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The Feed Gas Flow Effects on the NO_x Removal Performance through the Polyvinylidene Fluoride Hollow Fiber Membrane Module using H₂O₂ and HNO₃ as an Absorbent

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Abstract: Nitrogen oxides (NO_x), 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 NO_x contents. Alternatively, the polyvinylidene fluoride (PVDF) membrane module can be utilized to remove the NO_x using oxidant solutions to absorb the NO_x. The study aims to investigate the performance of the PVDF hollow fiber membrane module (HFMM) in removing NO_x using absorbent solutions consists of H₂O₂ and HNO₃. Throughout the experiment, the feed gas having 600 ppm NO_x 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 NO_x took place. The experimental results revealed that the efficiency of NO_x elimination declines as the feed gas flow rate is increased. This study's maximum NO_x reduction efficiency was 99.8%, at a 100 cm³/min feed gas flow.

Keywords: HNO₃; H₂O₂, NO_x elimination; pollutant gases; PVDF; reduction efficiency

1. Introduction

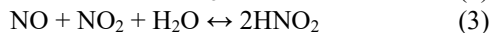
World energy consumption increases with the increasing human population due to daily activities that require various forms of energy¹. This huge energy consumption has caused various problems such as climate change, greenhouse gas emissions and depletion fossil fuel sources². Globally, around 64% of total electrical energy in 2019 was still produced by burning fuels from fossil such as oil, natural gas, and coal³. The burning of fossil fuels and gasoline-ethanol produce air pollutants such as SO_x, NO_x, CO, VOCs (volatile organic compounds)⁴, carbon particulates, and ash which can cause air pollution⁵, environmental damage⁶, and increase greenhouse gases (GHGs) emissions⁷. These pollutants in a certain range significantly affect human health, such as the body's respiratory system, especially in children and the elderly⁸. Meanwhile, the concern for the environment is acid rain resulting from photocatalytic reactions produced by air pollutants above, especially NO_x gas⁹. Among several types of Nitrogen Oxides, the gases most found in atmospheric air are Nitrogen Monoxide (NO) and Nitrogen Dioxide (NO₂), where

Nitrogen Monoxide takes up a percentage above 80% of NO_x gas¹⁰.

In general, NO_x gas can be removed mainly through dry and wet processes¹¹. The dry process comprises SCR (selective catalytic reduction)^{12,13} and NSR (NO_x 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 NH₄HSO₄ and NH₃ release to the atmosphere^{15,16}. In addition, it needs huge additional place and high investment cost¹⁷. The wet process has numerous benefits compared to the dry process, such as flexibility to feed gases, working at low temperatures, and no catalyst deactivation¹⁸. In the wet process for denitration, NO_x gases come through the absorbent solution and can be absorbed¹⁹. The challenge is that NO is extremely insoluble in water, therefore, it needs to be oxidized to easily soluble species in the absorbent solution²⁰. To convert NO to more solvable species in the wet process, several strong oxidants can be utilized such as H₂O₂, NaOH, Ca(OH)₂, NaClO₂, or KMnO₄²¹. The wet process for removing NO_x using an oxidant solution is usually conducted in a bubble reactor²². This study employed

PVDF-based HFMM to eliminate NO_x through a wet process using solutions of H₂O₂ and HNO₃ as absorbent. The shell side of HFMM acts as the reactor, while the fibers distribute the NO_x-containing gas before contact with the absorbent.

The reaction between NO_x gases and H₂O₂ and HNO₃ solution is as follows⁽²³⁾⁽²⁴⁾:



The addition of HNO₃, 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 NO_x in nitrogen. The chemicals used, H₂O₂ and HNO₃, 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 H₂O₂ and HNO₃ as presented in Reaction (1-5). Gas Analyzer ECOM-D recorded the NO_x concentrations to and from HFMM. The schematic of the experiment is presented in Figure 1.

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

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

$$R = \frac{X_{\text{in}} - X_{\text{out}}}{X_{\text{in}}} \times 100\% \quad (7)$$

$$\text{NOx}_{\text{loading}} = \frac{\text{NOx}_{\text{Abs}}}{\text{molH}_2\text{O}_2} \quad (8)$$

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

Where X_{in} and X_{out} , $Q_{G,\text{in}}$, 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.

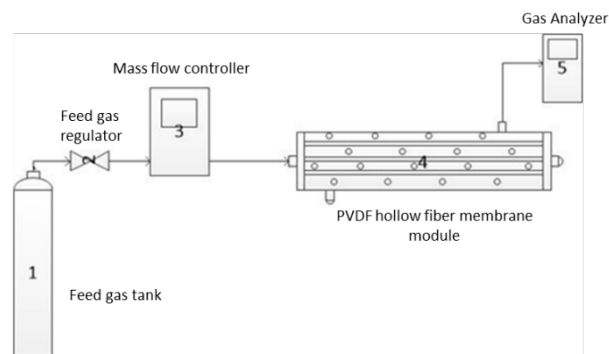


Fig. 1: The experimental diagram schematic.

3. Results and Discussion

The Figure 2 presents the dependency of the absorbed NO_x and the efficiency of NO_x elimination on the feed gas flow in the HFMM contains a mixture of 200 mL of H₂O₂ (0.1 M) and 200 mL of HNO₃ (0.5 M). The absorbed NO_x rises with an increase in the feed flow rate entering the HFMM due to the absorbed NO_x also increases. The absorbed NO_x increases from 4.1 to 8.0 x 10⁻⁵ mmol/s, and NO_x 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 NO_x 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 HNO₃ and 0.25 wt.% H₂O₂⁽²⁴⁾.

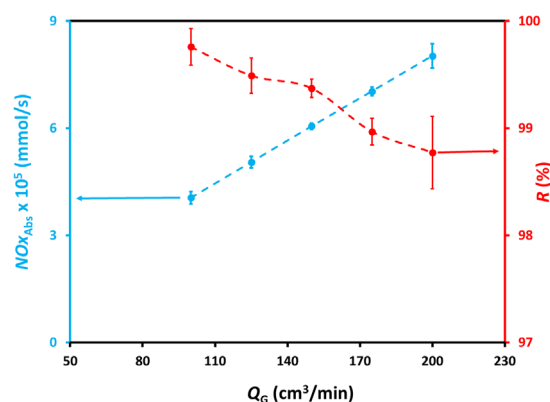


Fig. 2: The dependency of absorbed NO_x and NO_x elimination efficiency, R , on the feed gas flow, Q_G .

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 H₂O₂ (0.1M) and 200 mL HNO₃ (0.5M). The gas-liquid boundary layer declines with the feed gas flow, which enhances the absorbed NO_x^{(26),(27)}. Moreover, Equation (8) demonstrates that the mass transfer coefficient raises with the absorbed NO_x. 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 NO_x, in an HFMM containing 48 polysulfone-based fibers using absorbents of 25 mL 0.5 wt.% H₂O₂ and 25 mL of 0.5 M HNO₃²⁵.

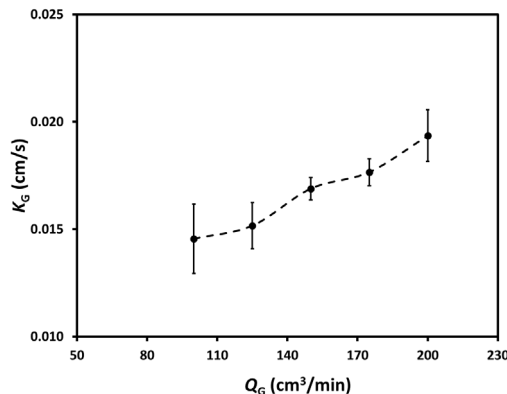


Fig. 3: The mass transfer coefficient, K_G , dependency, on the feed gas flow, Q_G .

Figure 4 shows the dependency of NO_x loading on the feed gas flow in the HFMM having 200 mL H₂O₂ (0.1 M) and 200 mL HNO₃ (0.5 M), where NO_x loading rises with increasing the feed gas flow entering the HFMM. As expressed in Equation (9), the NO_x loading is directly proportional to the absorbed NO_x. The absorbed NO_x is also directly proportional to the feed gas flow as expressed in Equation (6)¹¹.

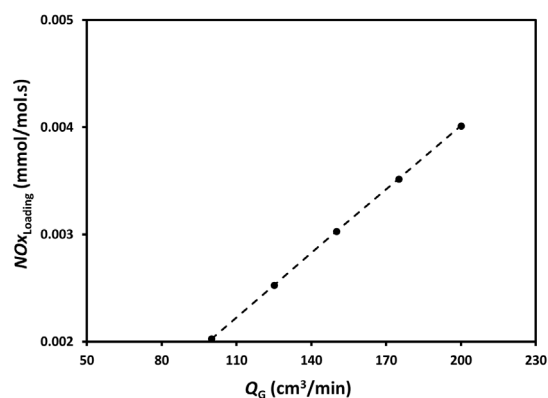


Fig. 4: The dependency of NO_x loading on the feed gas flow, Q_G .

4. Conclusion

The HFMM could be utilized to remove NO_x gases from the gas stream using absorbents of H₂O₂ and HNO₃. This study's maximum NO_x 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 NO_x removal. Meanwhile, the feed gas flow raises the absorbed NO_x, mass transfer coefficient, and NO_x loading.

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Nomenclature

A_m	membrane surface area (m ²)
K_G	overall mass transfer coefficient (m s ⁻¹)
$NO_{x,Abs}$	NO _x absorbed (mol s ⁻¹)
$NO_{x,loading}$	NO _x loading (mol NO _x mol H ₂ O 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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