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The Effect of pH on H_2O_2 and Nitrate Production in The Plasma Electrolysis Process

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Abstract. Plasma electrolysis is the newest method in the formation of environmentally friendly nitrogen fertilizers. Nitrogen fertilizer in the form of liquid nitrate from air injection in a K_2SO_4 electrolyte solution flowing direct current. Nitrate formation is influenced by the pH conditions of the electrolyte solution. This is related to the equilibrium of nitrate formation, which will decrease with decreasing pH. The results of this study, the effective plasma electrolysis process for the formation of nitrates, was carried out within 60 minutes with the initial acidity level of the K_2SO_4 electrolyte solution pH_o=6. During 60th minutes, the final processes pH_t=3, and the nitrate equilibrium shifts to the reactants to become nitrite, so at this point, the process is stopped so that there is no nitrate reduction. The pH condition also affects the formation of H_2O_2, which represents the presence of •OH as a nitrate forming radical. At pH=6, the amount of H_2O_2 produced was higher (0.62 mmol/L) than at 8.10 and 12 (0.42 mmol/L, 0.36 mmol/L, and 0.31 mmol/L). Nitrates produced at pH=6 were higher (1889 ppm) than at 8.10 and 12 (1635 ppm, 860 ppm, and 646 ppm).

INTRODUCTION

One of the important nutrients for plants is nitrogen. Its availability in the earth is very abundant, reaching 78% in the form of N_2 gas. N_2 gas cannot be used directly by plants as fertilizer because it is very difficult to break N_2 bonds into simple nitrogen compounds (NO_x)[1]. Nitrogen fertilizer is made in two forms, ammonia and nitrate. An old process and most commonly used in the fertilizer industry is the haber-bosch process to produce ammonia[2]. The weakness of Haber bosch is air emissions, so that the production of nitrogen fertilizers by plasma electrolysis was initiated in this study. Air plasma electrolysis is the latest technology that develops air plasma technology where plasma and air are formed in the liquid phase of electrolyte solutions with the help of electrical energy so that the intended nitrate compound can be directly in the form of a liquid[3]. This method effectively produces radical compounds that can help O_2 and N_2 gases from the air react with plasma to form large amounts of nitrate compounds. The working principle of making this liquid nitrate fertilizer is to inject air into the electrolyte solution where plasma is formed[4]. The application of this method is expected to have better performance and be more environmentally friendly when compared to conventional processes. The thing that needs to be considered in plasma electrolysis is the acid-base level of the electrolyte solution (pH) because it affects the formation of radicals that form nitrates. Previous research has succeeded in synthesizing liquid nitrate fertilizer with a concentration of up to a concentration of 700 ppm[5]. However, at the time of choosing the electrolyte, the researchers only considered whether the electrolyte could support the formation of nitrates in solution or not, not paying attention to the pH conditions and the formation of H_2O_2 as the equivalent of the nitrate forming •OH radical. In this research, it is necessary to analyze the pH of the plasma electrolysis operating conditions because it will be related to the formation of radicals that affect the production of nitrates. In addition, under certain acidity conditions, the absorption of NO_2 gas which is formed in the solution to be converted into NO_3 will decrease.

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MATERIAL AND METHODS

Equipments

Tools used in research are plasma electrolysis reactor with raw material that air injection (N_2 and O_2), 0.02 K_2SO_4 and operation condition in temperature 60ºC, 400 W, flowrate 0.8 lpm, and used tungsten for anode electrode and stainless-steel for the cathode. Other tools used UV-Vis Spectrophotometry Shimatzu 1800, analytical scales Metler Toledo, water bath, glassware in the laboratory.

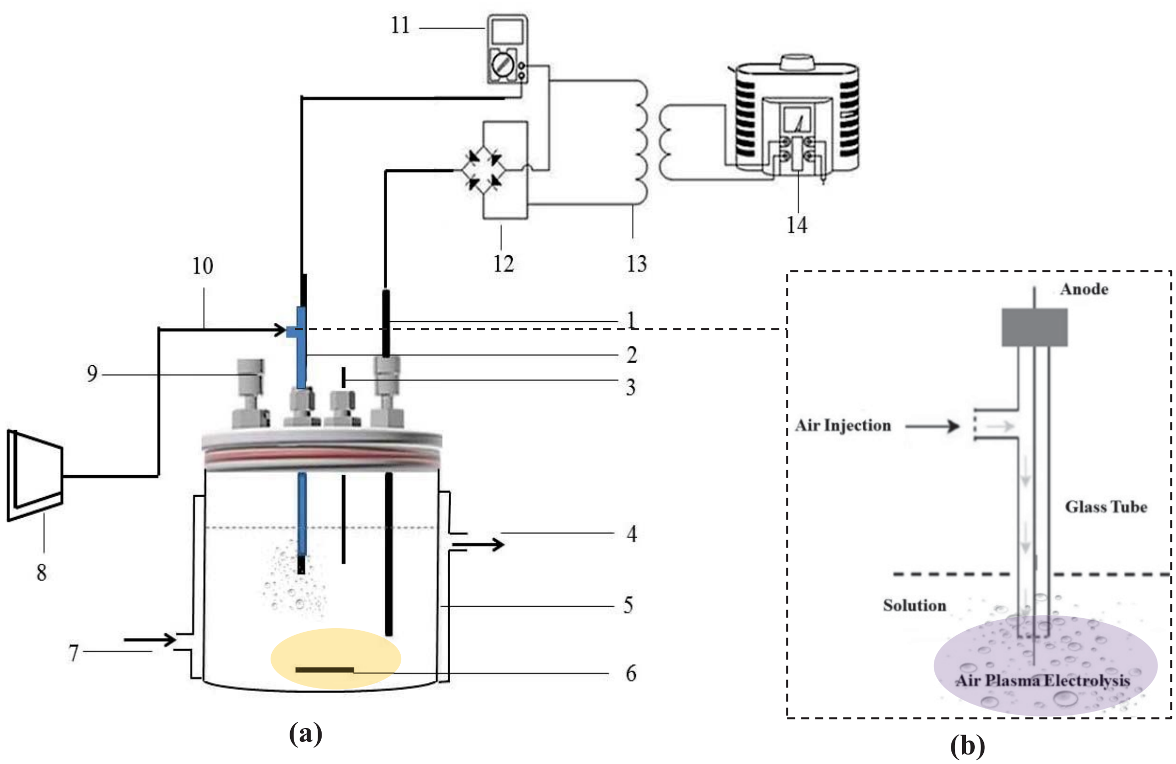

FIGURE 1. (a) Air Plasma Electrolysis Reactor (b) Illustration of air injection at a tungsten Picture description:

1. Cathode
2. Tungsten Anode
3. Temperature Sensor
4. Outlet Cooling Water
5. Cooling Jacket
6. Magnetic Stirrer Bar
7. Inlet Cooling Water
8. Aerator
9. Sample Port
10. Air Flow Injector
11. Multimeter and Power Analyzer
12. Diode Bridge
13. Transformator
14. Slide Regulator

Materials

Materials used including, air injection, distilled water, potassium sulfate, sulfuric acid, potassium permanganate, hach 2106169 nitriver 5 nitrate reagent powder.

Determination of H_2O_2

The measurement of the amount of H_2O_2 formed was carried out by the permanganometric titration method. The first stage before the titration process is dripping the sample with sulfuric acid (H_2SO_4) to provide an acidic atmosphere and prevent the formation of its MnO_2 compound from accelerating the decomposition of MnO_4^- ion because MnO_2 will affect the calculation quantity •OH. In an acidic environment, the MnO_4^- ion will be reduced to

$Mn^{2+,}$ thus prevent the permanganate ion decomposition reaction. The reaction that occurs can be seen in equation (1) below this.

$$2MnO_4^- + 5H_2O_2 + 6H + \rightarrow 5O_2 + 2Mn_2 + + 8H_2O \qquad (1)$$

After that, the heating and titration process is carried out. 0.01 N $KMnO_4$ solution was used as a titrant which will oxidize the reducing compound in the test solution to reach the endpoint of the titration. The endpoint of the titration is indicated by a change in the color of the solution from clear to pink. Apart from being a titrant, $KMnO_4$ also functions as an indicator in the titration process.

Determination of Nitrate

A total 1 mL of sample is added 10 ml distilled water and 1 g hach 2106169 nitriver 5 nitrate reagent powder, stirring and allowed to react for 30 minutes. The solution is put into the cuvette and read its absorbance at length wave 541 nm in UV-Vis Spectrophotometry Shimatzu 1800.

RESULTS AND DISCUSSION

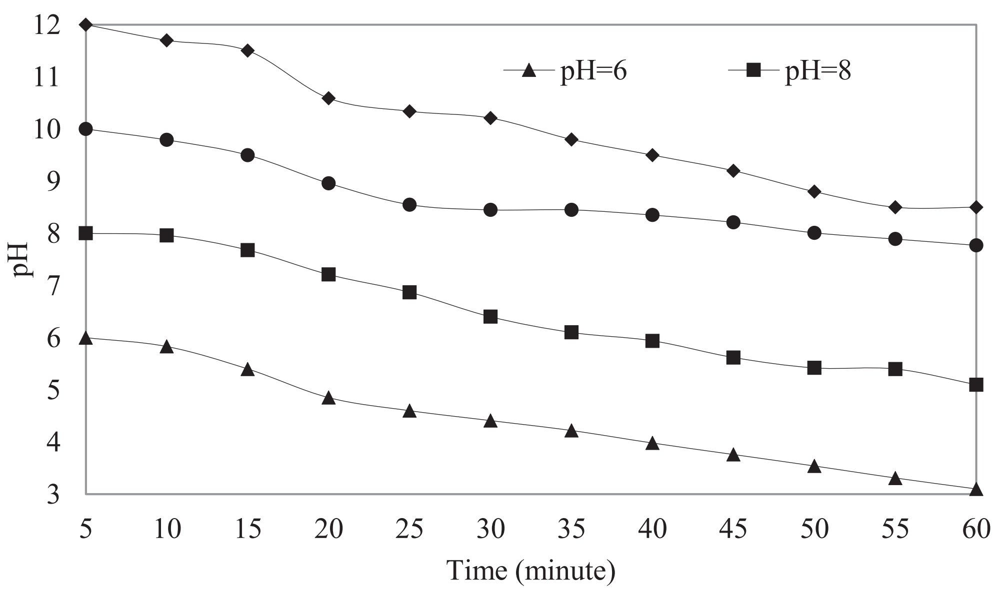

FIGURE 2. Initial pH (at Air Flow Rate of 0.8 lpm, 400W, Temperature 60°C)

Based on the consideration of nitrate equilibrium, the use of processing time should not be too long. So in this research, the synthesis of liquid nitrate was carried out with a processing time of 60^{th} minutes and a pH of 3-12. The greater the acidity value of the electrolyte solution used at various pH solutions, increasing the formation of the number of radicals produced during the electrolysis process. According to Le Chatelier, a low pH is a source of pressure for the system, and on the other hand, the system needs to adjust its pH so that it does not decrease further[6]. According to Jinzhang et al. (2008), by using a pH solution between 3-10.99, the reactive species •OH will increase at a smaller pH so that at pH=3 reactive species •OH is formed at most $15x10^{-4}$ mol/L than the one other pH. to determine the effectiveness of the nitrate formation that occurs[7]. Based figure 2 that both the control pH (6) and pH (8,10,12) decreased pH during 60^{th} minutes of the plasma electrolysis process. The final pH value varies, and in this study, a controlled pH (6) was used because in the 60^{th} minute the final value was pH=3. At low levels, the system will move the equilibrium between nitrate and nitrite to the reactants, where the nitrate concentration will decrease and be converted back into nitrite. If the resulting nitrate product has decreased, while the specific energy consumption continues to increase, the process must be stopped because it is no longer effective.

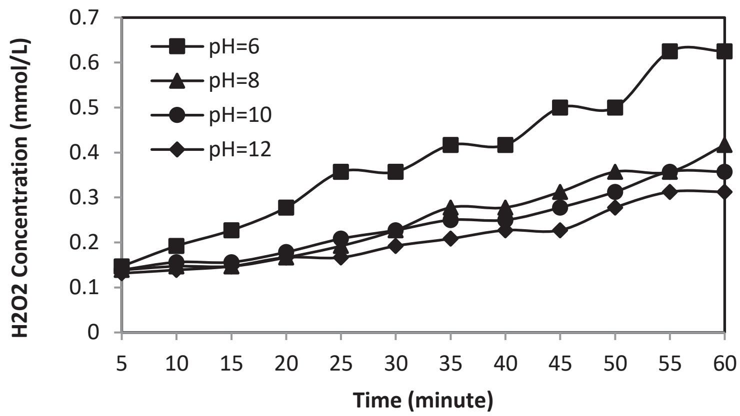

FIGURE 3. Effect of pH in H_2O_2 formation (at Air Flow Rate of 0.8 lpm, 400W, Temperature 60°C)

Figure 3 shows a series of H_2O_2 measurements at different pH. At controlled pH=6, the amount of H_2O_2 produced was higher (0.63 mmol/L) than at 8.10 and 12 (0.42 mmol/L, 0.36 mmol/L , and 0.31 mmol/L). A higher concentration of H_2O_2 represents •OH radical is obtained at a relatively lower pH. This could be attributed to the fact that there are more hydroxyl radicals stable at higher acidity. Therefore, the acid solution facilitates the formation of hydroxyl radicals. However, with a long reaction time, the hydroxyl radical concentration decreased with increasing pH. Because more hydroxyl radicals are generated in alkaline solutions, and more hydroxyl radicals can be degraded. As a result, H_2O_2 concentrations appear relative lower in a higher pH solution. H_2O_2 produce two •OH, and series of reactions propagate shown in reactions (2)-(4).

$H_2O_2 \rightarrow 2{\bullet}OH$ (2)

${\bullet}OH + H_2O_2 \rightarrow {\bullet}HO_2 + {\bullet}H_2O$ (3)

${\bullet}HO_2 + {\bullet}HO_2 \rightarrow H_2O_2 + O_2$ (4)

In alkaline pH condition the reaction mechanism in reaction (5)-(6)[8].

$3NO_3 + H_2O \rightarrow 2NO_2 + {\bullet}OH + OH^-$ (5)

${\bullet}OH \leftrightarrow H^+ + {\bullet}O$ (6)

The extra profits are manifold in the presence of the formation of H_2O_2 lies in a little NO_2 formed because NO_2 is quickly converted to NO_3 if H_2O_2 is present. So, with the right setting of the initial pH, the formed nitrate will be more optimal.

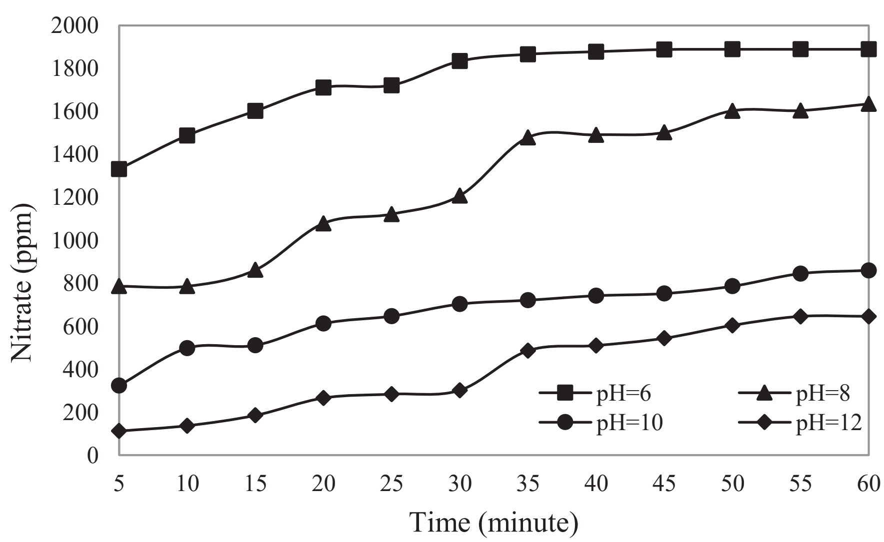

FIGURE 4. Effect of pH in nitrate production (at Air Flow Rate of 0.8 lpm, 400W, Temperature 60°C)

According to Le Chatelier low, pH is a source of pressure for the system. On the other hand, the system needs to adjust its pH to not experience a decrease in nitrate. The system will move the equilibrium between nitrate and nitrite to the reactants, where the nitrate concentration will decrease and be converted back into nitrite. HNO_2 is a weak acid (pKa HNO_2/NO_2 = 3,3) that reacts quantitatively to NO_2. Likewise with nitric acid (HNO_3), which is a strong acid that quantitatively leads to NO_3. As noted above, both types of acids can be generated in situ. in the plasma and then reacted. The production of HNO_2 and HNO_3 has the consequence of lowering pH. In the case of air as the carrier gas nitrogen oxides can be formed from well-known gas-phase reactions nitrogen and oxygen dissociate. Nitrogen oxides are influenced by pH resulting in the formation of acids and ions water as in the reaction (7)-(10)[9].

$$3NO_2 + H_2O \rightarrow 2H^+ + 2NO_3^- + NO \quad (7)$$

$$2NO_{2(g)} \rightarrow N_2O_{4(g)} + H_2O_{2(l)} \rightarrow HNO_{3(l)} + HNO_{2(l)} \quad (8)$$

$$NO_{2(g)} + NO_{(g)} \rightarrow N_2O_{3(g)} + H_2O_{(l)} \rightarrow 2HNO_{2(l)} \quad (9)$$

$$3HNO_{2(l)} \rightarrow HNO_3 + 2NO_{(g)} + H2O_{(l)} \quad (10)$$

NO produced by reactions (7) and (10) can also be is oxidized to NO_2 when air is used as working gas, thus increasing the nitrate concentration. Reaction hydroxyl radicals with NO_2 can also cause the formation of acids as in the reaction (11).

$$NO_2 + \bullet OH \rightarrow HNO_3 \quad (11)$$

Figure 4 details the effect of pH on nitrate formation. Higher nitrates were produced at control pH (pH=6) compared to pH=8, pH=10 and pH= 12. Nitrates produced at pH=6 were higher (1889 ppm) than at 8.10 and 12 (1635 ppm, 860 ppm, and 646 ppm). Overall when nitrates increase from pH=6 to pH=3, nitrates under other conditions follow the trend, but the nitrate concentration is lower because the efficiency of nitrate oxidation decreases with increasing pH[10].

CONCLUSIONS

Plasma electrolysis is effective as a method of producing liquid nitrate fertilizer by considering the pH conditions of the electrolyte solution. The level of acidity affects nitrate production, where the more acidic the nitrate will increase. However, according to the equilibrium of nitrate formation at low pH (pH=3) the equilibrium shifts to the reactants, which means that the nitrate will be reduced and shifted to the reactants (nitrite) so that the resulting nitrate is reduced. the amount of H_2O_2 formed is also the pH condition. H_2O_2 which represents the presence of OH radicals will increase in low pH conditions.

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