gas cylinder with 20% volume and 80% volume N_2 balance, and activator used Piperazine (PZ) and Monosodium glutamate (MSG). In this study, concentration of absorbent used was 30% wt. with 1% wt. activator.

2.2. Apparatus and procedure

The experimental set-up for CO_2 absorption shown in Figure 1. On the absorption process, feed gas with 20% of CO_2 (*balance* N_2) was flowed with various flow rates for about 200-600 mL/min through the shell side of membrane contactor which measured using gas flow meter**.** The solvents was flowed using a diaphragm pump into the tube side of membrane contactor at flow rate of 100 mL/min which measured using liquid flow meter. Flow rate of gas and liquid was counter-current. The outlet gas from the membrane shell also called sales gas, while the outlet absorbent from the membrane tube also called rich amine.

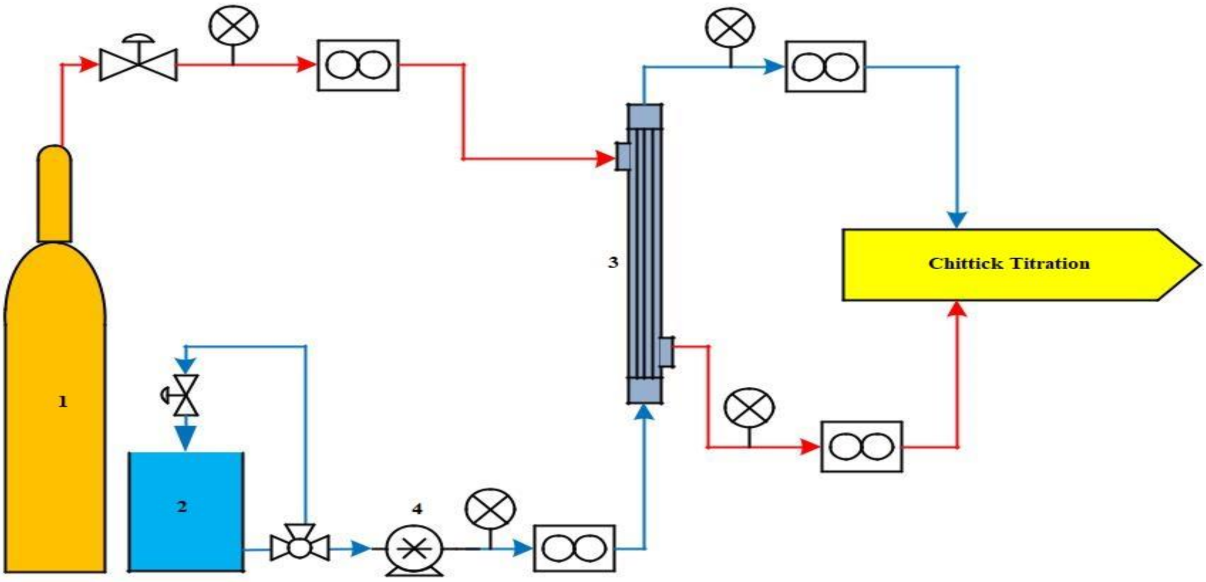

Figure 1. Experimental setup for CO_2 absorption. 1) Feed gas tube; 2) solvent tank; 3) HFMC; 4) liquid pump

CO_2 concentration in the solvent was analysed using chittick titration with 1 M HCl and indicator of methyl orange. While sales gas sample was taken and being bubbled into 1 M NaOH. Flow rate of sales gas bubbled into NaOH was depend on the value stated in the flow meter of sales gas and it was bubbled for 10 minutes. NaOH contained CO_2 titrated using 1 M HCl and assisted with pp and methyl orange indicators.

2.3. Data analysis

CO_2 concentration in the gas and liquid phase at inlet and outlet of membrane contactor module measured by chittick titration. Amount of CO_2 in gas phase use to calculated flux absorption and CO_2 removal with equation as follow:

$$J_{CO_2} = \frac{Q_{im}\ x\ C_{in} - Q_{out}\ x\ C_{out}}{A} \tag{1}$$

Where J_{CO2} is the CO_2 flux (mole/m^2.s), Q_{in} and Q_{out} are input and output of gas flow rate (mL/min), C_{in} and C_{out} are CO_2 concentration in feed gas and sales gas (mole/m^3), and A is inner surface area of the hollow fiber membranes (m^2). And the CO_2 removal rate is an important measure for absorption performance of the system and absorbents is calculated as follow:

$$\eta = \frac{Q_{in} \times C_{in} - Q_{out} \times C_{out}}{Q_{in}\ x\ C_{in}} x100\% \tag{2}$$

CO2 concentration in the absorbent as CO_2 loading it is determined by equation from Zhang, et al. [1]:

$$\alpha = \frac{mol(CO_2)}{mol(solvent)} = \left[\frac{\frac{(V_{gas} - V_{HCl})(P)(273K)}{(101325\,Pa)(T)(22{,}4L/mol)}}{C_1V_1} \right] \tag{3}$$

V_{gas} is volume change of saturated NaCl which is shown by measuring burette (mL), V_{HCl} is HCl volume that is required until the solvent sample changes in color (mL) ; from yellow to red, P is operational pressure (Pa), T is operational temperature (K), C1 is solvent concentrate (mole/L), and V_1 is the volume of solvent sample (mL).

3. Results and Discussion

3.1. Effect of feed gas flowrate on CO_2 absorption flux

The effect of feed gas flowrate on CO_2 absorption flux shown in Figure 2. The result shows that increasing of feed gas flowrate could enhance the CO_2 absorption flux for three kind of absorbents used. This can help explain to the reduction in gas boundary layer thickness due to the increase in gas flowrate. CO_2 mass transfer resistance will decrease due to reduction of gas boundary layer thickness and make it easier for CO_2 gas to diffuse from the bulk gas phase to the liquid phase [12]. Absorption occurs because of concentration difference between the gas phase and liquid phase. The feed of gas has higher CO_2 concentration will diffuse through the membrane pore and then dissolved into absorbent [14].

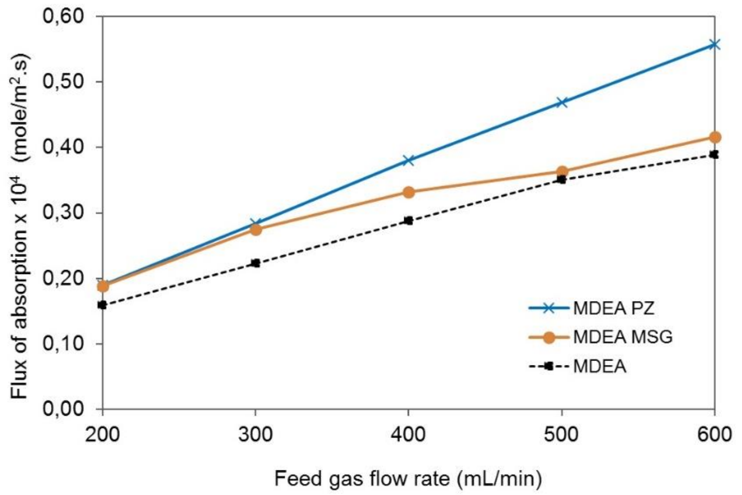

Figure 2. Effect of feed gas flowrate on CO_2 absorption flux in various solvent (CO_2: 20% vol, Q_{liq}= 100 mL/min)

Figure 2 shows that for the same operation conditions, the flux absorption with the MDEA, MDEA–MSG and MDEA–PZ solvents could arrive at the highest values of 3.8 x 10^{-5} mole.m-^{2}.s^{-1}; 4.1 x 10^{-5} mole.m-^{2}.s^{-1} and 5.5 x 10^{-5} mole.m-^{2}.s^{-1} respectively. The absorption flux of the MDEA-activated solutions are evidently better than that of the non-activated MDEA solution. Activators PZ and MSG, despite a little amount in the solutions, can effectively enhance absorption flux of membrane gas absorption. The activation of PZ is higher than that of MSG. It reveals that PZ is an efficient activator in membrane gas absorption for CO_2. PZ has a special molecular structure in which a symmetrical diamino cyclic structure exists. The symmetrical structure make PZ can easily binding the CO_2 molecule from absorbent.

3.2. Effect of Feed Gas Flowrate on CO_2 Removal

The effect of feed gas flowrate on CO_2 removal shown in Figure 3. Figure 3 shows that CO_2 removal decreased with the increase of feed gas flowrate for any given absorbent. At higher gas flowrate, the residence time of feed gas in the membrane contactor was reduced. Short residence time of feed gas in the membrane module will accelerate contact time between the gas and membrane surface and reduce the amount of diffused CO_2 from gas phase through the membrane pore to the liquid phase [15].

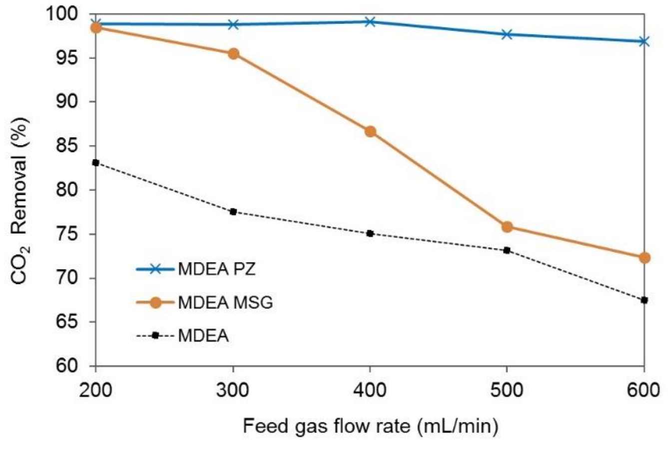

Figure 3. Effect of feed gas flow rate on CO_2 removal in various solvent (CO_2: 20% vol, Q_{liq}= 100 mL/min)

For the same operation conditions, the CO_2 removal with the MDEA, MDEA–MSG and MDEA–PZ solvents could arrive at the maximal values of 67%; 72%; and 96% respectively. PZ and MSG activators even in smaller amount can effectively increase CO_2 absorption performance in the membrane contactor.

3.3. Effect of Feed Gas Flowrate on CO_2 Loading

CO_2 *loading* defines as amount of mole CO_2 that is absorbed per mole absorbent. Figure 4 shows the effect of feed gas flowrate towards CO_2 *loading* on various kind of absorbent. The higher flowrate of the feed gas, the CO_2 *loading* value will be increase. The amount of CO_2 loading affected by the value of CO_2 absorption flux, the higher rate of CO_2 mass transfer from the surface of the membrane into the absorbent will shows the amount of CO_2 absorbed into the absorbent [9].

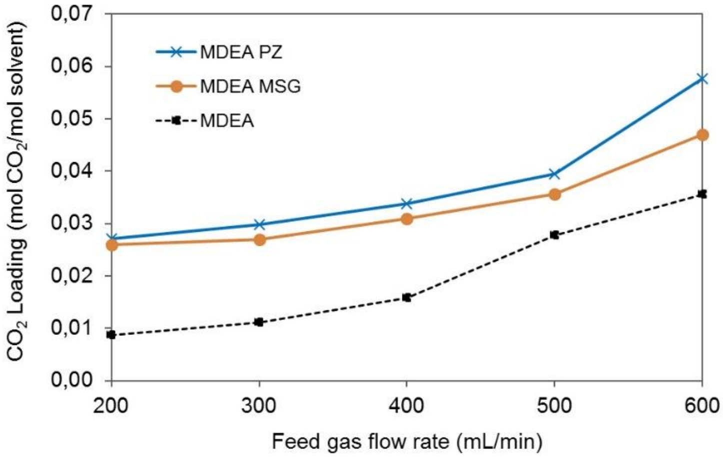

Figure 4. Effect of feed gas flow rate on CO_2 loading (CO_2: 20% vol, Q_{liq}= 100 mL/min)

Figure 4 shows that for the same operation conditions, the CO_2 loading with the MDEA, MDEA–MSG and MDEA–PZ solvents could arrive at the highest values of 0.036; 0.047; and 0.058 respectively. This value compared with the value of absorption flux of three various absorbent that MDEA-activated solutions are evidently better than that of the non-activated MDEA solution.

4. Conclusion

The best absorbent in the absorption process of CO_2 is activated MDEA. MDEA-PZ become the best absorbent for CO_2 absorption with comparison of separation efficiency 1.4 higher than unactivated MDEA absorbent. The highest absorption flux was obtained 5.5 x 10^{-5} mole.m-^{2}.s^{-1} with MDEA-PZ as absorbent and operation condition of gas flowrate 600 mL.min^{-1} and liquid flowrate 100 mL.min^{-1}. The highest CO_2 removal was 96% by utilizing MDEA-PZ solvent with operation condition of gas flowrate 200 mL.min^{-1} and liquid flowrate 100 mL.min^{-1}.

Acknowledgments

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