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The Effect of the Number of Fibers in Hollow Fiber Membrane Modules for NO_x Absorption

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Abstract. As a type of gas that contributes to air pollution, nitrogen oxide (NO_x) has harmful effects on humans and the environment. Among several types of NO_x, nitric oxide (NO) and nitrogen dioxide (NO_2) are most commonly found in air. The utilization of membranes as reactors is a system that combines chemical reactions with the separation process through membranes to increase the conversion of the reaction. This study investigated the absorption process by utilizing a hollow fiber membrane module (polysulfone) as a bubble reactor with H_2O_2 (0.5 wt.%) and HNO_3 (0.5M) as the absorbent. NOx feed gas was flown into the tube side of the membrane; the shell side was filled with static H_2O_2 and HNO_3 and the shell input and the tube output flow were closed to create gas bubbles. The experimental results showed that the absorption efficiency increased, but the mass transfer coefficient and flux decreased as the number of fibers in the membrane module increased at the same feed gas flow rate. The NO_x loading is relatively constant as the amount of fiber in the membrane module increased at the same feed gas flow rate. The experimental results also showed that the mass transfer coefficient, flux, and NO_x loading increased with increasing feed gas flow rate, but the absorption efficiency decreased when using the same number of fibers in the membrane module. The maximum NO_x absorption efficiency achieved in this study was 94.6% at the feed gas flow rate of 0.1 L/min, using a membrane module with 48 fibers.

Keywords: Absorption efficiency; Hollow fiber; Mass transfer coefficient; NO_x loading

1. Introduction

Currently, atmospheric pollution is a significant problem across the globe; apart from SO_2, the most dangerous and toxic gas is NO_x (nitrogen oxide). NO_x is produced from the reaction between nitrogen (N) and oxygen (O) during the combustion process at high temperatures. Among several types of NO_x, such as N_2O, nitrogen monoxide (NO), N_2O_3, nitrogen dioxide (NO_2), N_2O_4, and N_2O_5, NO and NO_2 are the ones most often found in atmospheric air, with NO comprising >90% of the total amount of gas (Kumar et al., 2015). Furthermore, 49% of NO_x comes from motor vehicles, 27% comes from the activities of the electricity generation industry, and 19% comes from household activities. NO_x has also been reported to have the ability to cause acid rain, form fog fumes, decrease water quality, destroy ecosystems, and contribute to global warming (Choi et al., 2014; Gao et al., 2018; Kartohardjono et al., 2019a; Sun et al., 2019). In addition, NO_x is also having harmful effect on the human being (Kartohardjono et al., 2019b).

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The reduction of NO_x in exhaust gases, such as those from boilers and the nitric acid (HNO_3) industry, is currently attracting much attention due to increasingly stringent environmental regulations; for example, the annual average quality standard for NO_2 in ambient air is set at 0.053 ppm (Indonesia, 1999). Several technologies have been pioneered for this purpose, including Selective Catalytic Reduction, Selective Non-Catalytic Reduction, adsorption, and absorption using column contactors (Kartohardjono et al., 2019b). Similarly, the absorption of NO_x using membrane technology has also been developed; in this type of system, the contactors offer several advantages: a continuous process that is easy to operate, low energy consumption, easy scale-up, low separation costs, and the ability to produce high-quality products (Kartohardjono et al., 2017)

Hollow fiber membrane contactors have been widely used as gas-liquid contactors due to the large ratio between their surface area for contact and the equipment volume (Lipnizki and Field, 2001). Furthermore, gas absorption through the membrane contactor also the integrates separation and absorption processes to exploit the benefits of both. Moreover, the hollow fiber membrane module has two different spaces for each fluid, shell, and tube. The in-flowing liquid provides selective absorption to certain gas species, while the porous membrane acts as the contacting interface between the liquid and gas phases, allowing the unidirectional transport of gas into the liquid. For example, the gas component to be removed is absorbed into the solution when the gas stream contacts with the liquid (Wang and Yu, 2017). The hollow fiber membrane module also provides a large ratio of surface area to volume, which is very beneficial for gas-liquid contact (Anggraini et al., 2019). Additionally, the mass transfer between phases that occurs in membrane modules is driven by differences in the concentration of the inter-phase components and pressure drops.

In contrast, the use of membranes as reactors involves the combination of chemical reactions with the separation process through membranes with the usual intention of increasing the conversion of the reaction. A bubble reactor is a type of reactor that is in two phases of gas and liquid; it is a cylindrical vessel with a gas distributor (sparger) at the bottom. The fluid in the gas phase flows into the vessel and, in the process, gas bubbles are formed and move through the liquid inside the vessel. The advantages of this type of reactor include high mass transfer rates, high density, and low operating and maintenance costs (Shaikh and Al-Dahhan, 2013). Bubble reactors are widely applied in chemical, petrochemical, biochemical, metallurgical, and materials industries.

A number of studies have investigated the use of membranes as additional units in processes involving bubble reactors or columns. Xia et al. (2013) immersed a hollow fiber membrane module in a liquid cylindrical bubble column reactor to test the hydrodynamic effect induced by an installed sparger. Moreover, Adewuyi et al. (2014) investigated if a membrane could remove the remaining moisture from the results of NO_x gas absorption using $Na_2S_2O_8$ solvents from a bubble reactor made from glass. The present study was conducted to examine the utilization of hollow fiber membrane modules to reduce NO_x from gas mixtures using a mixture of hydrogen peroxide (H_2O_2) and HNO_3 as the absorbent. It was expected that the fibers in the membrane module would increase the contact area between NO_x and the absorbent solution to enhance the NO_x absorption.

2. Materials and Methods

2.1. Materials

The schematic diagram of NO_x absorption using a hollow fiber membrane module with the bubble reactor principle is shown in Figure 1. The modules used in this study were supplied by PT GDP Filter Bandung. The following modules were used: 16, 32, and 48 fibers, each with a 4 cm diameter and a 25 cm length. Moreover, the feed gas (NO_x = 600 ppm), HNO_3, and H_2O_2 were purchased from Energy Indogas Nusantara Indonesia and Merck Indonesia, respectively. The outer diameter of the polysulfone-based fibers was 2 mm and the inner diameter was 1.8 mm.

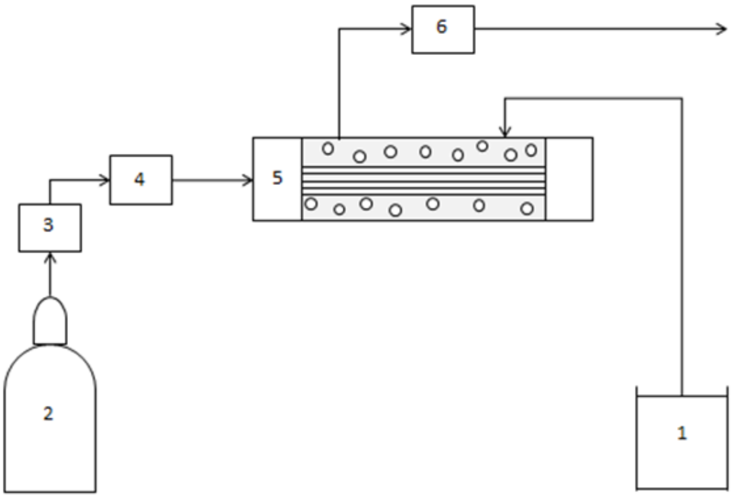

Figure 1 Schematic diagram of the experiment: (1) Absorbent tank; (2) NO_x feed gas; (3) Mass flow controller; (4) Gas analyzer; (5) Hollow fiber membrane module; (6) Gas analyser

2.2. Methods

As shown in Figure 1, the NO_x feed gas was flown into the lumen side of the membrane fibers; the shell side was filled with the static absorbent, which was a mixture of HNO_3 0.5M and H_2O_2 0.5% w/t at 1:1. The feed gas containing NO_x of about 600 ppm at a given flow rate penetrated the membrane fibers and created bubbles on the surface of the fiber in contact with the absorbent liquid in the shell side of the membrane module. The gas moved to the surface of the absorbent solution in the membrane module and exited through the top of the module, where the NO_x concentration and gas flow rate were measured. Furthermore, the inlet and outlet gas compositions to and from the membrane contactor were analyzed using the ECOM-D Combustion Gas Analyzer; the flow rates were measured using a mass flow meter (Shanghai Cixi Instruments). The independent variables used in this study were the number of membrane fibers, which were 16, 32, and 48, and the feed gas flow rates of 0.1, 0.125, 0.15, 0.175, and 0.2 L/min.

The amount of NO_x absorbed (NO_x abs) by the absorbent and the absorption efficiency, *R*, from the experiment were calculated using Equation 1 and Equation 2, respectively.

$$NOx_{Abs} = (x_i F_i - x_o F_o)\frac{P}{RT} \tag{1}$$

$$R = \frac{NOx_{Abs}}{x_i F_i} x100\% \tag{2}$$

The mass transfer coefficient, K_G, flux, *J*, and NO_x loading were calculated using Equations 3, 4, and 5, respectively.

$$K_G = \frac{Q_G}{A} ln\left(\frac{x_i}{x_o}\right) \tag{3}$$

$$J = \frac{NOx_{Abs}}{A} \tag{4}$$

$$NOx_{Loading} = \frac{NOx_{Abs}}{n_{Absorbent}} \tag{5}$$

where *x*i and F_i and x_o and F_o are the NO_x concentration and flow rate in the inlet and outlet membrane module, respectively. *P*, *T,* and *R* are the pressure, temperature, and gas constant, respectively. Q_G, A, and $n_{absorbent}$ are the feed gas flow rate, membrane fibers surface area, and absorbent mole, respectively.

3. Results and Discussion

Absorption tests were used to investigate the effects of the number of membrane fibers and the feed gas flow rate on NO_x absorption efficiency, mass transfer coefficient, mass transfer flux, and NO_x loading. The absorption percentage, *R*, is a parameter that describes how much NO_x is absorbed in comparison to the initial amount of NO_x. As seen in Figure 2, the NO_x absorption efficiency increases as the number of fibers in the membrane module increases at the same feed gas flow rate. However, the NO_x absorption efficiency decreases with the increase in the feed gas flow rate when the number of fibers in the membrane module is the same. The increasing number of membrane fibers caused the percentage of NO_x absorption to increase due to the higher surface-to-volume ratio; this indicates that the amount of contact between the gas-liquid phases increases at the same volume so it enhances the amount of NO_x absorbed by the absorbent solution in the membrane module. In this study, the NO_x absorption efficiency increased by 0.4% from 94.2% to 94.6%when the number of fibers in the membrane module increased from 16 to 48 at the feed gas flow rate of 0.1 L/min. The increase was insignificant because the absorption efficiency was already high in the membrane module with the lowest number of fibers. The same trend was reported by Wang and Yu (2017) in a study that used a hollow fiber polypropylene membrane contactor to reduce the NO_x gas content with a feed gas composition of 184.8 ppm and a gas flow rate of 100 mL/min. They used a solvent that was a mixture of water with H_2O_2 0.2% w/t and NaCl 5% w/t. The feed gas flow rate ranged from 0.05 to 0.25 L/min at a temperature of 323 K. In the present study, the highest absorption efficiency was 94.6% at 0.1 L/min gas flow rate, with a membrane module with 48 fibers, while Wang and Yu (2017) stated the maximum absorption in hydrophobic polypropylene hollow fiber membrane modules with 3000 fibers was ~92% at a 0.05 L/min feed gas flow rate. However, in a wet process of oxidation-absorption in a bubble reactor, the maximum conversion was found to be as high as 94.5% using $Na_2S_2O_8$ and CaO_2 as the oxidants to remove 345 ppm NO_x with a feed gas flow rate of 2 L/min (Wang et al., 2018).

An increase in the feed gas flow rate can increase the amount of NO_X absorbed. Thus, based on Equation 2 this can increase the absorption efficiency. However, based on Equation 2 an increase in the feed gas flow rate can also reduce the absorption efficiency. The decrease in absorption efficiency caused by increasing the feed gas flow rate indicates that the amount of NO_x present in the feed gas is has a greater effect than increasing the amount of NO_x absorbed (Kartohardjono et al., 2019b). In the present study, the highest NO_x absorption efficiency achieved was 94.6% at the feed gas flow rate of 0.1 L/min when the number of fibers in the contactor was 48. Furthermore, the mass transfer process consisted of three consecutive steps: (i) diffusion from the bulk gas phase to the outer surface of the membrane; (ii) diffusion through the membrane pores; and (iii) dissolution into the absorption liquid and liquid phase diffusion/chemical reaction (Kartohardjono et al., 2019c). In this case, the increase in the gas flow rate reduced the residence time of the gas so as to reduce the contact time between the gas and the membrane module; consequently, this made it possible for the incoming feed gas to not be absorbed into the membrane module (shell-side bypass). In the present study, the NO_x absorption efficiency was decreased by 0.6% from 94.6% to 94.0% when the feed gas flow rate increased from 0.1 to 0.2 L/min. The efficiency of NO_x absorption in this study was already high, at around

93.8%, even in the membrane module with the lowest number of fibers (16 fibers) and at the highest feed gas flow rate (0.2 L/min), as shown in Figure 2.

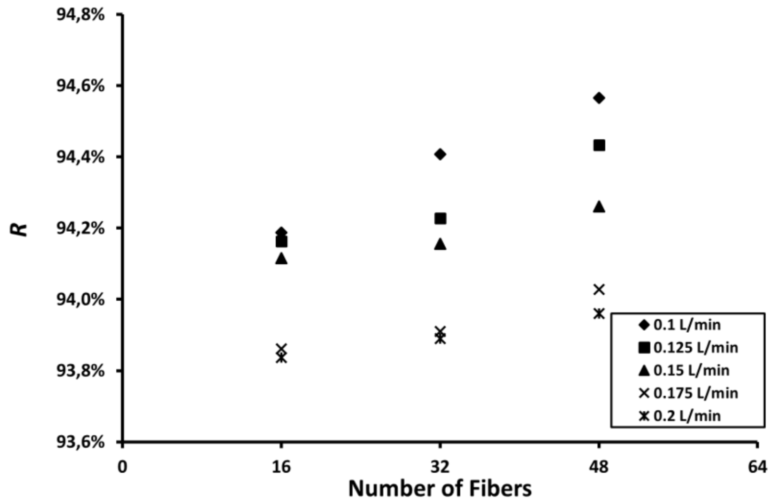

Figure 2 The NO_x absorption efficiency, R, as a function of the number of fibers, at a feed gas flow rate, Q_G, ranging from 0.1 to 0.2 L/min

Mass transfer flux (J) is a parameter describing the number of moles of NO_x transferred along the membrane module per area unit and time. As seen in Figure 3, the flux, J, increases as the gas flow rate increases and decreases as the number of membrane fibers increases in accordance with those expressed in Equation 4. When the gas flow rate increases, the amount of cumulative gas moving in each unit area also increases. Furthermore, an increase in the amount of NO_x gas leads to an increase in the concentration between the phases, making it more of a driving force for mass transfer occurring at each of the membrane sides. Moreover, the increase in the gas flow rate reduces the number of boundary layers on the shell side of the membrane, which makes it easier for NO_x to move from the gas phase to the membrane surface. Based on Equation 4, this will increase the flux, J. This finding is in accordance with the results reported by (Wang and Yu, 2017). However, with regard to the variations in the number of membrane fibers, the flux in mass transfer decreased as the number of membrane fibers increased. Thus, the packing density of the membrane is larger with respect to the thickness of the boundary layer, which is dependent on the geometry of the membrane. In the present study, the maximum mass transfer flux was 3.02 mole/m^{2}s, which was found at a gas flow rate of 0.2 L/min using the 16-fiber membrane. This is different from the findings reported in previous research where the maximum mass transfer flux was 4×10^{-5} mole/m^{2}h (Wang and Yu, 2017).

Moreover, the mass transfer coefficient (K_L) illustrates the effectiveness of the membrane and solvent in absorbing NO_x per area unit of the module. As seen in Figure 4, the mass transfer coefficient increased as the gas flow rate increased. This is because the thickness of the boundary layer decreased as the gas flow rate increased in order to decrease the mass transfer resistance on the boundary layer in the gas phase. An increase in the number of membrane fibers resulted in a greater packing density, which led to a decrease in the mass transfer coefficient. However, the packing density affects the flow characteristics in the membrane; a higher value causes a channeling phenomenon leading to a reduction in the mass transfer coefficient as the number of membrane fibers increases. This finding is similar to the results reported in previous research where the mass transfer coefficient values decreased with increasing packing density or by increasing the number of membrane fibers (Kartohardjono et al., 2016).

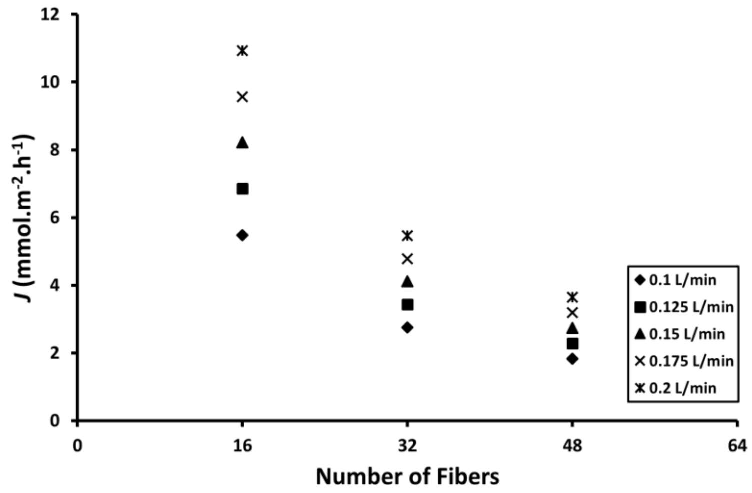

Figure 3 The mass transfer flux, J, as a function of the number of fibers, at a feed gas flow rate, Q_G, ranging from 0.1 to 0.2 L/min

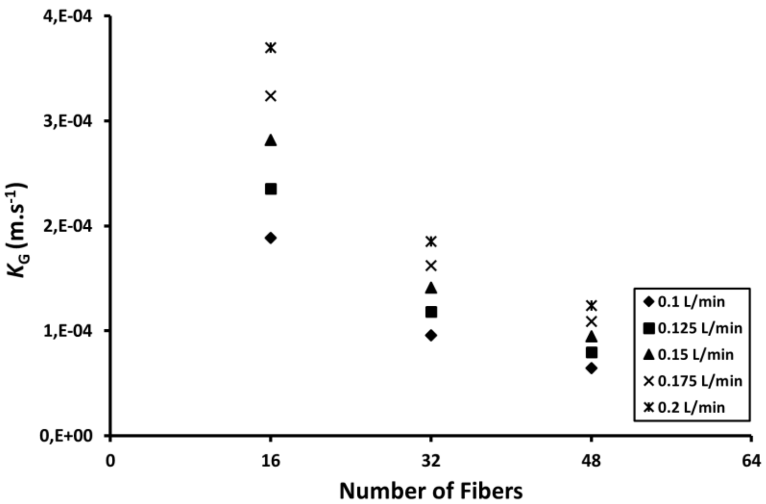

Figure 4 The mass transfer coefficent, K_G, as a function of the number of fibers, at a feed gas flow rate, Q_G, ranging from 0.1 to 0.2 L/min

NO_x loading is a parameter that describes the number of moles of NO_x to be absorbed per unit time per unit of mole of H_2O_2 in the absorbent solution. As seen in Figure 5, NO_x loading increased as the feed gas flow rate increased for the membrane modules with the same number of fibers, but it was relatively constant as the number of fibers in the membrane modules increased at the same feed gas flow rate. With the addition of the gas flow rate, an increase in the concentration gradient and a decrease in the boundary layer was observed. This led to a more complete mass transfer and an increase in the overall number of moles of NO_x that were transferrable. Furthermore, reducing the thickness of the boundary layer caused more NO_x to be absorbed into the solvent thereby increasing the NO_x loading by increasing the feed gas flow rate (Figure 5). As the number of membrane fibers increased, the area of the effective contact between the phases also increased. The addition of the contact area increased the solvent's ability to absorb NO_x. Therefore, with the same number of solvent moles, the solvent has the ability to absorb more NO_x due to the increasing contact between the solvent and the gas. However, the increase in the amount of absorbed NO_x was not significant because, at the feed gas flow rate applied, the efficiency was already high (>90%) so only a small amount of NO_x can be absorbed further. Consequently, the NO_x loading was relatively constant as the number of fibers in the membrane modules increased (Figure 5).

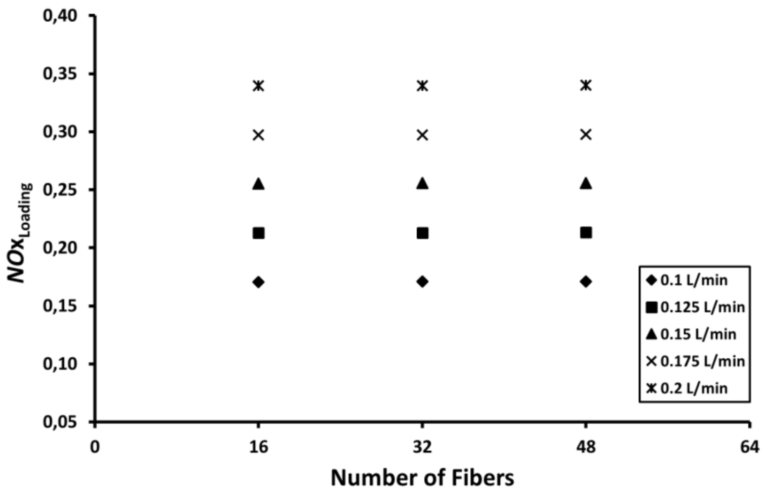

Figure 5 NO_x loading ((mmol NO_x/mol H_2O_2)/h), as a function of the number of fibers, at a feed gas flow rate, Q_G, ranging from 0.1 to 0.2 L/min

4. Conclusions

This study utilized hollow fiber membrane modules to absorb NO_x using a mixture of HNO_3 0.5M and H_2O_2 0.5% w/t as the absorbent. The feed gas flow rate and the number of membrane fibers were the main variables used in this study. The aim was to understand their effects on the overall mass transfer coefficient, flux, absorption efficiency, and NO_x loading. The experimental results showed that the mass transfer coefficient, flux, and NO_x loading increased by increasing the feed gas flow rate, while the absorption efficiency decreased. The highest NO_x absorption efficiency achieved in this study was 94.6% at the feed gas flow rate of 0.2 L/min with the membrane module with 48 fibers in the contactor. Moreover, the mass transfer coefficient and flux decreased while the absorption efficiency increased as the number of fibers in the contactor increased at the same feed gas flow rate. The NO_x loading was relatively constant as the number of fibers in the contactor increased at the same feed gas flow rate. In this study, the increase in the efficiency of NO_x absorption was insignificant when the amount of fibers in the membrane module increased from 16 to 42 at the feed gas flow rate of 0.1 L/min. However, the NO_x absorption efficiency decrease was insignificant if the gas flow rate increased from 0.1 to 0.2 L/min on a membrane module with 48 fibers. The NO_x absorption efficiency achieved in this study was already high (about 93.8%), even for the membrane module with the lowest number of fibers (16 fibers) and at the highest feed gas flow rate (0.2 L/min).

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