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Abstract: Nitrogen oxides (NOx), which can be found in the combustion process of coal-fired power plants, are pollutant gases that are dangerous to the environment and human life. The conventional technology used the dry method such as SCR (Selective Catalytic Reduction) and SNCR (Selective Non-Catalytic Reduction) to clean the gas stream from NOx contents. Alternatively, the polyvinylidene fluoride (PVDF) membrane module can be utilized to remove the NOx using oxidant solutions to absorb the NOx. The study aims to investigate the performance of the PVDF hollow fiber membrane module (HFMM) in removing NOx using absorbent solutions consists of H_2O_2 and HNO_3. Throughout the experiment, the feed gas having 600 ppm NOx in nitrogen was introduced to the membrane fiber, then diffused in the pores of membrane to the outer surface of the fiber in the shell side of the HFMM, where the reaction between oxidant and NOx took place. The experimental results revealed that the efficiency of NOx elimination declines as the feed gas flow rate is increased. This study's maximum NOx reduction efficiency was 99.8%, at a 100 cm^3/min feed gas flow.

Keywords: HNO_3; H_2O_2, NOx elimination; pollutant gases; PVDF; reduction efficiency

1. Introduction

World energy consumption increases with the increasing human population due to daily activities that require various forms of energy[1]. This huge energy consumption has caused various problems such as climate change, greenhouse gas emissions and depletion fossil fuel sources[2]. Globally, around 64% of total electrical energy in 2019 was still produced by burning fuels from fossil such as oil, natural gas, and coal[3]. The burning of fossil fuels and gasoline-ethanol produce air pollutants such as SOx, NOx, CO, VOCs (volatile organic compounds)[4], carbon particulates, and ash which can cause air pollution[5], environmental damage[6], and increase greenhouse gases (GHGs) emissions[7]. These pollutants in a certain range significantly affect human health, such as the body's respiratory system, especially in children and the elderly[8]. Meanwhile, the concern for the environment is acid rain resulting from photocatalytic reactions produced by air pollutants above, especially NOx gas[9]. Among several types of Nitrogen Oxides, the gases most found in atmospheric air are Nitrogen Monoxide (NO) and Nitrogen Dioxide (NO_2), where Nitrogen Monoxide takes up a percentage above 80% of NOx gas[10].

In general, NOx gas can be removed mainly through dry and wet processes[11]. The dry process comprises SCR (selective catalytic reduction)[12,13] and NSR (NOx storage and reduction)[14]. The disadvantage of the dry process is not suitable for small and medium-sized industries, and the use of ammonia can lead to the establishment of NH_4HSO_4 and NH_3 release to the atmosphere[15,16]. In addition, it needs huge additional place and high investment cost[17]. The wet process has numerous benefits compared to the dry process, such as flexibility to feed gases, working at low temperatures, and no catalyst deactivation[18]. In the wet process for denitration, NOx gases come through the absorbent solution and can be absorbed[19]. The challenge is that NO is extremely insoluble in water, therefore, it needs to be oxidized to easily soluble species in the absorbent solution[20]. To convert NO to more solvable species in the wet process, several strong oxidants can be utilized such as H_2O_2, NaOH, $Ca(OH)_2$, $NaClO_2$, or $KMnO_4$[21]. The wet process for removing NOx using an oxidant solution is usually conducted in a bubble reactor[22]. This study employed

PVDF-based HFMM to eliminate NOx through a wet process using solutions of H_2O_2 and HNO_3 as absorbent. The shell side of HFMM acts as the reactor, while the fibers distribute the NOx-containing gas before contact with the absorbent.

The reaction between NOx gases and H_2O_2 and HNO_3 solution is as follows[23)24)]:

$$2NO_2 \leftrightarrow N_2O_4 \quad (1)$$
$$NO + NO_2 \leftrightarrow N_2O_3 \quad (2)$$
$$NO + NO_2 + H_2O \leftrightarrow 2HNO_2 \quad (3)$$
$$3HNO_2 \leftrightarrow 2NO + HNO_3 + H_2O \quad (4)$$
$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \quad (5)$$

The addition of HNO_3, which acts as an autocatalyst, enhances the rate of reaction (5).

2. Materials and Methods

The HFMM consists of 40 fibers sizes of 0.5 and 1.5 mm inside and outside diameters and 40 cm in length. PT EIN Indonesia supplies feed gas containing 600 ppm NOx in nitrogen. The chemicals used, H_2O_2 and HNO_3, are analytical grades supplied by Merck Indonesia. Throughout the experiment, the feed gas flowed into the lumen fiber in the membrane module and was adjusted by mass flow controller CX Series supplied by Shanghai Cixi Instruments. The feed gas diffuses in the fibers' pores and passes through to the shell side, and contact absorbent solutions to react with H_2O_2 and HNO_3 as presented in Reaction (1-5). Gas Analyzer ECOM-D recorded the NOx concentrations to and from HFMM. The schematic of the experiment is presented in Figure 1.

The absorbed NOx, NOx_{Abs}, efficiency of removal, R, NOx loading, *NOx-loading*, and overall mass transfer coefficient, K_G, can be determined by Eq. (6-9)[25)] [5, 11]:

$$NOx_{Abs} = (X_{in} - X_{out})\frac{Q_{G,in}P}{RT} \quad (6)$$

$$R = \frac{X_{in}-X_{out}}{X_{in}} x100\% \quad (7)$$

$$NOx_{loading} = \frac{NOx_{Abs}}{molH_2O_2} \quad (8)$$

$$K_G = \frac{Q_G}{A_m} ln\left(\frac{X_{in}}{X_{out}}\right) \quad (9)$$

Where X_{in} and X_{out}, $Q_{G,in}$, T, P, and R are the concentration of inlet and outlet gases in HFMM, feed gas flow rate, temperature, pressure, and ideal gas constant, respectively.

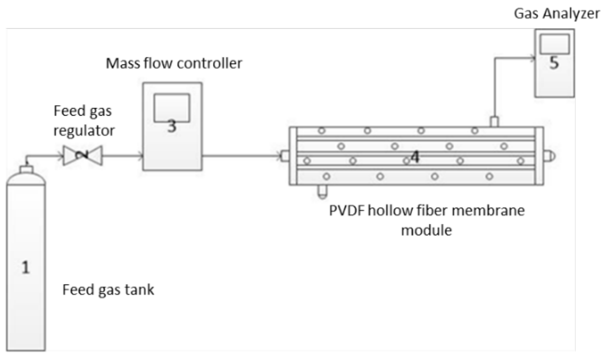

Fig. 1: The experimental diagram schematic.

3. Results and Discussion

The Figure 2 presents the dependency of the absorbed NOx and the efficiency of NOx elimination on the feed gas flow in the HFMM contains a mixture of 200 mL of H_2O_2 (0.1 M) and 200 mL of HNO_3 (0.5 M). The absorbed NOx rises with an increase in the feed flow rate entering the HFMM due to the absorbed NOx also increases. The absorbed NOx increases from 4.1 to 8.0 x10^{-5} mmol/s, and NOx absorption efficiency decreases from 99.8 to 98.8% by doubling the feed gas flow from 100 to 200 mL/min because the less gas residence time in the HFMM[11)]. A previous study showed a slight decline in NOx reduction efficiency from 94.6 to 94.0% by doubling the feed gas flow from 100 to 200 mL/min in a polysulfone membrane module containing 48 fiber using 50 mL absorbent solution of 0.25 M HNO_3 and 0.25 wt.% H_2O_2[24)].

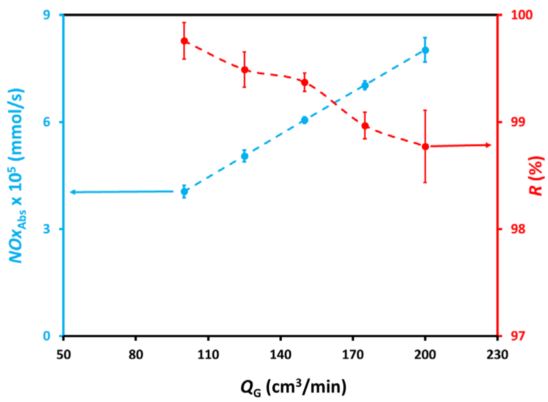

Fig. 2: The dependency of absorbed NOx and NOx elimination efficiency, R, on the feed gas flow, Q_G.

The mass transfer coefficient, K_G, as shows in Figure 3, is enhanced by increasing the feed gas flow in the HFMM using a mixture of 200 mL of H_2O_2 (0.1M and 200 mL HNO_3 (0.5M). The gas-liquid boundary layer declines with the feed gas flow, which enhances the absorbed NOx[26),27)]. Moreover, Equation (8) demonstrates that the mass transfer coefficient raises with the absorbed NOx. As presented in Figure 3, the overall mass transfer coefficients increased from 0.014 to 0.019 cm/s or by approximately 42% by doubling the flow of the feed gas from 100 to 200 mL/min. Similar results have also been presented in the previous study where the overall mass transfer coefficient increased from around 0.007 to 0.013 cm/s when the feed gas flow was doubling flow from 100 to 200 mL/min, containing 600 ppm NOx, in an HFMM containing 48 polysulfone-based fibers using absorbents of 25 mL 0.5 wt.% H_2O_2 and 25 mL of 0.5 M HNO_3[25].

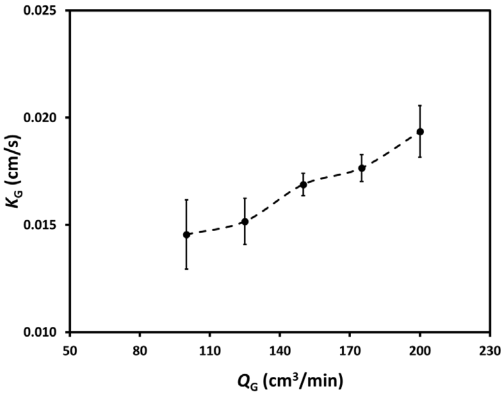

Fig. 3: The mass transfer coefficient, K_G, dependency, on the feed gas flow, Q_G.

Figure 4 shows the dependency of NOx loading on the feed gas flow in the HFMM having 200 mL H_2O_2 (0.1 M) and 200 mL HNO_3 (0.5 M), where NOx loading rises with increasing the feed gas flow entering the HFMM. As expressed in Equation (9), the NOx loading is directly proportional to the absorbed NOx. The absorbed NOx is also directly proportional to the feed gas flow as expressed in Equation (6)[11].

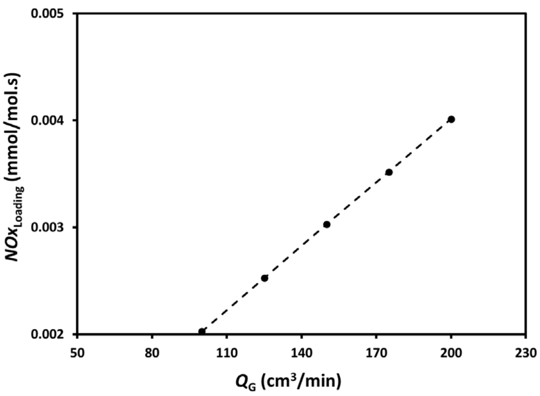

Fig. 4: The dependency of NOx loading on the feed gas flow, Q_G.

4. Conclusion

The HFMM could be utilized to remove NOx gases from the gas stream using absorbents of H_2O_2 and HNO_3. This study's maximum NOx removal efficiency was 99.8% at a feed gas flow of 100mL/min. The increase in the feed gas flow rate causes a decline in the efficiency of NOx removal. Meanwhile, the feed gas flow raises the absorbed NOx, mass transfer coefficient, and NOx loading.

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Nomenclature

Am	membrane surface area (m^2)
K_G	overall mass transfer coefficient ($m\ s^{-1}$)
NOx_{Abs}	*NO*x absorbed ($mol\ s^{-1}$)
NOx,loading	*NO*x loading (mol NOx mol $H_2O_2^{-1}$)
$Q_{G,in}$	feed gas flow rate ($m^3\ s^{-1}$)
P	pressure (bar)
R	ideal gas constant ($J\ mol^{-1}\ K^{-1}$)
T	temperature (K)
X_{in}	*NO*x inlet concentration (ppm)
X_{in}	*NO*x outlet concentration (ppm)

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