Spectroscopic of Radicals Formed and Nitrate Production by Contact Glow Discharge Air Plasma Electrolysis

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Abstract. This research’s aims to determine the hydroxyl radicals formed and the production of liquid nitrate in the nitrate synthesis process using plasma electrolysis. Nitrate synthesis has been carried out by various methods including Haber Bosch nitrogen fixation. The synthesis of Haber Bosch nitrate actually causes high gas emissions and is not environmentally friendly. This has led to the synthesis of nitrate which does not cause emissions and is environmentally friendly, namely by plasma electrolysis. The methodology used in plasma electrolysis to produce liquid nitrate fertilizer, by injecting air into the tungsten anode and K$_2$SO$_4$ electrolyte. The hydroxyl analysis formed was carried out by looking at the IR spectrum measured using FTIR spectroscopy at an absorption band of 500 cm$^{-1}$ to 4000 cm$^{-1}$. Analysis of the nitrates formed was carried out using a UV-VIS spectrophotometer. The results obtained were that at $t = 10$ minutes OH and NH$_3$ radicals were formed at a wavelength of 3331.47 cm$^{-1}$ and 1634.63 cm$^{-1}$. The nitrate produced at 0.02 M K$_2$SO$_4$ with an airflow rate of 0.2 lpm resulted in an optimal nitrate of 269.12 ppm with an energy consumption of 82.95 kJ/mmol and a yield of 21.7% mol.

1. Introduction

The concept of plasma was first put forward by Langmuir. Langmuir defines plasma as gas ionized in a discharge electricity, so the plasma can also be defined as the mixing of neutral brushes of electrons, radicals, positive and negative ions[1,3,6]. Mixing of ions which are positively charged with electrons which are negatively charged have properties very different from gases in general and the matter in this phase called the plasma phase [2-5]. So in simple terms, plasma is defined as an ionized gas and is known as the fourth phase of matter after the solid, liquid, and gas phases [2,5-6].

Plasma is an area electron collision reactions are very significant to occur[7]. Plasma can occur when the temperature or energy of a gas is increased, allowing the gas to ionize will cause the gas to release its electrons which under normal circumstances surround the nucleus. Plasma is made by utilizing electric voltage,
namely by exposing two electrodes in free air [8,11,12]. At the same time, the electric voltage begins to flow (electrical discharge) This phenomenon is called an electrical breakdown. The greater the electric voltage applied to the electrodes, the greater ions and free electrons formed[9,11-12]. Plasma Discharge is plasma discharge which can be operated at atmospheric pressure [10]. A discharged plasma with a dielectric barrier is formed in the electric field non-uniform, which occurs in the area around the enabling electrode the ionization and formation of high-energy electrons in the area[5,10,13]. Research on Nitrate synthesis from air using plasma technology is starting developed by Birkeland-Eyde (1903). Air plasma nitrogen fixation process provides advantages including simple, operable and process instantaneous, high energy for a very fast reaction, resulting smaller units, and generally do not cause pollution [14,16,18].

Air plasma nitrogen fixation is generally carried out by reaction of nitrogen with oxygen or hydrogen to produce nitrogen oxides (nitric acid) or ammonia [15,17,19]. The use of plasma electrolysis incorporates the principle of plasma formation in the gas phase by electrolysis. Plasma electrolysis technology is a process electrolysis is carried out at a voltage high enough to form electric sparks due to the excitation of electrons, giving rise to plasma in the electrolyzed solution. The plasma will produce reactive species in large quantities thereby increasing the breaking of bonds in water and nitrogen in the air. On plasma electrolysis to produce liquid fertilizer nitrate, using air injection as the main feedstock for its nitrogen source required. Plasma electrolysis is a method of electrolysis where The plasma is generated by direct current (DC) between the electrodes and the electrolyte surface at the surroundings. Plasma electrolysis stems from conventional electrolysis developed by increasing the operating voltage to very high up to formed plasma.

Plasma electrolysis or contact glow discharge electrolysis (CGDE) is a non-conventional electrolysis, where plasma is produced by direct current or DC at the electrode, anode or cathode, and the liquid electrolyte at surroundings [20-22]. There is an anode with an oxidation reaction and a cathode with a reaction reduction. Plasma electrolysis can break down water molecules into \( \cdot \text{OH} \) and radicals hydrogen (\( \cdot \text{H} \))[5,13,19-20]. \( \cdot \text{OH} \) is the strongest oxidizing agent with an oxidation potential of 2.8 mV. Plasma electrolysis is an electrochemical process which is energized by a DC current with a high enough voltage at the two electrodes and electrolyte surface to produce plasma in solution (Sangupta et al., 1991). some of the H\(_2\)O molecules break down into H\(_2\), O\(_2\) and H\(_2\)O\(_2\) as a result of attacks from H\(_2\)O\(^+\) (gas) from the anode plasma. The reactive species \( \cdot \text{OH}, \cdot \text{H} \) and H\(_2\)O\(^+\) diffuse across the plasma layer towards the electrolyte stream then reacts one with the ones other or react with the active substrate in solution[23-25,27,29]. Nitrate synthesis process using plasma electrolysis causes the discharge to form channels that are conductive so that the electrons are very energized high yield in water can ionize, dissociate and / or recombine water molecules[26,28,30].

2. Material and Methods

2.1. Material
The main ingredients used in research include air (N₂ and O₂). Aquades used to dilute K₂SO₄ electrolyte becomes electrolyte solution with the desired concentration. 0.02 M Potassium Sulfate (K₂SO₄) Sulfate serves as an electrolyte solution that can increase the conductivity of solution.

2.2. Instrument
Shimadzu UV VIS Spectofotometer, FTIR spectroscopy, the plasma electrolysis reactor. Plasma electrolysis reactor is made of a beaker tube which has a diameter inside of 14 cm. There is a cover at the top of the reactor which is equipped with two electrodes, namely the cathode and anode, and is equipped with a sensor temperature and condenser are illustrated in Figure 1. The cathode is cylindrical solid made of stainless steel SS-316 with a diameter of 6 mm. While the anode is made of tungsten and has a special assembly for the housing air injection from the compressor to the anode which will then be channeled to in the electrolyte solution.

![Figure 1. Air Plasma Electrolysis Reactor](image)

2.3. Methods
Before synthesizing liquid nitrate fertilizer using a reactor plasma electrolysis, first it is necessary to test the performance of the reactor. Testing conducted to obtain the characteristics of plasma formed in the glow zone discharge with a certain voltage range. Every 20 V increase in voltage, the current value is measured and the data is taken in temperature : 60°C and flow rate : 0.2 lpm. Spectroscopic characterization of radical formed was analyzed by FTIR spectroscopy. Nitrate production formed was analyzed by Shimadzu UV VIS spectrophotometer.

3. Results and Discussion
3.1. Glow Discharge Zone
Value of a certain voltage will have a certain current value for each concentration variation electrolytes and variations in air flow rate. In addition, this data is also needed for knowing the voltage value required to make each variation possible at the same power. The same power value indicates the same plasma performance. The voltage used in the plasma electrolysis process must be above the voltage critical. Figure 3 is a current-voltage characteristic curve the process of plasma electrolysis using a 0.02 M K₂SO₄ solution.
In this study, the electrolyte used was K₂SO₄ because it has excellent conductivity for electrolysis and capable of generating highly reactive species, such as the Na₂SO₄ compound in studies previously, however, this compound is more reactive due to the elemental potassium. Based on Figure 2, it can be seen that the curve shows a decrease first until you reach a point (V_d) and then climb back up. In this electrolysis process, the zone of decline is called the transition zone, where the current value is inversely proportional to the value of the voltage due to the formation of the air shroud in around the anode, which results in the formation and breaking process gas bubbles from the solution causing an oscillation in the current. The sheath can blocking the flow of electrons towards the anode. The electron is then excited and causing the gas to ionize and form plasma. Point V_d is a turning point, called the critical voltage or midpoint voltage [9,11,27-28]. Then the ascending curve represents the glow discharge zone, where the current begins to increase as the voltage increases, the plasma is more stable, and the light emitted becomes brighter. In this zone also reactive species more has been formed so that it is in this zone that the nitrate synthesis process is carried out.

Glow discharge zone was chosen as the process zone because in this zone the number of OH radicals produced, have been able to produce an effective reaction and plasma that is stable and bright. The glow discharge zone occurs after passing ohmic zone or Faraday electrolysis which is characterized by the appearance of gas bubbles around the anode occurs and has passed the transition zone where it starts. The formation of a gas shroud caused by the bursting of gas bubbles causes the current to oscillate [7,22]. The hallmark of the zone glow discharge is the value of the current rising when the voltage is increased, the gas shroud formed is stable, the plasma light is bright and the sound when processing is sufficient toned [1,4,8-9].

3.2. Spectroscopy FTIR Analysis for Radical Formed

The FTIR spectrum of a 0.02 K₂SO₄ electrolyte solution at an operating time of 10 minutes shown in Figure 2.
From Figure 3, FTIR wavelengths are in the frequency band between 500 to 4000 cm\(^{-1}\). At the operating time \(t = 10\) minutes, it was shown that the radicals formed were •OH and NH\(_3\) which were shown at the peak of the absorption band 3329.58 cm\(^{-1}\) and 1634.57 cm\(^{-1}\). The FTIR peak shows that •OH radicals are still formed but the amount is less than at \(t = 10\) minutes. This is because the •OH radicals are oxidized to NO\(_2\) and NO\(_3\). This is in accordance with the picture which is shown in Figure 4 as follows.

![Figure 3. Air Plasma Electrolysis FTIR Spectra](image)

**Figure 3.** Air Plasma Electrolysis FTIR Spectra

![Figure 4. Radical Formed by Fotolisis UV[24]](image)

**Figure 4.** Radical Formed by Fotolisis UV[24]
In Figure 4, nitrogen with an injection rate of 2 mg-N/L forms ammonia (NH$_3$) at t=0 minutes and •OH radicals which are indicated by the number of H$_2$O$_2$ compounds. Synthesis of nitrates using air plasma electrolysis with raw material abundant availability will result in cheap financing. So that the composition of the air is an important factor in nitrate synthesis. Fixation experiments nitrogen to NO and NO$_2$ using a limited air plasma at the N$_2$/O$_2$ ratio in the 0.25-4 range. In the experiment, the NO concentration increased to the ratio feed reaches 3. NO$_2$ concentration reaches its peak at the same ratio feed with 1. At an N$_2$/O$_2$ feed ratio of about 1, both NO and NO$_2$ selectivities approximate 50%, but at a higher feed ratio, both experimentally has increased NO selectivity, while NO$_2$ selectivity shows opposite trend. This is logical, since NO$_2$ production by oxidation of NO becomes less on the increase in the N$_2$ fraction. When the N$_2$/O$_2$ feed ratio is below 1 (60%) then the NO$_2$ selectivity formed was only 40%. This is because of the rate of formation NO$_2$ decreases. Meanwhile, the hydroxyl radical (•OH) that comes from breaking water bonds can also react with NO$_2$ to form nitrate ions or with NH$_3$ to form various intermediate species leading to the formation of NO$_3^-$ ions too, due to its nature which is a strong oxidizing agent with very high energy. This is what underlies the position where the plasma is formed directed to the anode position. The formation of nitrate in this reaction is dominated by role OH radicals and the nature of •OH radicals in oxidizing NH$_3$ forming NO$_3^-$ which occurs rapidly [24]. Product The final nitrogen obtained is in the form of nitrate, the ammonium being formed will quickly be oxidized to ammonia which will be further oxidized to nitrate. At higher energies, the number of radicals produced will also be more and with high stress will produce a radical variation more [8,26,28]. With increasing radicals and •OH radicals produced, the more nitrate products will be obtained.

3.3 Nitrate Production
Species •OH is the reactive species with the highest levels of oxidation that can be oxidizes nitrogen from the air to nitrate. •OH radical species are widely produced by plasma due to gas ionization from the joule heating effect of water from the solution [9]. The water molecule will split into •OH because of the high energy electrons which is excited to the plasma. •OH radicals have a very short residence time, which is about 3.7 x 10$^{-9}$ seconds [18]. The •OH radicals formed can recombines with each other to form H$_2$O$_2$. In addition to the N$_2$ gas that it reacts with •OH becomes nitrate, O$_2$ gas which is a component in air reacts with H$_2$O molecules to form H$_2$O$_2$ and O$_3$ [5,9]. Increasing the air rate can increase the formation of H$_2$O$_2$ compounds, which is presumed will increase the reaction of nitrogen or other intermediate NO$_X$ compounds to nitrate directly or via •OH first, where H$_2$O$_2$ is formed from each other •OH radicals react and dissociate again to produce •OH [9,24]. The air injected into the anode will react with reactive species form nitrate compounds which will dissolve directly in the electrolyte solution. In this study, nitrate production is shown in Table 1.
Table 1. Nitrate Production by Air Plasma Electrolysis

| Flow rate (lpm) | Operation time (menit) | Nitrate Production (ppm) | Nitrate Production (mmol) | Specific Energy Consumption (KJ/mmol) |
|-----------------|------------------------|--------------------------|---------------------------|-------------------------------------|
| 0.2             | 1                      | 63.92                    | 1.546                     | 23.28                               |
|                 | 2                      | 98.56                    | 2.384                     | 30.20                               |
|                 | 3                      | 161                      | 3.895                     | 27.73                               |
|                 | 4                      | 164.16                   | 3.971                     | 36.26                               |
|                 | 5                      | 190.4                    | 4.606                     | 39.08                               |
|                 | 10                     | 255.68                   | 6.185                     | 58.21                               |
|                 | 15                     | 269.12                   | 6.510                     | 82.95                               |
|                 | 20                     | 254.1                    | 6.147                     | 117.14                              |

Based from Table 1, The air that is injected into the anode will react with reactive species form nitrate compounds which will dissolve directly in the electrolyte solution. the predominant reactive species for nitrate formation is \( \cdot \)OH. \( \cdot \)OH radicals will more is formed at the anode therefore plasma is directed to form at the anode. visually, 600 watts of power is effectively used at a lower flow rate of 0.2 lpm. the highest amount of nitrate that can be formed is at a K\(_2\)SO\(_4\) concentration of 0.02 M in the 15th minute with a nitrate of 269.12 ppm with an energy consumption of 82.95 kJ / mmol and a yield 21.7% by mol. Based on Table 1 also, the smallest specific energy consumption is at the first minute in the electrolyte concentration of 0.02 M, namely 23.28 kJ / mmol, and change / delta The smallest specific energy consumption is between the 3rd minute and 4th minute. This shows in the 4th minute the most efficient increase in the amount of nitrate compared to other measured points. nitrate formation process requires more \( \cdot \)OH radicals than with other radical species due to the reaction pathway of nitrate formation via \( \cdot \)OH radicals has the largest reaction rate constant [18,24,26]. Energy density will increase the amount of NO\(_2\) production but then the amount of NO\(_2\) decreased dramatically at a certain point which is caused by the NO\(_2\) formed reacts with N radicals to form N\(_2\)O. After 15 minutes, nitrate production has decreased. This is because NO\(_2\), which is in the dissolved gas phase, reacts with O\(_3\) and N radicals will cause the equilibrium in the solution to shift towards the left so that the nitrate formed will be encouraged to turn into NO\(_2\) in order to achieve equilibrium. specific energy consumption will continue to increase with increasing time. As the processing time increases, the amount of energy consumed will also increase which results in high processing costs for electrical energy needs. One of the goals of nitrate synthesis using plasma electrolysis is lower operating costs. So this research has encouraged parameter characterization in order to reduce the specific energy consumption. The reduction in specific energy consumption has a good impact because the process costs required for electrical energy needs will be lower. Specific energy consumption is the ratio between the electrical energy required for the production of nitrate (mmol). Thus, the greater the amount of nitrate produced, the specific energy
consumption decreases, where the increase in air flow rate to the optimum point gives the resulting nitrate more and more. Process conditions that are no longer efficient are indicated by an increase in air flow rate resulting in decreased nitrate production accompanied by an increase in energy consumption [20,24,27].

**Conclusion**

This research concludes that plasma electrolysis by air injection at the anode can be applied as a method for liquid nitrate synthesis. This of course becomes enlightenment for the production of liquid fertilizer. In this study, one of the influential radicals is hydroxyl radical. The hydroxyl radical test was carried out using FTIR at a wavelength range of 500 to 4000 cm⁻¹. The production of liquid nitrate reaches 269.12 ppm which is produced from the plasma electrolysis process that has met the plant's need for nitrate fertilizer at 100-300 ppm.

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