Effect of solution pH and conductivity on nitrate synthesis by air contact glow discharge electrolysis method

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Abstract. This study aims to determine the effect of pH of the solution and conductivity on the yield of nitrates formed. The method is carried out by plasma electrolysis made from air injection. The electrolyte solution used is a mixture of K2HPO4 and K2SO4. The pH condition of the solution is getting longer decreasing also has an effect due to acidic nitrate ions which are more formed if dissolved in water. If the condition of the solution the more acidic, the absorption power of NO2 gas formed in the solution to NO3 will decrease further, so that over time resulting in the production of nitrates in the solution will decrease. The research results showed that for 120 minutes the processing time was large The pH decreases due to the formation of acidic nitrates. Decreased pH can also be caused by H2O2 production. In minute 0 to minute 5, a significant decrease in pH of 2.99. This is due to accretion nitrate product for 5 minutes the process is very significant that is equal to 1277 ppm. While the decrease in pH at minute 5 to minute 120 is less significant, where the pH decreases around 0.09 to 0.02 due to increase nitrate products are not as large as 5 minutes of processing time. Then, the more acidic the solution causes nitrate production to decrease. In acidic conditions, absorption of NO2 gas formed in the solution to be converted to NO3 will decrease. The concentration of an electrolyte solution affects the conductivity of a solution, where the higher the concentration of an electrolyte solution, the conductivity of a solution will also be even greater. The amount of conductivity will affect the speed at which a plasma is formed.
1. Introduction
Plasma electrolysis or contact glow discharge electrolysis (CGDE) is non-conventional electrolysis, in which plasma is produced by direct or DC at an electrode, anode or cathode, and the surrounding liquid electrolyte [1-3]. In plasma electrolysis, many produce reactive species such as $\text{H}_2\text{O}_2$, OH, H, $e^-$, HO$_2^-$, and others. As a method rich in generating free radical species, this method can be used to induce unusual chemical reactions in a solution [1,4]. The reaction zones in plasma electrolysis are divided into two types. The first zone is located in the liquid phase near the surface between the electrolyte and plasma. The second zone is located around the electrodes. This reaction zone is illustrated in Figure 1 below.

![Figure 1. Plasma Electrolysis Reaction Zone](image)

In the plasma process, electrolytic gas bubbles form around the electrodes. If there is an increase in heat, there will be joule heating which results in the evaporation of the electrolyte solution, so that a thin layer or gas sheath is formed around the electrode [3-5]. The pH of a solution is between 3–10.99, the reactive species $\cdot$OH will increase at a smaller pH so that at pH = 3 reactive species $\cdot$OH that is formed at most reaches $15.10^{-4}$ mol/L compared to other pH. The longer the electrolysis process, the lower the pH of the solution. This is because the more acidic the solution becomes, the greater the plasma produced so that the production of hydroxyl radicals ($\cdot$OH) and hydrogen radicals ($\cdot$H) will increase. In acidic conditions, the absorption power of NO$_2$ gas which is formed in the solution to be converted into NO$_3$ will be reduced [1,2,4]. at a low pH of 4 has a higher nitrate yield than at a high pH (7). According to Le Chatelier, low pH is a source of stress for the system and conversely, the system needs to adjust its pH so that it does not decrease further. Thus, the system will move the equilibrium between nitrate and nitrite towards the reactants, where the nitrate
concentration will decrease and be converted back into nitrite [3-4]. Therefore, at low pH, it will produce a balance of the system against nitrite and reduce the nitrate concentration. If the resulting nitration product has decreased, while the specific energy consumption continues to increase, then the process needs to be stopped because it is no longer effective. So, based on the consideration of the nitrate equilibrium, the use of processing time should not be too long. So this research on liquid nitrate synthesis was carried out with a 30 minute process time with a pH of 3-12 to determine the effectiveness of nitrate formation that occurs [5-7].

The conductivity value of the water used can be increased by adding electrolyte compounds to the water, so that plasma can be formed in the electrolysis process[2,4,8]. If the conductivity value of a solution is too low, the available charge carrier becomes small in the system, then the resistance becomes very large and the required operating voltage must also be high to initiate the formation of plasma. Production of active species such as •OH, •H, and H₂O₂ radicals will also increase along with the increase in the conductivity of the solution. Thus, the conductivity value of a solution will affect the production of OH radicals which is characterized by increased H₂O₂ production[5,7,8]. The greater the acidity in the electrolyte solution used in the pH variation of the solution, increasing the formation of the number of electrons produced during the electrolysis process[9-10]. Research about pH and conductivity in nitrate synthesis not yet more do. The novelty from this research is how to know the effect of pH and conductivity for the nitrate synthesis process.

2. Material and Methods

2.1. Materials
The main ingredients used in the study include air (N₂ and O₂) Aquades used to function to thin the electrolyte solution used is a mixture of K₂HPO₄ and K₂SO₄ into an electrolyte solution with the desired concentration. Electrolyte solution used is a mixture of K₂HPO₄ and K₂SO₄ that can increase the conductivity of the solution. The concentration used is a mixture of K₂HPO₄ and K₂SO₄ electrolyte solution used was 0.01 and 0.02 M.

2.2. Instrument
In this study, the main tool in the form of a plasma electrolysis reactor is a batch equipped with a jacket which is an insulator as a place for cooling water to circulate and circulate using a pump. The air plasma electrolysis reactor scheme used is shown in the following figure 2.
Figure 2. (a) Schematic Air Plasma Electrolysis Reactor for Synthesis of Liquid Nitrate Fertilizers, (b) Air Injection with Glass Sheath

Caption: 1. Thermometer, 2. Anode, 3. Cathode, 4. Glass casing, 5. Baffle, 6. Electrolyte solution, 6. Electrolyte solution, 7. Cooling jacket, 8. Magnetic bar, 9. Magnetic stirrer, 10 Coolant water in, 11. Coolant water comes out, 12. Air inlet injector, 13. Compressor, 14. Multimeter, 15. Bridge diode, 16. Transformer, 17. Slide regulator.

The air plasma electrolysis reactor is made of a beaker tube which has an inner diameter of 14 cm, while the outer diameter for the cooling system is 19 cm. There is a lid on the top of the reactor which is equipped with two electrodes, namely the cathode and anode, and is equipped with a thermometer. Solid cylindrical cathode made of stainless steel SS-316 with a diameter of 6 mm. While the anode is made of tungsten and is equipped with a special circuit for the injection of air from the compressor to the anode which will then be channeled into the electrolyte solution. Electric circuits to generate electricity in plasma electrolysis reactors using electronic devices such as transformers, slide regulators, diode bridges to control voltage, and multimeters to measure electric current and voltage.

2.3. Methods
Before synthesizing liquid nitrate fertilizer using a plasma electrolysis reactor, it is first necessary to test the reactor performance. Tests carried out to obtain the characteristics of plasma formed in the glow discharge zone.
with a certain voltage range. For every voltage increase of 20 V, the current value is measured and the data taken. If the current value obtained is fluctuating, the current value is recorded for 1 minute then the average value is taken. Furthermore, the current measurement data can be made voltage range curves that are used with an increase of 20 V to the current. Plasma characterization tests were performed on each variation of electrolyte concentrations.

Electrolyte concentration variations used were a combination of 0.01 K₂HPO₄ and 0.01 K₂SO₄, a combination of 0.01 K₂HPO₄ and 0.02 K₂SO₄, and a combination of 0.02 K₂HPO₄ and 0.01 K₂SO₄. The value of the voltage and current ranges in the glow discharge zone can be determined by the plasma being formed is larger and stable when the magnitude of the current and voltage is directly proportional again. After creating a voltage-to-current curve, then making a voltage-to-power curve to determine the magnitude of the voltage used for variable variations at the same power. Measuring nitrate concentration with UV-Vis spectrophotometry. To find out the levels of nitrate (NO₃⁻) in a solution/water can using a UV-Visible Spectrophotometer with a measurement range of 0.01 mg to 1.0 mg NO₃⁻ N/L with cuvette thickness (path length) 1 cm or more, at length wave 543 nm.

3. Results and Discussion

3.1. Characterization of Currents and Stresses in Variations in the mixture of K₂HPO₄ and K₂SO₄ Electrolyte Solutions.

In this research, K₂HPO₄ and K₂SO₄ compounds are used as electrolyte solutions which are inert electrolytes that do not react with active species in the plasma. Ion K⁺ in the solution has the potential to react with nitrate compounds that are formed to form KNO₃ compounds whose existence is needed by plants[11-12]. Beside the phosphate and sulfate content in the solution is also expected to meet the nutrients needed for plants.

This research was conducted with variations in the composition of electrolyte solutions, namely a combination of 0.01 M K₂HPO₄ and 0.01 M K₂SO₄, a combination of 0.01 M K₂HPO₄ and 0.02 M K₂SO₄, a combination of 0.02 M K₂HPO₄ and 0.01 M K₂SO₄, and 0.02 M K₂SO₄. Current-voltage characteristic curve profiles on the variation of electrolyte solution composition are shown in Figure 3.
In Figure 3 it is known that 0.02 M K$_2$SO$_4$ enters the glow discharge zone first, then followed by a combination of 0.01 M K$_2$HPO$_4$ and 0.02 M K$_2$SO$_4$, a combination of 0.02 M K$_2$HPO$_4$ and 0.01 M K$_2$SO$_4$, and finally by a combination 0.01 K$_2$HPO$_4$ and 0.01 K$_2$SO$_4$. The use of variations in the composition of electrolyte solutions provides different solution conductivity. The greater the concentration of electrolyte used, the greater the conductivity value. This will affect whether or not the plasma is formed quickly due to the influence of whether or not electrons are sent in solution [11]. 0.02 M K$_2$SO$_4$ solution has a conductivity of 4.72 mS, a combination of 0.01 M K$_2$HPO$_4$ and 0.02 M K$_2$SO$_4$ has a conductivity of 3.48 mS, a combination of 0.02 M K$_2$HPO$_4$ and 0.01 M K$_2$SO$_4$ has a conductivity of 3.37 mS, and by a combination of 0.01 K$_2$HPO$_4$ and 0.01 K$_2$SO$_4$ has a conductivity of 2.4 mS. Solutions with greater conductivity will require high energy to achieve the stability of a plasma[12-14]. For example, at a voltage of 440 V, 0.02 M K$_2$SO$_4$ solution has a higher current value than other solutions. In determining the amount of voltage used in each variation of the composition of the electrolyte solution at the same power, the current-voltage curve is then converted to a power-voltage curve.
3.2. Effect of solution pH on nitrate synthesis

The pH condition of the solution which decreases more and more also has an effect due to acidic nitrate ions which are more formed when dissolved in water. If the condition of the solution becomes more acidic, the absorption of NO$_2$ gas formed in the solution to become NO$_3$ will decrease, so that over time the production of nitrates in the solution will decrease[2,10,11]. This is also supported by the experiment of the synthesis of liquid nitrate fertilizer by air plasma electrolysis method using K$_2$SO$_4$ 0.02 M electrolyte solution which shows that the pH value of a solution decreases with time. The decrease in pH during the processing time is shown in Figure 4 as follows.

![Figure 4. Relationship of pH with Processing Time in Synthesis of Liquid Nitrate Fertilizer by Plasma Electrolysis Method [0.02 M K$_2$SO$_4$ Solution, 600 Watt Power, 1.2 lpm Air Flow Rate, Anode Depth 2 cm, Temperature 60°C, Volume 3 L]](image)

Relationship of pH with processing time in synthesis of nitrate can be seen in Table 1.
Table 1. Relationship of pH with Processing Time in Synthesis of Liquid Nitrate Fertilizer by Plasma Electrolysis Method [0.02 M K₂SO₄ Solution, 600 Watt Power, 1.2 lpm Air Flow Rate, Anode Depth 2 cm, Temperature 60°C, Volume 3 L]

| Processing time (minute) | pH   | Nitrate Concentration |
|-------------------------|------|-----------------------|
|                         |      | ppm | mmol |
| 0                       | 7.24 | 0   | 0    |
| 5                       | 4.25 | 1277| 61.78|
| 10                      | 4.2  | 1364| 65.99|
| 15                      | 4.18 | 1491| 72.13|
| 20                      | 4.09 | 1529| 73.97|
| 30                      | 4    | 1606| 77.70|
| 60                      | 3.79 | 1988| 96.18|
| 90                      | 3.76 | 2055| 99.42|
| 120                     | 3.74 | 1991| 96.32|

Table 1 shows that during the 120 minutes of processing time the pH decreased due to the formation of acidic nitrates. The decrease in pH is also caused by the production of H₂O₂. In the 0th minute to the 5th minute, the pH decrease was quite significant at 2.99. This is because the addition of nitrate products during the 5 minute process is very significant at 1277 ppm. While the decrease in pH at minute 5 to minute 120 is less significant, where the pH has decreased around 0.09 to 0.02 because the addition of nitrate products is not as big as at 5 minutes of processing time. Then, the more acidic a solution is, the less nitrate production will be. In acidic conditions, the absorption power of NO₂ gas formed in the solution to be converted to NO₃ will decrease. This is also obtained the following table 2[15].

Table 2. Effects of pH on Nitrite and Nitrate Equilibrium

|            | pH 4 | pH 7 |
|------------|------|------|
| Initial Nitrate (mg/L) | 0    | 0    | 50  | 50  | 100 |
| NO₂ (mg/L) | 7    | 3    | 90.1| 81.6| 98.1|
The longer the processing time is used, the conversion decreases. This is because the increase in nitrate products decreases even though air injection into the system is stable at 0.4 lpm. However, at a certain time the nitrate produced did not increase or decrease, so that at that time the production of nitrates was inefficient. Nitrogen conversion is the ratio of nitrate products produced in mmol to the amount of air injected into the system. Air injected into the system is freely available and does not require a fee, so that whatever air is injected into the system is not a problem, then the aspect that needs to be considered is the resulting nitrate product, which will be better if the nitrated product produced is high[2,4,16]. On the other hand, the specific energy consumption will increase as time goes on. This can affect the costs incurred, wherewith the increase in energy used, the expenditure will increase as well. If the nitrated product produced has decreased, while the specific energy consumption continues to increase, then the process needs to be stopped because it is no longer effective. So, based on the previous explanation by considering the amount of nitrate produced, nitrogen conversion, and energy used, the use of the processing time should not be too long. Therefore in this research, the synthesis of liquid nitrate fertilizer was carried out with a processing time of 30 minutes.

3.3. Effect of Conductivity on Synthesis Nitrate
In this research, K₂HPO₄ and K₂SO₄ compounds are used as electrolyte solutions which are inert electrolytes which do not react with active species in the plasma. Potassium and phosphate content in the electrolyte solution is expected to meet the nutrients needed for plants, where potassium and phosphorus are known as primary macronutrients for plants other than nitrogen[17-18].

The concentration of an electrolyte solution affects the conductivity of a solution, where the higher the concentration of an electrolyte solution, the conductivity of a solution will also be even greater. The amount of conductivity will affect the speed at which a plasma is formed. However, if the concentration of the solution used is too high, such as more than 1% wt, the energy consumption becomes very wasteful and the temperature will be increasingly difficult to control. The electrical conductivity of a solution at 20°C can be seen in the following table 3.
### Table 3. Electrical Conductivity of the Solution at 20°C

| Electrolyte                  | Conductivity (mS/cm) |
|------------------------------|----------------------|
|                              | 0.5% mass | 1% mass |
| Kalium Dihidrogen Fosfat (KH₂PO₄) | 3         | 5.9     |
| Kalium Hidrogen Fosfat (K₂HPO₄)  | 5.2       | 9.9     |
| Kalium Sulphate (K₂SO₄)       | 5.8       | 11.2    |

The mechanism of nitrate formation is known that •OH radicals as reactive species play an important role in nitrate formation. In the anode part, more •OH radicals will be formed, while in the cathode part there will be more •H radicals, so in this study the plasma formed will be directed at the anode. Furthermore, the air injected at the anode will react with the reactive species to form nitrates in the electrolyte solution. Production of nitrate can be seen Table 4.

### Table 4. Concentrations and Amounts of Nitrates Formed in Variations in Electrolyte Solution Composition [700 Watt Power, 0.8 lpm Air Flow Rate Anode Depth 1.5 cm, Temperature 60°C]

| Time (minute) | 0.01 M K₂HPO₄ and 0.01 M K₂SO₄ | 0.02 M K₂HPO₄ and 0.01 M K₂SO₄ | 0.01 M K₂HPO₄ and 0.02 M K₂SO₄ | 0.02 M K₂SO₄ |
|---------------|---------------------------------|---------------------------------|---------------------------------|--------------|
|               | ppm    | mmol   | ppm    | mmol   | ppm    | mmol   | ppm    | mmol   |
| 5             | 1109.00| 26.83  | 1307.50| 31.63  | 1032.00| 24.96  | 1133.50| 27.42  |
| 10            | 1249.00| 30.21  | 1384.00| 33.48  | 1075.50| 26.02  | 1427.50| 34.53  |
| 15            | 1524.00| 36.87  | 1466.00| 35.46  | 1099.50| 26.60  | 1480.50| 35.81  |
| 20            | 1866.50| 45.15  | 1601.00| 38.73  | 1451.50| 35.11  | 1495.00| 36.16  |
| 30            | 2213.50| 53.54  | 1784.50| 43.17  | 1664.00| 40.25  | 1529.00| 36.99  |

From table 4, the highest nitrate production was obtained in a combination of 0.01 M K₂HPO₄ and 0.01 M K₂SO₄ electrolyte solutions with a yield of 2213.50 ppm, followed by a combination of 0.02 M K₂HPO₄ and 0.01 M K₂SO₄ with nitrate yield of 1784.50 ppm, then a combination of 0.01 M K₂HPO₄ and 0.02 M K₂SO₄ with a nitrate yield of 1664 ppm, and the lowest nitrate yield obtained in a 0.02 M K₂SO₄ solution with a result of 1529 ppm. The lower the conductivity value of a solution, the higher the nitrate produced. Nitrate production from highest to lowest is achieved by a combination of 0.01 M K₂HPO₄ and 0.01 M K₂SO₄, combination of 0.02 M K₂HPO₄ and 0.01 M K₂SO₄, combination of 0.02 M K₂HPO₄ and 0.02 M K₂SO₄, a combination of 0.01 M K₂HPO₄ and 0.02 M K₂SO₄.
K₂SO₄, and 0.02 M K₂SO₄ with each conductivity value of 2.4 mS, 3.37 mS, 3.48 mS, and 4.72 mS. At the same power usage, which is 700 Watt, the magnitude of the voltage used for each variation of the combination of solutions will be different, where the higher the conductivity of a solution, the smaller the process voltage used will be. The magnitude of the average process voltage for 30 minutes the processing time for each variation of the combination where the sequence from the smallest to the large is 0.02 M K₂SO₄ by 403 V, a combination of 0.01 M K₂HPO₄ and 0.02 M K₂SO₄ is 510 V, a combination of 0.02 M K₂HPO₄ and 0.01 M K₂SO₄ is 522 V, and a combination of 0.01 M K₂HPO₄ and 0.01 M K₂SO₄ is 547 V. Increasing voltage will affect the number and type of reactive species that are produced [6]. At low stresses, •OH and •H radicals will be produced, while at higher voltages, •O radical production begins to be detected and an increase in •OH and •H radical production. quick or concise compared to the help of •H and •OH radicals whose pathways for the formation of nitrates are more gradual[4,5,7].

4. Conclusion
The conclusion of this research is that plasma electrolysis is effective for nitrate synthesis under glow discharge conditions. The pH and conductivity factors greatly affect the amount of nitrate produced. At the beginning of the process the pH of the solution from 10.99 will decrease over time until it reaches pH 3. After pH 3 there is no decrease in pH anymore due to equilibrium. Conductivity is affected by the type of electrolyte used. In this study, a combination electrolyte of 0.01 M K₂HPO₄ and 0.01 M K₂SO₄ with a conductivity value of 2.4 mS resulted in the highest nitrate yield up to 2213.50 ppm.

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