

# Flue gas carbon capture using hollow fiber membrane diffuser-separator

D Ariono<sup>1</sup>, A S Chandranegara<sup>1</sup>, S Widodo<sup>1,2</sup>, Khoiruddin<sup>1</sup>, I G Wenten<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

<sup>2</sup>PPPTMGB LEMIGAS, Balitbang KESDM, Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, Jakarta, 12230, Indonesia

Email: igw@che.itb.ac.id

**Abstract.** In this work, CO<sub>2</sub> removal from flue gas using membrane diffuser-separator was investigated. Hollow fiber polypropylene membrane was used as the diffuser while pure water was used as the absorbent. Separation performance of the membrane diffuser-separator as a function of CO<sub>2</sub> concentration (6-28%-vol.) and flow rate (gas: 0.8-1.55 L.min<sup>-1</sup> and liquid: 0.2-0.7 L.min<sup>-1</sup>) was investigated and optimized. It was found that CO<sub>2</sub> removal was significantly affected by CO<sub>2</sub> concentration in the feed gas. On the other hand, CO<sub>2</sub> flux was more influenced by flow rates of liquid and gas rather than concentration. The optimized CO<sub>2</sub> removal (64%) and flux ( $1 \times 10^{-4}$  mol.m<sup>-2</sup>.s<sup>-1</sup>) were obtained at the highest gas flow rate (1.55 L.min<sup>-1</sup>), the lowest liquid flow rate (0.2 L.min<sup>-1</sup>), and 6.2%-vol. of CO<sub>2</sub> concentration. Outlet gas of the membrane diffuser system tends to carry some water vapor, which is affected by gas and liquid flow rate. Meanwhile, in the steady-state operation of the separator, the gas bubbles generated by the membrane diffuser take a long time to be completely degassed from the liquid phase, thus a portion of gas stream was exiting separator through liquid outlet.

## 1. Introduction

Carbon Dioxide (CO<sub>2</sub>) is a major source of global warming phenomenon. One attempt to control the emission of greenhouse gas is by removing CO<sub>2</sub> from flue gas. On the other hand, the separation of CO<sub>2</sub> from the gas stream is an important step in some industrial processes and is needed for technical, economic, and environmental reasons. In the liquefied natural gas (LNG) industry, CO<sub>2</sub> must be separated to prevent several problems such as a freezing problem in low-temperature chillers, corrosion in the process equipment, reduction of the caloric value of gas flow, and a decrease of pipeline capacity [1].

Generally, CO<sub>2</sub> removal is performed by solvent absorption, solid adsorption, and membrane-based separation. Solvent-based separation is currently the well-established technology. It has high selectivity and capacity as well as simplicity in solvent regeneration [2,3]. However, solvent absorption which traditionally uses packed columns, has some disadvantages such as high regeneration energy as well as difficulty in obtaining an accurate estimate of the gas-liquid mass transfer area and a limited range of gas and liquid flow rates due to operational problems including flooding, loading, channeling, and foaming [4,5]. Membrane technology has been considered as the promising alternative for conventional technologies in various processes including separation, purification, chemical reaction, and contacting processes [6–17]. Membrane technology offers interesting features such as lower energy consumption, relatively low operating expenditure, smaller footprint, easy to scale-up, easy to operate, and more process intensive [18–21]. Recently, using membrane as a contactor of two streams has been widely studied [22–24]. The gas-liquid contacting process using hollow fiber membranes is a hybrid process that combines the advantages of conventional reactive absorption technology with membrane contactor processes. This process is



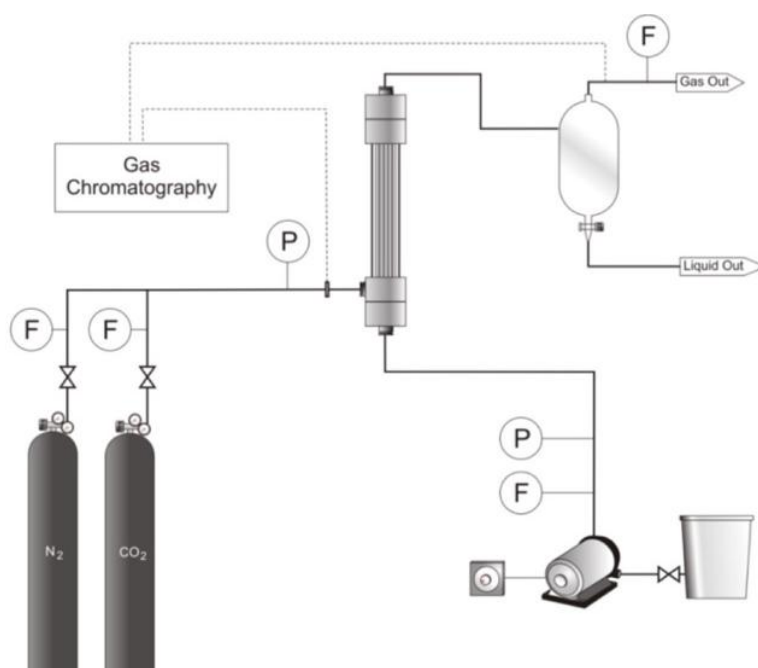
expected to be used as an alternative technology that has the potential to overcome operational problems encountered in conventional absorption processes.

Although much research has been done regarding the separation of CO<sub>2</sub> using hollow fiber membrane contactor, there is still little commercial plant found with such technology. This is associated with several drawbacks that hinder their commercialization [25–29]. According to Luis et al. [30], there are four main factors that need to be considered to make the contactor membrane a competitive technology against conventional contactor: solving membrane wetting phenomenon, fabricating a high durability and low cost membrane, selecting an appropriate and environmentally friendly solvent or absorbent, and investigating the influence of other component in the gas stream.

In this study, a new configuration of a membrane-based contacting process is proposed. A unique configuration, a series membrane diffuser–separator is used for CO<sub>2</sub> removal from flue gas. Hollow fiber membrane serves as a micro bubble generator resulting in a two-phase fluid. In this configuration, the mass transfer will occur on the bubble surface. This is different from the membrane contactor which keeps the inter phase area remained in the membrane pore. By filling the pore with gas it is expected that the membrane wetting does not occur and the CO<sub>2</sub> separation performance is expected to be stable in a long-term operation.

## 2. Materials and Method

CO<sub>2</sub> and N<sub>2</sub> gasses were obtained from PT BOC. Polypropylene membrane was supplied by GDP Filter Indonesia (average pore size: 0.04–0.05 µm). For all of the experiments, pure water was used as the solvent (absorbent).



**Figure 1.** Experimental set-up of hollow fiber membrane diffuser-separator

The equipment used in this research was a set of tools that can be divided into three main tools, namely the absorbent tank, diaphragm pump, membrane module, separator, and gas chromatography (GC Shimadzu). The CO<sub>2</sub>/N<sub>2</sub> gas mixture was passed to the membrane module via a dead-end shell, in which the lumen was continuously absorbed by water. The gas stream was dispersed in a micro bubble in the water stream, where the mass transfer occurred on the bubble surface. This two-phase flow was then separated through the gravity separator. To obtain the gas-liquid separation data, the gravity separator was operated under both closed and steady valve conditions with a 14 cm liquid height. The absorption experiments were conducted at room temperature and atmospheric pressure. Gas in and out

of the system was analyzed using GC after 10 minutes of operation. The equipment scheme used in the study is shown in Figure 1. Analysis of reactant and product samples was carried out with Gas Chromatograph GC-Shimadzu with Porapax column equipped with TCD system. Argon was used as carrier gas.

### 3. Results and Discussion

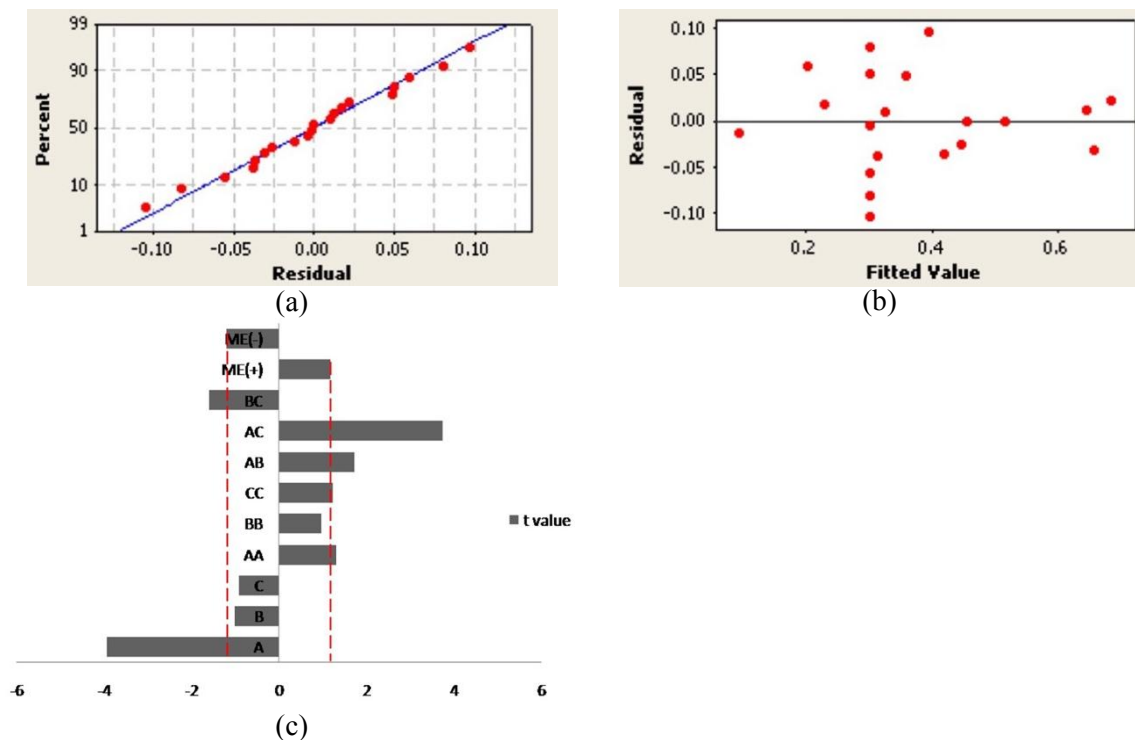
#### 3.1. Effect of operating parameters on CO<sub>2</sub> removal

Data on the effect of operating variables on CO<sub>2</sub> separation were obtained from the analysis of inlet gas and outlet gas in a closed separator system. In the absence of a liquid outflow, it was assumed that all the gas exit through the gas outlet and the absorbed CO<sub>2</sub> still remained in the liquid phase. Modeling using regression for the effect of CO<sub>2</sub> concentration, gas flow rate, and liquid flow rate on CO<sub>2</sub> separation resulted in the following equation:

$$Y_1 = 1.51757 - 0.05841(A) - 0.77880(B) - 0.63684(C) + 0.00047(A^2) + 0.31381(B^2) + 0.80335(C^2) + 0.01091(AB) + 0.03337(AC) - 0.42762(BC) \quad (1)$$

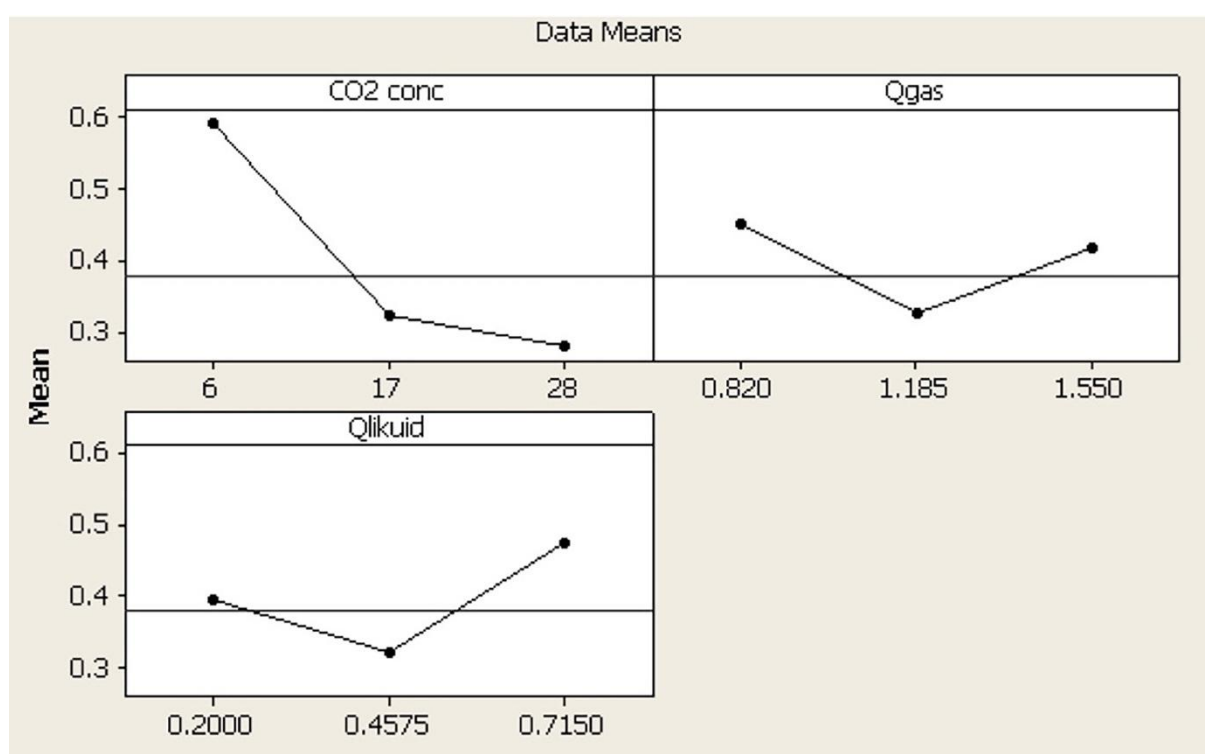
where  $Y_1$  is CO<sub>2</sub> separation (0-1),  $A$  is CO<sub>2</sub> concentration (%Volume),  $B$  is gas flow rate (L.min<sup>-1</sup>), and  $C$  is liquid flow rate (L.min<sup>-1</sup>)

The validity of the equation was evaluated by comparing actual data distribution to the model shown in Figure 2. With  $R^2 = 89.81\%$ , the equation was able to represent the actual data distribution of the experiment. Looking at the normal probability plot curve in Figure 2, the actual distribution of the data is close to the normal distribution line which indicates that the model is satisfied. Plots of residual versus fitted value does not show the tendency of a particular pattern.



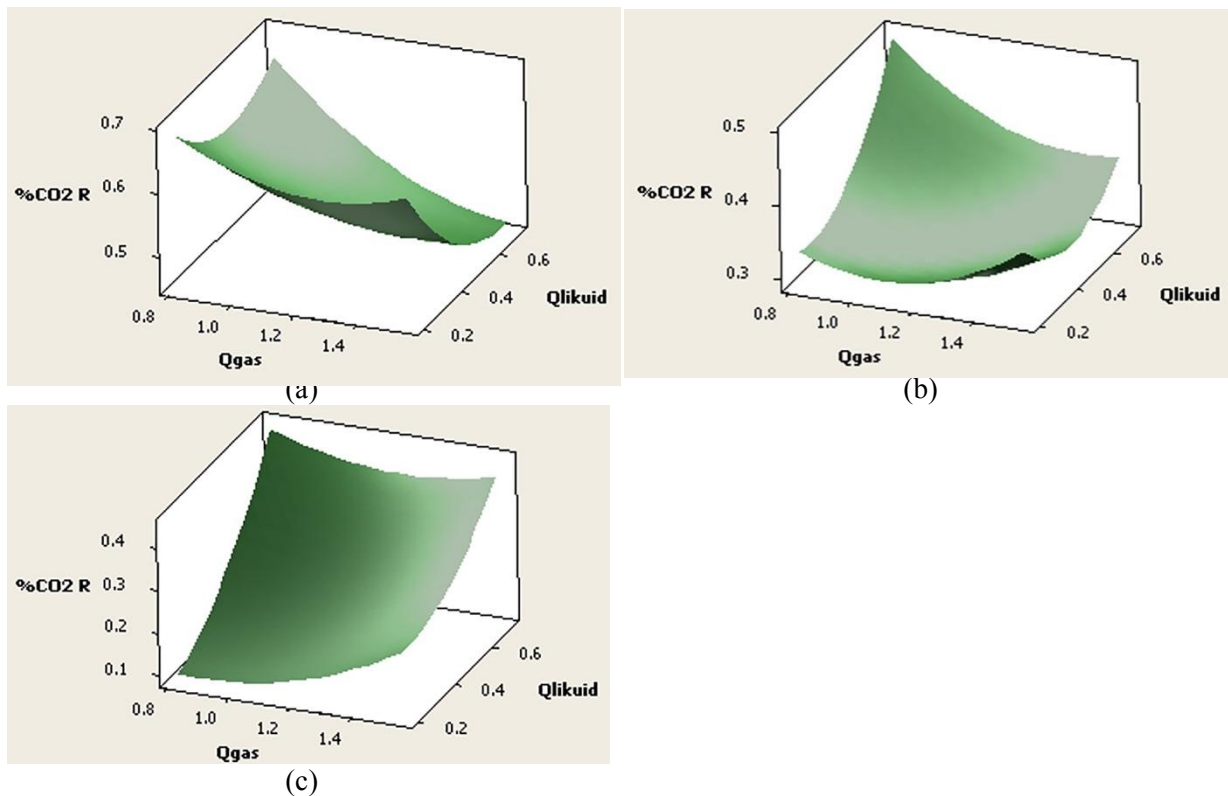
**Figure 2.** Analysis the effect of operating variables on CO<sub>2</sub> separation. (a) residual vs. predicted response, (b) normal probability plot of residual, and (c) Pareto diagram

A Pareto diagram is constructed based on the model to determine the effect of experimental variables on the CO<sub>2</sub> separation (Figure 2). The diagram shows that the variable A (CO<sub>2</sub> concentration in the feed) has the highest effect on the separation of CO<sub>2</sub>. Variable B (gas flow rate) and variable C (liquid flow rate) have no significant effect on CO<sub>2</sub> separation result. This shows that within the range of operating condition used in this study, the increase in CO<sub>2</sub> concentration in the feed from 6-28%-vol will decrease CO<sub>2</sub> separation significantly, while the increase of gas flow rate in the range of 0.82-1.55 L.min<sup>-1</sup> and the increase of liquid flow rate in the range 0.2-0.72 L.min<sup>-1</sup> only able to slightly increase CO<sub>2</sub> separation. In other words, a higher CO<sub>2</sub> concentration requires larger flow rate to achieve the desired separation value. The interaction of CO<sub>2</sub> concentration feed and the liquid flow rate (AC) shows a significant value in the positive direction. It means the larger liquid flow rate tends to bind the higher CO<sub>2</sub> from the gas which results in an increased CO<sub>2</sub> separation. The behavior of CO<sub>2</sub> separation due to the change of operating variables is shown in **Figure 3**.



**Figure 3.** Effect of operating variables on CO<sub>2</sub> separation

**Figure 4** shows that the highest CO<sub>2</sub> separation will be achieved under larger liquid flow rate and smaller gas flow rates. At low CO<sub>2</sub> concentration (6%-vol) the increase of gas flow rate will decrease CO<sub>2</sub> separation, especially at a higher liquid flow rate. While at higher feed CO<sub>2</sub> concentration, the CO<sub>2</sub> separation will decrease significantly, but with the same gas flow rate and liquid flow rate profile. At a low feed concentration conditions, CO<sub>2</sub> is well absorbed and has reached equilibrium. It appears that the increase in CO<sub>2</sub> concentration in the feed greatly affects the separation of CO<sub>2</sub>. Water as absorbent has a finite physical absorption capacity expressed by the Henry constant of 0.8317. At low concentrations of feed CO<sub>2</sub>, water is able to absorb CO<sub>2</sub> until it reaches equilibrium. At high gas flow rates, the formation of the gas bubble will increase so the gas-liquid contact area will decrease. The increase in liquid flow rate causes greater turbulence in the lumen side of the membrane resulting in lower gas-liquid contact time. At high gas and liquid flow rates, separation becomes inefficient due to the shorter contact time.

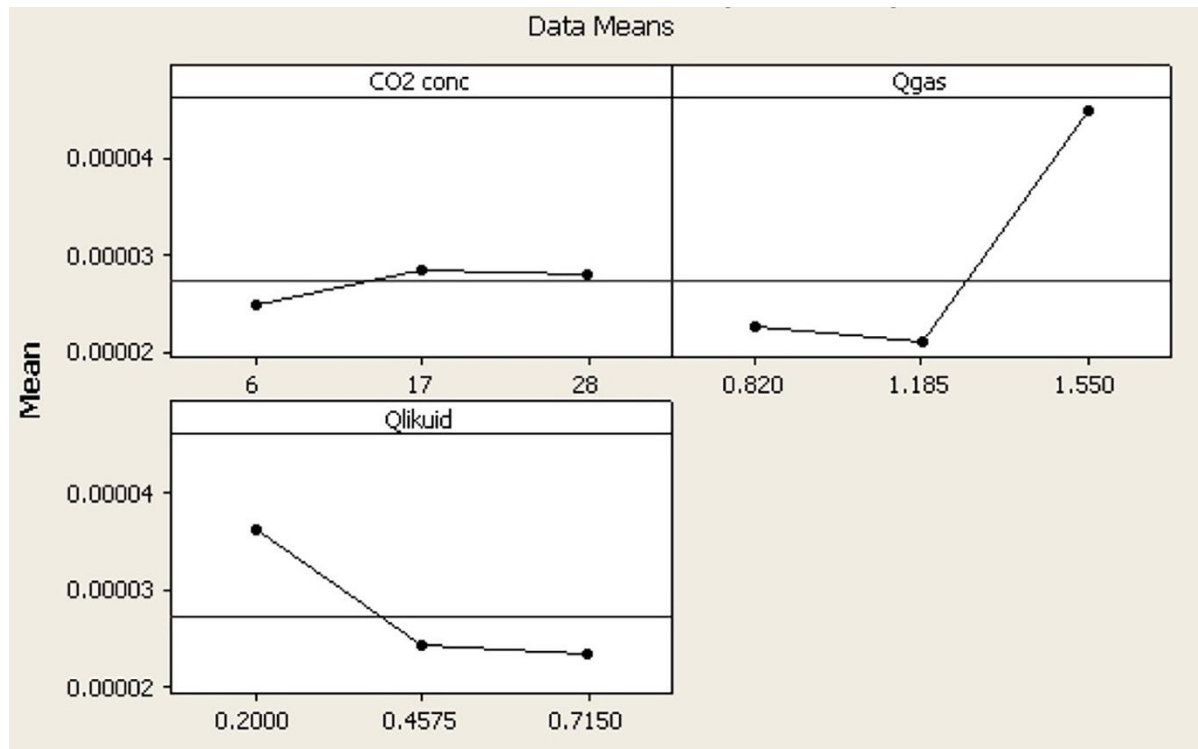


**Figure 4.** Influence of operation variable on separation of  $CO_2$ .  $CO_2$  in feed (a) 6%-vol., (b) 17%-vol., and (c) 28%-vol

### 3.2. $CO_2$ flux

The effect of variables on  $CO_2$  flux is shown in

Figure 5. It is showed that the flux of  $CO_2$  is more influenced by the gas and liquid flow rates than the  $CO_2$  concentration in the feed. The increase in gas flow rate initially causes the flux to decrease due to the formation of larger air bubbles in the liquid which reduces gas-liquid contacting area. However, at a further increase of gas flow rate, there is a significant increase in  $CO_2$  flux. This indicates that at high gas flow rates, a greater gas intensity is more dominant than the reduction of contact area due to the magnification of gas bubble size. In other words, a high gas flow rate creates a large gas-liquid contact area with a larger number of bubbles of large size. While at a lower gas flow rate, small diameter bubbles are produced with fewer amounts. This is similar to the effect of higher liquid flow rate. At a larger liquid flow rate, the decrease of  $CO_2$  flux is due to the shorter contact time which associated with a higher superficial velocity in the lumen side of the membrane. Meanwhile, the increase in  $CO_2$  concentration in the feed tends to increase the flux value due to the increasing amount of transferred  $CO_2$ . However, the flux increase is not significant.



**Figure 5.** Effect of operating variable on CO<sub>2</sub> flux

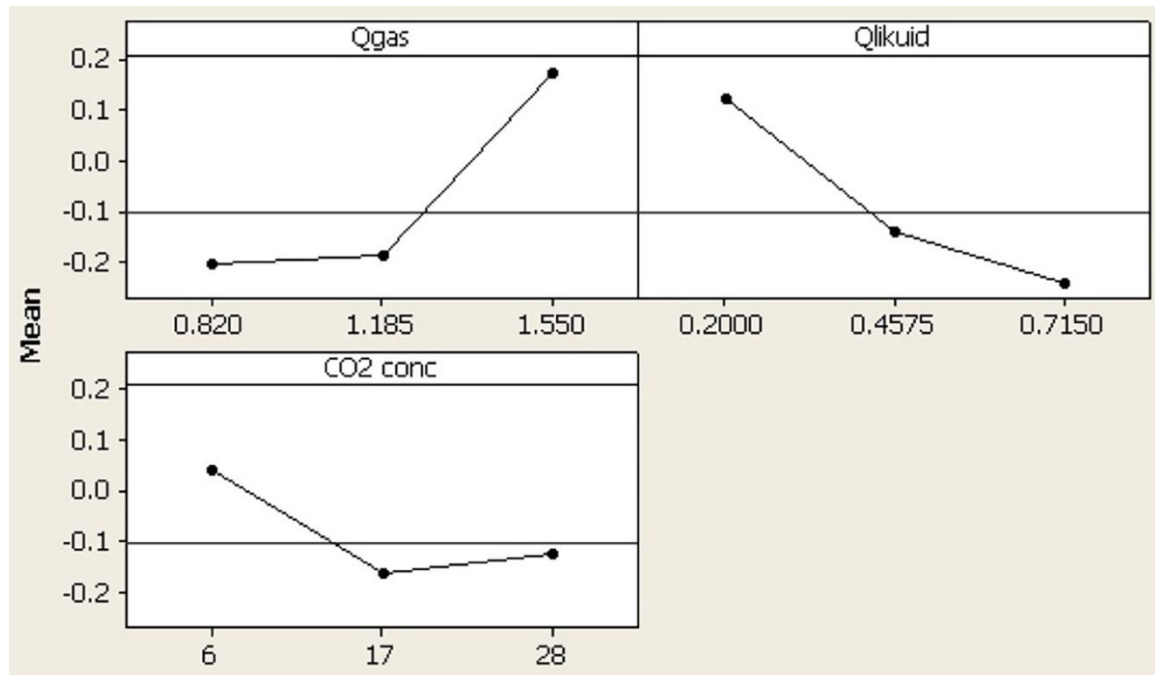
### 3.3. Gas-liquid separation

The observation of the separator performance (gas-liquid separation) was evaluated from two parameters, namely how much water is incorporated into the carried-over/re-entrainment phases and how many gas bubbles are carried into the liquid phase outlets. The data retrieval for the water which is incorporated in the gas phase was carried out under closed separator conditions. The effect of the gas flow rate and the liquid flow rate on the gas difference is given in Figure 6.

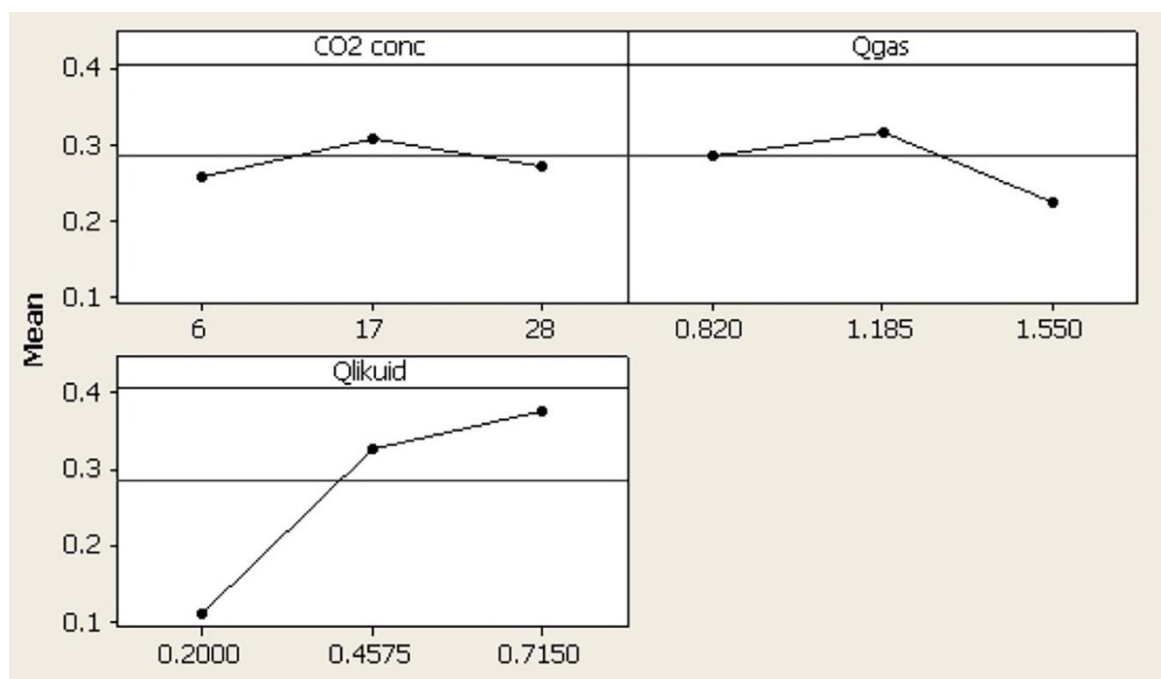
The positive differential values of flow rate indicate that the feed gas flow rate is higher than the output gas. This is due to the presence of CO<sub>2</sub> in the liquid phase so that the flow rate of the outlet gas is decreased. The negative value of gas flow rate difference indicates that the feed gas is smaller than residue gas. The increasing gas flow rate at the outlet is caused by carried water vapor after contact between gas and liquid in the separator. The positive gas difference value indicates that the reduction of gas volume due to the transfer of CO<sub>2</sub> to the liquid phase is more dominant than the amount of water vapor that moves to the gas stream. Meanwhile, the negative gas difference value shows that the water vapor carried to the gas phase is more dominant than the transfer of CO<sub>2</sub> to the liquid phase.

The increase of the gas flow rate causes the larger bubbles in liquids and decrease the contact area between gas-liquid. Thus the displacement of water into the vapor phase is lower and the transfer of CO<sub>2</sub> to the liquid phase is more dominant than the movement of water to the vapor phase. Conversely, an increase in the liquid flow rate will increase the turbulence in the lumen causing the bubble gas to be more easily fragmented and dispersed in the liquid, so the contact area is increased. This increase in contact area causes the water vapor carried in the gas phase to be more dominant than the transfer of CO<sub>2</sub> to the liquid phase. Meanwhile, the increase of CO<sub>2</sub> concentration in the feed did not significantly affect the gas flow rate difference. The amount of gas loss in the liquid flow is seen from the decrease in the gas flow rate as the separator is operated steadily against the gas flow rate (the separator is closed). The effect of operating variables on gas loss is depicted in

Figure 7. The graph shows that the  $\text{CO}_2$  concentration in the feed almost has no effect on the amount of gas involved in the liquid phase. The most influential variable is the liquid flow rate. The increase of the liquid flow rate in the fixed volume of the separator will reduce the residence time in the separator. The lower residence time causes gas bubbles have not been fully degassed. They remain in the liquid phase and are carried in the liquid stream.



**Figure 6.** Effect of operating variable on the difference of gas flow rate





**Figure 7.** Effect of operating variable on gas loss in the liquid phase

The residence time needed for the gas bubble to be released from the liquid is expressed in Table 1. It shows that the residence time of 0.57-3.4 minutes in this experimental range is not sufficient for degassing of less than 5 microns bubbles. It takes 5.13 minutes for all 5-micron gases to be discharged from the liquid. This data also shows that the bubbles diameter generated by the membrane diffuser are distributed at <10 microns. This is also similar to the effect of the gas flow rate on the amount of gas loss. Initially, the increase in gas flow rate causes higher gas loss since the gas bubbles are dispersed in the liquid. However, the increase in gas flow rate further causes the larger bubbles which make it easier to separate and require only a short degassing time. This causes the loss of gas carried in the liquid phase decreases significantly.

**Table 1.** Degassing time of gas bubbles in the liquid

$dp$ (micron)	1	5	10	12	15	20	25	50
$Uc$ (gas velocity) (m/s)	1.8E-07	4.6E-04	0.013	0.033	0.097	0.40	1.17	34.6
Degassing time (s)	794.7	307.8	10.4	4.3	1.4	0.35	0.12	0.004
Degassing time (minute)	13.2	5.13	0.17	0.07	0.024	0.006	0.002	6.74E-05

#### 4. Conclusions

The hollow fiber gas-liquid contacting process, a hybrid process combining the advantages of both conventional reactive absorption and membrane contactor processes, is considered as an alternative technology which can potentially overcome the drawbacks of conventional processes. However, membrane contactor still has not been commercialized for CO<sub>2</sub> removal due to wetting problem. A distinct concept of using membrane technology as contacting device is introduced to overcome wetting problem. In series membrane diffuser-separator is used to generate micro-bubble in the lumen side wherein the mass transfer takes places instead of maintaining interfacial area in the pore of membrane. Separation performance of the membrane diffuser-separator as function of CO<sub>2</sub> concentration (6-28 %-vol), gas flow rate (0.82-1.55 L.min<sup>-1</sup>), and liquid flow rate (0.2-0.72 L.min<sup>-1</sup>) was investigated and optimized. It was found that CO<sub>2</sub> removal was significantly affected by CO<sub>2</sub> concentration in feed gas. On the other hand, CO<sub>2</sub> flux was more influenced by flow rates of liquid and gas than CO<sub>2</sub> concentration. The optimized CO<sub>2</sub> removal (64%) and flux ( $1 \times 10^{-4}$  mol.m<sup>-2</sup>.s<sup>-1</sup>) were obtained at the highest gas flow rate (1.55 L/min), the lowest liquid flow rate (0.2 L/min), and 6.2%-vol. of CO<sub>2</sub>. Outlet gas of the membrane diffuser system tend to carry several water vapor which is affected by gas and liquid flow rate. Meanwhile in the steady-state operation of the separator, the gas bubbles generated by the membrane diffuser take a long time to be completely degassed from the liquid phase, thus a number of gas was exiting separator through the outlet of liquid stream.

#### References

- [1] Boucif N, Corriou J P, Roizard D, Favre E 2012 *AIChE J.* **58** 2843-55
- [2] Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C 2011 *Chem. Eng. Res. Des.* **89** 1609-24
- [3] Aaron D, Tsouris C 2005 *Sep. Sci. Technol.* **40** 321-48
- [4] Mansourizadeh A, Ismail A F 2009 *J. Hazard. Mater.* **171** 38-53
- [5] Ahmad A L, Sunarti A R, Lee K T, Fernando W J N 2010 *Int. J. Greenh. Gas Control* **4** 495-8
- [6] Drioli E, Curcio E 2007 *J. Chem. Technol. Biotechnol.* **82** 223-7
- [7] Wenten I G, Dharmawijaya P T, Aryanti P T P, Mukti R R, Khoiruddin 2017 *RSC Adv.* **7** 29520-39
- [8] Ariono D, Purwasasmita M, Wenten I G 2016 *J. Eng. Technol. Sci.* **48** 367-87
- [9] Khoiruddin, Widiasta I N, Wenten I G 2014 *J. Food Eng.* **133** 40-45
- [10] Strathmann H, Grabowski A, Eigenberger G 2013 *Ind. Eng. Chem. Res.* **52** 10364-79
- [11] Rathore A S, Shirke A 2011 *Prep. Biochem. Biotechnol.* **41** 398-421



- [12] Wenten I G, Widiasta I N 2002 *Desalination* **149** 279–85
- [13] Ariono D, Khoiruddin, Subagio, Wenten I G 2017 *Mater. Res. Express* **4** 24006
- [14] Wenten I G, Khoiruddin 2016 *J. Eng. Sci. Technol.* **11** 916–34
- [15] Khoiruddin, Aryanti P T P, Hakim A N, Wenten I G 2017 *AIP Conf. Proc.* **1840** 90006
- [16] Purwasasmita M, Kurnia D, Mandias F C, Khoiruddin, Wenten I G 2015 *Food Bioprod. Process.* **94** 180–6
- [17] Khoiruddin K, Hakim A N, Wenten I G 2014 *Membr. Water Treat.* **5** 87–108
- [18] Ma L, Dong X, Chen M, Zhu L, Wang C, Yang F, Dong Y 2017 *Membr.* **7**
- [19] Yang X, Wang R, Fane A G, Tang C Y, Wenten I G 2013 *Desalin. Water Treat.* **51** 3604–27
- [20] Wardani A K, Hakim A N, Khoiruddin, Wenten I G 2017 *Water Sci. Technol.* **75** 2891–9
- [21] Wenten I G, Khoiruddin, Arfianto F, Zudiharto 2013 *Desalination* **314** 109–14
- [22] Himma N F, Anisah S, Prasetya N, Wenten I G 2016 *J. Polym. Eng.* **36** 329–62
- [23] Purwasasmita M, Nabu E B P, Khoiruddin, Wenten I G 2015 *J. Eng. Technol. Sci.* **47** 426–46
- [24] Wenten I G, Julian H, Panjaitan N T 2012 *Desalination* **306** 29–34
- [25] Lv Y, Xu C, Yan G, Guo D, Xiao Q 2013 *Adv. Mater. Res.* **616–618** 1541–5
- [26] Li J-L, Chen B-H 2005 *Sep. Purif. Technol.* **41** 109–22
- [27] Zhang Z, Wu X, Wang L, Zhao B, Li J, Zhang H 2017 *RSC Adv.* **7** 13451–7
- [28] Lv Y, Yu X, Tu S-T, Yan J, Dahlquist E 2010 *J. Memb. Sci.* **362** 444–52
- [29] Bottino A, Comite A, Costa C, Di Felice R, Varosio E 2015 *Sep. Sci. Technol.* **50** 1860–9
- [30] Luis P, Van der Bruggen B, Van Gerven T 2011 *J. Chem. Technol. Biotechnol.* **86** 769–75