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The Effect of pH on H₂O₂ 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 K₂SO₄ 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 K₂SO₄ electrolyte solution pH₀=6. During 60th minutes, the final processes pH=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 H₂O₂, which represents the presence of •OH as a nitrate forming radical. At pH=6, the amount of H₂O₂ 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 N₂ gas. N₂ gas cannot be used directly by plants as fertilizer because it is very difficult to break N₂ 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 O₂ and N₂ 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 H₂O₂ 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 NO₂ gas which is formed in the solution to be converted into NO₃ will decrease.

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 $60^\circ C$, $400 W$, 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.

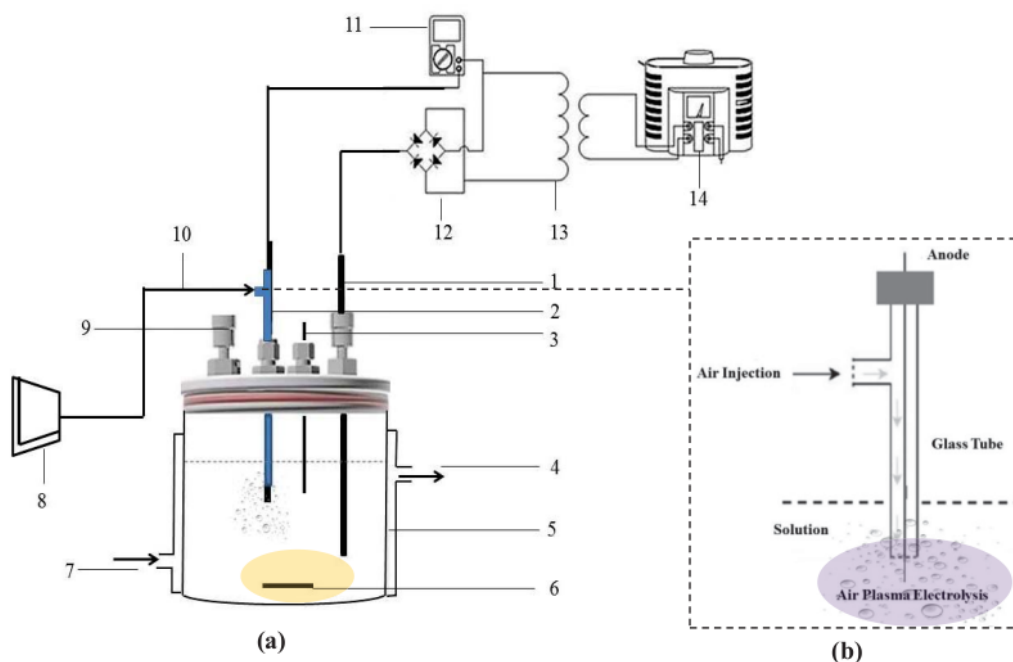


FIGURE 1. (a) Air Plasma Electrolysis Reactor (b) Illustration of air injection at a tungsten

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

Materials

Materials used including, air injection, distilled water, potassium sulfate, sulfuric acid, potassium permanganate, hach 2106169 nitrivier 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 $\bullet OH$. In an acidic environment, the MnO_4^- ion will be reduced to

Mn²⁺, thus prevent the permanganate ion decomposition reaction. The reaction that occurs can be seen in equation (1) below this.



After that, the heating and titration process is carried out. 0.01 N KMnO₄ 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, KMnO₄ 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 nitrive 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

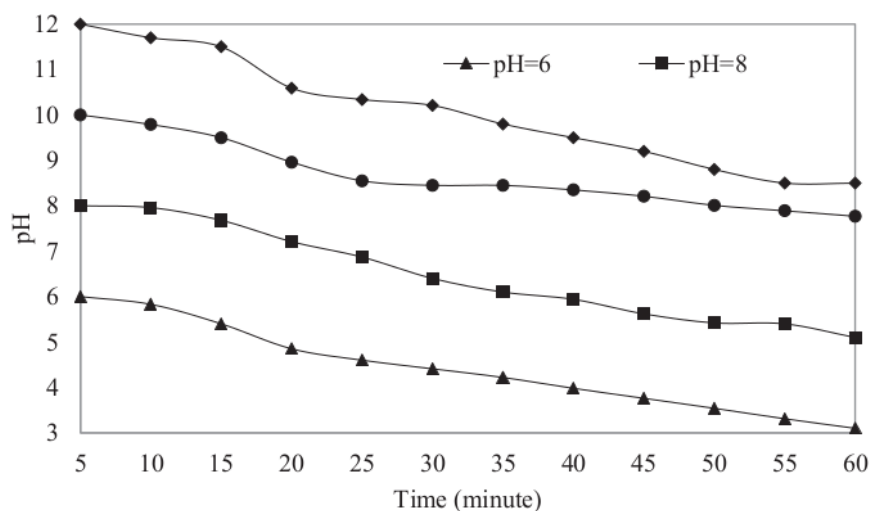


FIGURE 2. Initial pH (at Air Flow Rate of 0.8 lpm, 400W, Temperature 60°C)

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 60th 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 60th minutes of the plasma electrolysis process. The final pH value varies, and in this study, a controlled pH (6) was used because in the 60th 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.

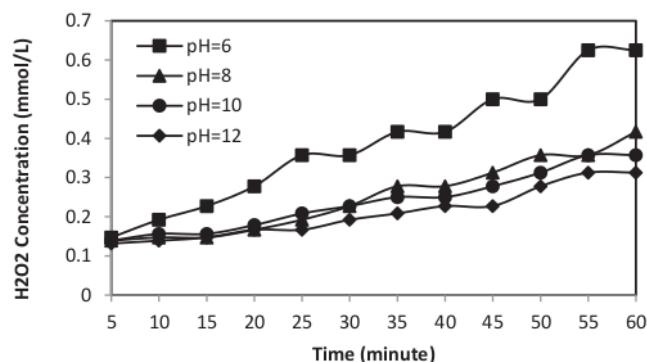
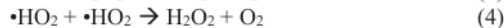
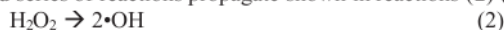
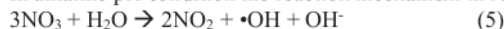


FIGURE 3. Effect of pH in H₂O₂ formation (at Air Flow Rate of 0.8 lpm, 400W, Temperature 60°C)

Figure 3 shows a series of H₂O₂ measurements at different pH. At controlled pH=6, the amount of H₂O₂ 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 H₂O₂ 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, H₂O₂ concentrations appear relative lower in a higher pH solution. H₂O₂ produce two •OH, and series of reactions propagate shown in reactions (2)-(4).



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



The extra profits are manifold in the presence of the formation of H₂O₂ lies in a little NO₂ formed because NO₂ is quickly converted to NO₃ if H₂O₂ is present. So, with the right setting of the initial pH, the formed nitrate will be more optimal.

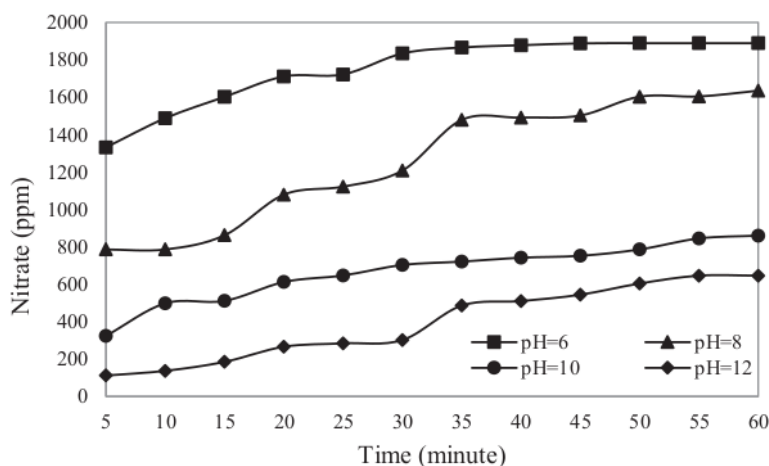
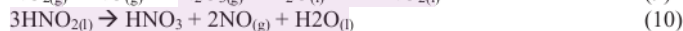
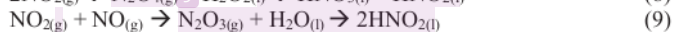
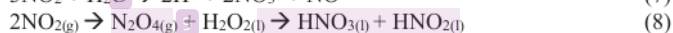


FIGURE 4. Effect of pH in nitrate production (at Air Flow Rate of 0.8 lpm, 400W, Temperature 60°C)

According to Le Chatelier law, 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. HNO₂ is a weak acid (pKa HNO₂/NO₂ = 3,3) that reacts quantitatively to NO₂. Likewise with nitric acid (HNO₃), which is a strong acid that quantitatively leads to NO₃. As noted above, both types of acids can be generated in situ. in the plasma and then reacted. The production of HNO₂ and HNO₃ 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].



NO produced by reactions (7) and (10) can also be oxidized to NO₂ when air is used as working gas, thus increasing the nitrate concentration. Reaction hydroxyl radicals with NO₂ can also cause the formation of acids as in the reaction (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 H₂O₂ formed is also the pH condition. H₂O₂ which represents the presence of OH radicals will increase in low pH conditions.

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