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Studi Pendahuluan Produksi Nitrat Sebagai Bahan Baku Pupuk Dengan Metode *Plasma Discharge*

Preliminary Study Of Nitrate Production By Plasma Discharge As Potential Fertilizer Material

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ABSTRACT

Nitrogen-based fertilizer production mainly involves the Haber-Bosch process, which synthesizes Ammonia via a chemical reaction of N_2 from the air and H_2 under high temperature and pressure conditions in the presence of a catalyst. However, the environmental concern for greenhouse gas emissions and high energy consumption triggers other Nitrogen fixation method development. The non-thermal plasma oxidation of N_2 into Nitrate is a promising method since it has lower energy consumption and a more suitable process condition with a better environmental profile. This study tested the designed plasma discharge reactor tube to produce nitrate from air N_2 with varying voltage, time, and airflow rate operating conditions. Nitrate concentration was analyzed using a UV-Vis spectrophotometer. The results show that nitrate concentration changes linearly with the applied voltage in a constant airflow rate and length of treatment time. The highest performance of the plasma discharge reactor was achieved on a 6 kV applied voltage with a flow rate of 0.2 L/min and a treatment time of 40 minutes where the obtained nitrate concentration was 7.7 ppm, which indicated the potential plasma discharged nitrate production for green fertilizer application. Further study shall be carried out to enhance the performance.

Keywords: *airflow; fertilizer; nitrate; nitrogen; plasma discharge*

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INTRODUCTION

Fertilizer application is important for plan growth by maintain soil fertility condition so it is able to provide essential nutrients needed for plants. Fertilizers can improve not only soil structure but also increase soil productivity. For the time being, Farmer’s using mostly of inorganic chemical fertilizer which has several disadvantages, such as decrease the soil quality and texture, diminish organic substances,and disrupt the balance of nutrients contained in the soil with the excessive dose used for long period. The used of inorganic chemical fertilizer can caused environmental pollution which affects to the nearby ecosystem. In addition, the higher price and limitation of raw material availability may caused an issue. Therefore, the development of alternative process to produce fertilizer material is needed at this time.

Various Nitrogen-based fertilizers are mainly produced using the Haber-Bosch process by combining N_2 from the air with H_2, which is typically obtained from steam reforming of methane from natural gas, in the high temperature and catalytic process to form Ammonia (NH_3). A subsequent thermochemical process then oxidizes the NH_3 produced by the Haber-Bosch process to form Nitrate (NO_3^-), which can react with NH_3 to produce Ammonium nitrate (NH_4NO_3) as a significant component in fertilizer. Nitrate is a preferable source of Nitrogen because it has higher mobility in the soil matrix due to ion exchange reactions of the latter as soils are strong cation exchangers (Graves et al. 2019; Wu et al. 2021). Despite the contribution to increasing agricultural productivity, Haber-Bosch's process has some disadvantages with the current manufacturing system and synthetic nitrogen fertilizer utilization. The Haber-Bosch process reduces energy incentive consumption with intense temperature and pressure conditions, leading to scalability production issues and high capital cost. Additionally, the Haber-Bosch process has become one of the highest contributors to greenhouse gas emissions to the environment from large-scale manufacturing (Peng et al. 2018; Rouwenhorst et al. 2021).

Necessary macro-nutrient elements for plant growth are Nitrogen (N), Phosphorus (P), and Kalium (K), which could be provided by regular fertilization. The concentration and ratio of fertilizer ingredients have an effect on the plant's growth and yield at a certain stage and dose given (Abdullah 2017). The application of fertilizer with higher nitrogen content is able to promote the vegetative growth phase of orchid plants as nitrogen is the main constituent element of proteins and enzymes for photosynthesis (Burhan 2017). Nitrogen-based fertilizer applications at the early stage of soybean plant growth increase the yield and nutrient efficiency linearly with the fertilizer dose. Uptake of nitrogen from fertilizer is needed to balance the nitrogen supply from N_2 fixation to meet the overall N demand for soybean plants to fulfill photosynthetic capacity for optimum yield (Pratama et al. 2017). Mangiring et al. (2017) studied the effect of shading and nitrogen fertilizer to production and quality of Pennisetum purpureum as fodder forage. The result showed that nitrogen dose affects the grass quality produced for its nitrate, fiber, and protein content.

The new technologies are continuously developed to manufacture Nitrogen-based fertilizer in a lower cost and environmentally clean process. Nitrogen fixation using Non-Thermal Plasma (NTP) technology offers some potential benefits, such as low temperature and pressure system, green technology with the carbon-free process as NTP solely uses water, and access to on-site small scale production, which result in a more efficient and less energy-intensive process. In NTP, N_2 is primarily dissociated through vibrational excitation instead of highly energetic species, which requires less energy input (Peng et al. 2018; Subramanian et al. 2021; Ranieri et al. 2021). NTP can generate the formation of reactive Oxygen Nitrogen species in the air at ambient temperature and pressure without a catalyst by the high energy electrons generated from the discharge to convert N_2 and O_2 to NO_x form since the energy in the electronic vibration mode could be delivered to nitrogen fixation reaction to attain the enormous activation energy. The reaction between N_2 and O_2 under plasma includes transformation from N_2 to $N_2(V)$ by the electrons present in the plasma. $N_2(V)$ tends to react with an activated Oxygen atom (O^*) to form NO_x, and an activated Nitrogen atom (N^*) can react with O_2 to produce NO_x further. Nowadays, the non-thermal atmospheric pressure plasma technology is considered to replace the conventional nitrogen fixation method because it can fix the atmospheric Nitrogen in the form of NO, NO_2^-, and NO_3^- which can all be used as fertilizers with the lowest energy consumption rate. These nitrogen derivatives are in mobile and soluble forms of Nitrogen in soil, making them more suitable for plant uptake (He et al. 2018; Lamichhane et al. 2021).

The prominent non-thermal plasma source for NO_x production includes dielectric barrier discharge (DBD), glow, spark, and arc type of discharges. These non-thermal sources typically have lower power requirements and are easier to operate. The use of non-thermal plasmas is preferred as they can generate higher concentrations of NO_x due to their non-equilibrium behavior. In order to control the NO_x synthesis, the operating conditions, which include electrical parameters, discharge regimes, and the process parameter, such as gas composition, flow rate, and temperature, became key factors that affect the NO_x concentrations and overall energy efficiency (Pei et al. 2020; Li et al. 2018)

In this study, the designed plasma discharge reactor tube was tested to produce nitrate from air N_2 as a component for fertilizer application. This study uses a variation of applied voltage, treatment time, and airflow rate operating condition to analyze the effect.

MATERIALS AND METHODS

1. Plasma Discharge Reactor

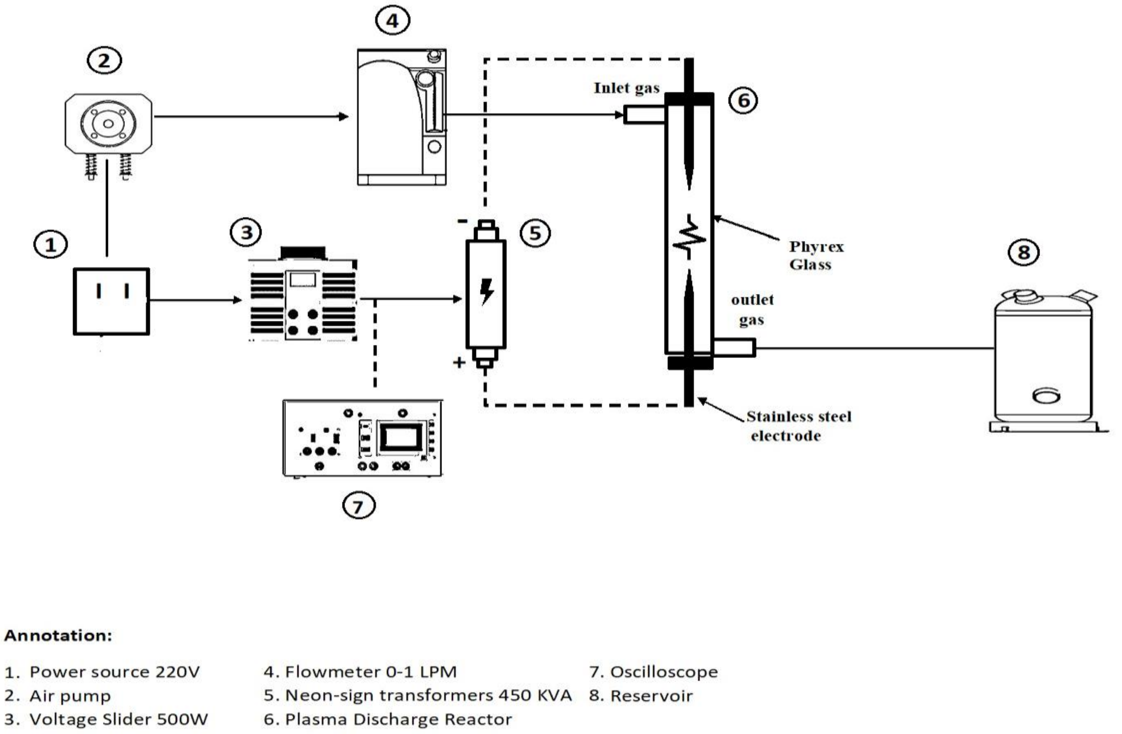

Figure 1. System design of nitrate production plasma discharge reactor

Figure 1 illustrates the design of the plasma discharge nitrate production system. The plasma discharge reactor is designed using stainless steel electrodes size 4 mm in diameter and 15 cm long. The reactor body uses a pyrex glass measuring 1mm thick, 20 cm long, 4 cm in diameter, which is formed by adding a 2 mm nipple hole at the end of the tube as air in and out. The cover of the reactor tube uses teflon material with holes in the middle for the installation of electrodes and as a place for the plasma discharge process to occur. The overall device system of this experiment consisted of an AC high voltage transformer (neon sign tubes transformer type: T151122, Prim 220 V / Sec 15 kV, 450 VA) connected to a stainless steel plasma reactor electrode. To set the desired output voltage, the neon sign transformer is connected to a Voltage slider regulator (TDGC-OKI 500 Watt) and connected in parallel with a digital oscilloscope (Hantek 5000 series) to be measured ensure that the variable output voltage reading is appropriate. The airflow rate is controlled by an airflow meter (Wiebrok LZM-6T 0 – 1 LPM) drawn from free air through a pump (Amara AA 350). An 8 mm silicone hose connects the airflow rate from the air pump to the reservoir.

Initial trials ensure that there are no air leaks in the performance design of the tool system by looking at the value of the air rate on the flowmeter that is flowed by the pump to the reactor inlet until the outlet to the reservoir is measured the same. Plasma discharge is formed from the electrode poles (+) and (–) separated by a distance (0.5 cm); the parameters used to produce nitrate from free air include output voltage (3.4 kV and 6 kV), airflow rate (0.2, 0.4, respectively), and 1 L/min), treatment time (20, 30, and 40min), with a 2x3x3 factorial design of the parameters used, 18 test data were obtained. The test was carried out using 1 L of distilled water with a pH value of 5,8, which was fed with air from the plasma discharge ionization process results. The stages of the testing process include plasma generation in the reactor, plasma formation, and air flow to plasma and reservoir. plasma production from the distance between two electrodes which are given a high voltage through a transformer connected to a voltage shifter and an oscilloscope. the free air captured using an air pump with an air flow rate controlled by an airflow meter flows into a plasma reactor. The air that passes through the plasma reactor undergoes an ionization process and then flows into a reservoir that already contains distilled water.

2. Sample Analysis

The performance of the plasma discharge reactor to produce nitrate was conducted in a reservoir containing 1 L aquadest under three investigated parameters (voltage, airflow rate, and treatment time). 10 mL of sample were taken every 20, 30, and 40 minutes and diluted with water to 50 mL in a flask. Nitrate concentration was analyzed following (APHA 2012) Section 4500 NO_3-B method and measured with Shimadzu UV-VIS spectrophotometer (UV-1700). Sample and standard solutions were added 1 mL HCl 1 M before being measured using a UV-Vis spectrophotometer. Concentration of calibration standard solution was 0.1 mg/L; 0.5 mg/L; 1 mg/L; 2 mg/L; 3 mg/L and 5 mg/L (R>0.998). The Standards and samples were measured from the difference between absorbance data at 220 nm, and multiple absorbance data at 275 nm due to dissolved organic matter also may absorb at 220 nm and NO_3^- does not absorb at 275 nm.

RESULTS AND DISCUSSION

Characterization of Plasma. The experimental results reveal that the performance of the plasma discharge tube reactor in synthesizing nitrate production from the air is affected by three parameters, namely output voltage, airflow rate, and treatment time. This preliminary study is also to see the plasma formed from applying the voltage magnitude using a transformer-neon sign voltage source with a plasma discharge tube reactor. It was found that with the use of 0.5 cm electrode distance by adjusting the voltage to 2 kV and 3 kV plasma discharge was not visible, plasma discharge began to appear when the voltage was set to a value of 3.4 kV. Figure 2 shows that the change in voltage used produces a different plasma color, when the voltage of 3.4 kV plasma produced is purple, while when 6 kV changes slightly, the color results are close to white, see figure 2.

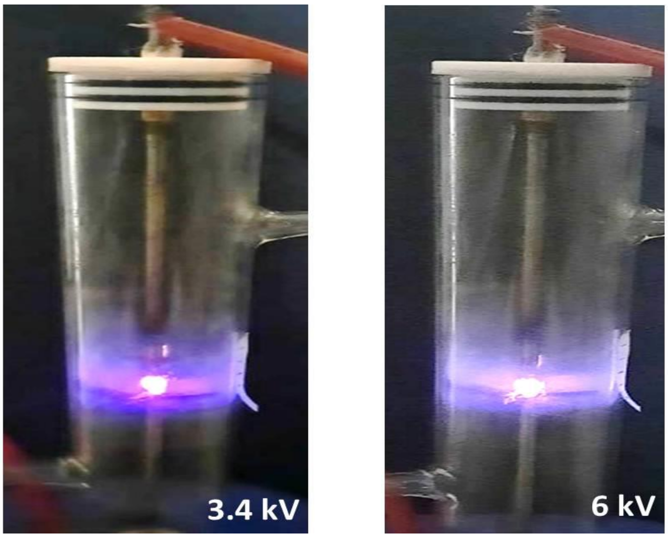

Figure 2. Plasma yield of 3,4 kV and 6 kV

Nitrate Production. Figure 3 shows that nitrate production increases with changes in voltage accompanied by variations in the time of the test, with the value of the airflow rate being constant continuously. This increase in production is due to changes in the magnitude of the electric field generated as the voltage increases in ionizing gas that passes through the gap in the plasma discharge reactor. This result is as per the research of Supeno and Kruus (2000); the increase in the voltage supplied to the reactor makes the plasma radiation produced increase and affects the rate of the reaction process in increasing production yields.

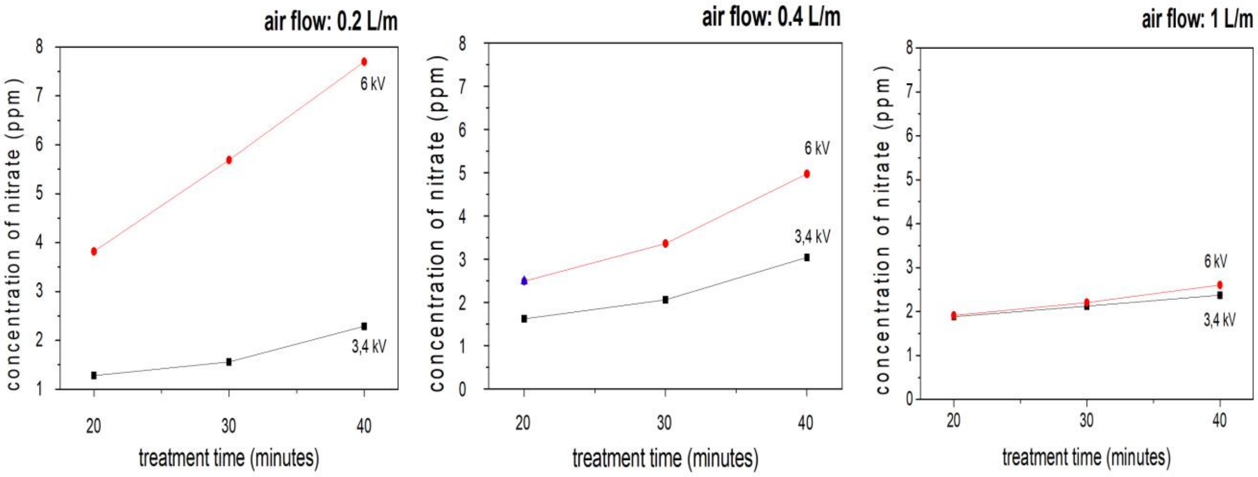

Figure 3. Effects of voltage on nitrate production

In observations during the experiment in Figure 4, nitrate production has an increasing trend when the airflow rate is 0.2, 0.4, 1 L/min with a voltage of 3.4 kV and a treatment time of 20-40 minutes. However, when 6 kV increases the voltage with an airflow rate of 0.4 L /min, the results obtained are lower than the results when using a flow rate of 1 L/min. This upward and downward trend is most likely influenced by the character of the plasma discharge formed on the magnitude of the voltage and the distribution rate of the ionized air molecules passing through the reactor. From the data obtained, adding treatment time has a linear effect on nitrate production under any operating conditions. The addition of treatment time and voltage will increase the degree of heat generated by the plasma discharge. It will affect the condition of the reactor body and electrodes, which is likely to impact the amount of nitrate levels produced.

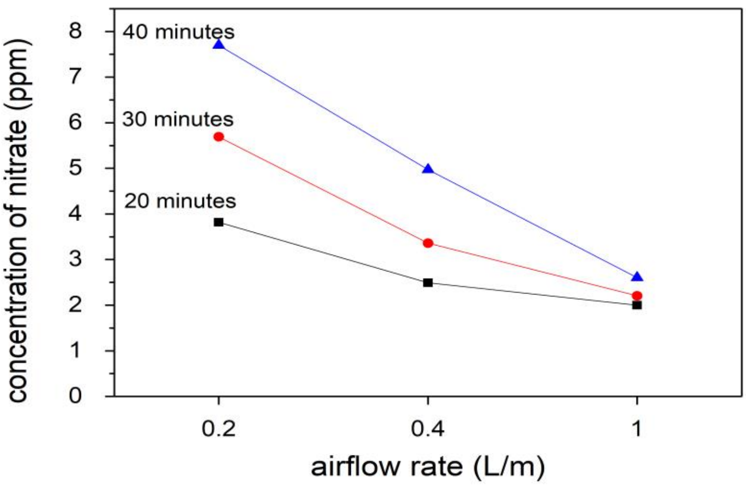

Figure 4. Effect of air flow rate on nitrate production

pH of effluent. The pH of air plasma-treated water decreased after the treatment from the initial pH 5.8. The effluent pH drops to 3-4 after the plasma process. It is primarily due to the accumulation of NO_3^- in the water (Graves et al. 2019). Figure 5 shows that the pH value in this test decreased with increasing voltage and treatment time which was inversely proportional to the concentration of nitrate produced with the same operation and treatment. The decrease in the pH value is due to the flow of air entering the water reservoir experiencing an increase in temperature resulting from the accumulation of ionized airflow, plasma discharge, and heat from the reactor body.

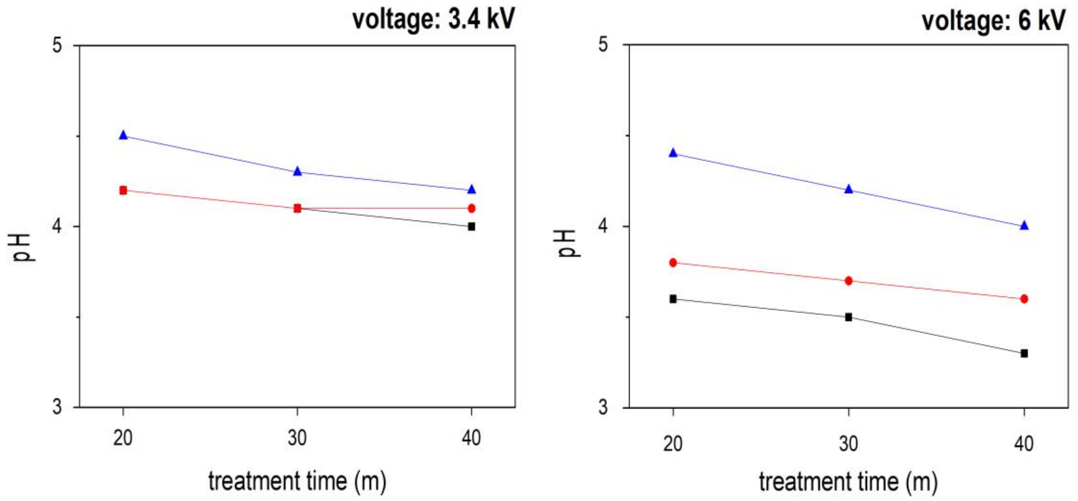

Figure 5. Change in pH of effluent after 20, 30, and 40 minutes in different condition with air flow rate 0.2 L/m (—■—), 0.4 L/m (—●—), and 1L/m (—▲—)

CONCLUSIONS

In this study, the plasma discharge reactor tube model's design was tested to produce nitrate from air N_2. The experimental data found that different operating conditions (voltage variation, treatment time, and air rate) affect the production results. The results show that nitrate changes linearly with changes in the applied voltage with a constant airflow rate and length of treatment time. The highest production is obtained when the voltage is 6 kV with a flow rate of 0.2 L/min with a treatment time of 40 minutes. Further studies should be carried out on the ability of plasma reactors to withstand heat and nitrate production with higher voltage or power experiments, material selection, and electrode spacing without changing the treatment time and airflow rates that have been investigated at this time.

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