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Research Article
Air Injection Effect on Energy Consumption and Production of Hydroxyl Radicals at Plasma Anode

Tulus Sukreni, Nelson Saksono and Setijo Bismo

Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, 16424, Depok, Indonesia

Abstract

Background and Objective: Plasma anode has been known as a very productive method of producing hydroxyl radicals that oxidize effectively in almost all organic and non-organic liquids. This research was conducted to investigate the effect of air injection and anode depth variation on required energy for plasma generation and production of hydroxyl radicals. **Materials and Methods:** A batch reactor (diameter 130 mm, height 190 mm) with tungsten electrodes (cathode diameter 6 mm and anode diameter 0.5 mm) was used by applying a continuous cooling system. The experimental parameters were composed of different rate of air injection (0, 2, 4 and 6 L min^{-1}) and various depth of anode (5, 25, 45 and 65 mm). The current was observed at various voltage (20-700 V) in 30 sec for each voltage. **Result:** The energy consumption of plasma formation was getting smaller at a higher rate of air injection, while at deeper anode position, the energy consumption found higher. Although the $^{\cdot}OH$ production became lower at a higher rate of air injection, the process efficiency observed higher. **Conclusion:** This research clarified that air injection on plasma anode and the anode depth position affected the energy consumption and production of hydroxyl radicals where the addition of air injection and variation of the anode depth could reduce energy consumption and also improved process efficiency.

Key words: Air injection, anode depth, energy consumption, hydroxyl radical, plasma anode

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Corresponding Author: Tulus Sukreni, Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, 16424, Depok, Indonesia Tel: +62 81229799924

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INTRODUCTION

The research on plasma electrolysis which is a part of advanced oxidation process (AOP) technology is still being developed. The plasma formed at the anode in electrolyte solution under certain conditions can produce free radicals, especially non-faradaic radical hydroxyl ($^{\cdot}OH$)[1]. Hydroxyl radicals are strong oxidizers that can oxidize almost all organic and non-organic liquids. However, the energy efficiency, which is the ratio of $^{\cdot}OH$ generated to the energy consumption during plasma electrolysis process, still needs to be improved due to the high-energy use in plasma formation[2,3]. During electrolysis plasma process, plasma formation which is preceded by the formation of the sheath on certain electrode caused by Joule heating requires the greatest energy consumption[1,4].

Increasing the energy efficiency of the process can be performed by optimizing the operating conditions, such as changing the depth of anode and adding the gas bubbles to the reactor that affect lower energy consumption or higher production of OH. In depth variations of 0.5, 10 and 20 mm, it was seen that at a deeper anode position, more energy was used for creating a continuous sheath[5]. In the previous experiment, the contact area of the anode increased with the deeper the anode was in the solution[5]. Therefore, the energy consumption for the sheath formation became larger. The plasma electrolysis process in this experiment used the anodes with the same surface area, so the change of energy consumption was only a function of the anode depth position.

The addition of gas bubbles into the solution also affects the energy of plasma formation where discharge propagation was much easier in bubbling water than that at no bubbling water[6], so it drastically reduced the required input power. The gas type, gas injection rate and gas injection mechanism greatly affect the plasma characteristics formed[7]. The gas used in this experiment was the air which is injected directly into the plasma through the anode sheath with a certain flow rate to give a more significant effect on the energy consumption. In this experiment, the plasma electrolysis process was carried out with variation of anode depth and air flow rate to determine the effect of each variable on energy consumption, the production of hydroxyl radicals and efficiency of the process.

MATERIALS AND METHODS

The research was conducted from May-December, 2017 in Intensification Laboratory of Chemical Engineering Department, University of Indonesia. The main tool used in this study is a plasma electrolysis reactor in which the circuit of equipment can be seen in Fig. 2. The plasma electrolysis reactor is made of a transparent tube with diameter of 130 mm and height of 190 mm equipped with cylindrical cathode with diameter of 6 mm and anode of 0.5 mm made of tungsten-coated glass (quartz). The voltage source of the electrode reactor came from the State Electricity Company (PLN) and has been controlled by using slide regulator, transformer and bridge diode. The reactor was filled with 2 L of electrolyte solution with concentration of 0.02 M Na_2SO_4. The air was injected into the reactor using a compressor with certain rate measured by a flow meter.

The process of plasma formation began with a normal (conventional) electrolysis characterized by the formation of gas bubbles on the electrode. At this stage, the increase of the voltage was directly proportional with the increase of the current. The current flowing at certain voltage was observed for 30 sec with multi-meter. After the voltage was increased surpassing the breakdown voltage (V_B), gas bubbled from hydrogen, oxygen and water vapor and form gas layers that enclose the anode. Measurements were performed for the voltage, current, time and temperature of the solution from the beginning of the electrolysis to the formation of stable plasma electrolysis. Based on the data obtained, a curve of voltage-current characteristic was created to determine the value of V_B and I_B at different anode depth and variation of air injection rate. The plasma energy consumption (E_B) can be calculated using the equation:

$$E_B = V_B \times I_B$$

The measurement of the $^{\cdot}OH$ generated was based on the amount of H_2O_2 in solution under certain conditions where

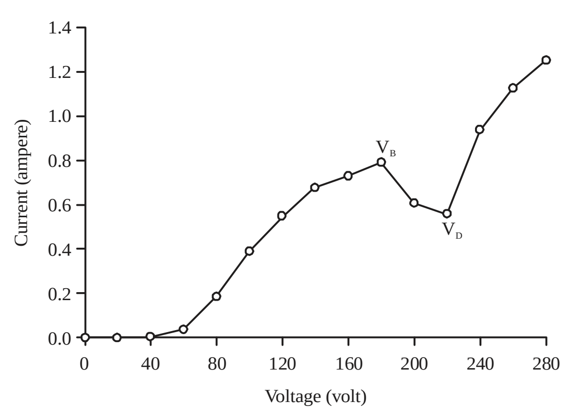

Fig. 1: Curve of voltage-current characteristic[9] of 0.02 M Na_2SO_4 electrolyte solution at 15 mm depth of anode and temperature 65 °C

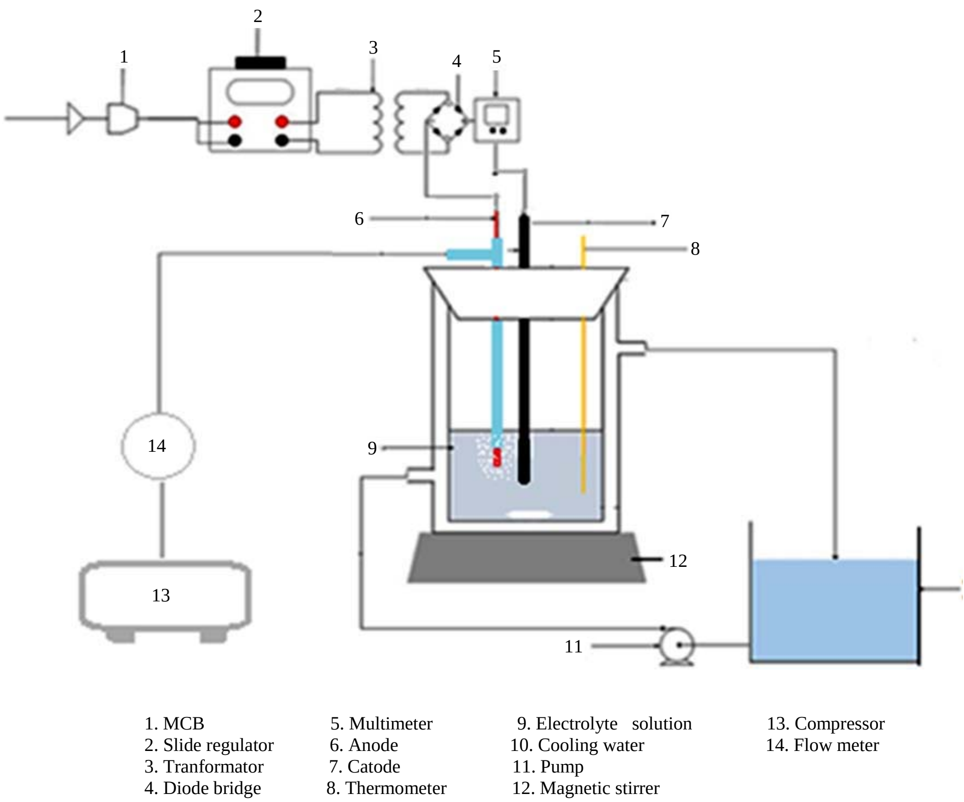

Fig. 2: Schematic of a plasma electrolysis reactor circuit

the measurement of H_2O_2 concentration was performed by using titration permanganometric method. The measurement conditions during plasma electrolysis process were carried out at temperature 55°C and voltage 700 V for 5 min. The analysis was performed on 25 mL sample taken from the solution, added strong acid (H_2SO_4 8 M) and then heated. After reaching temperature of 80-90°C, the solution was titrated with potassium permanganate ($KMnO_4$) 0.01 N.

Plasma formation: The process of plasma formation begins with the formation of the gas sheath which caused by the joules heating around the anode. The phenomenon of the gas sheath formation to the plasma formation in the plasma electrolysis process can be illustrated using the characteristic curve of current (I) and voltage (V)[8]. The I-V curve has certain characteristic during the occurrence of plasma electrolysis (Fig. 1)[9], from the figure can be identified several zones:

- **Ohmic zone $0<V<V_B$:** The current has a linear increase with the increase of voltage by the Ohm's law. In this zone occurs conventional electrolysis, which characterized by the presence of gas bubbles around the anode. The higher the voltage, the greater the current flow until it reaches the breakdown voltage (V_B)[10]. The absence of current line at the beginning of the curve, at very low voltage (0-40 V) indicates the absence of current flow since the electrolysis process has yet occurred
- **Transition zone: $V_B<V<V_D$:** The current begins to decrease as the voltage increases due to the formation of the gas sheath around the anode. The oscillations occur in the current due to the formation and breakdown of gas bubbles simultaneously. The voltage that causes the current to reach its lowest point is called the midpoint voltage (V_D)[11]
- **Plasma zone: $V> V_D$:** The current begins to increase as the voltage increases and the light emitted becomes brighter. The colors emitted correspond to the metal ions in the electrolyte solution[3]

The characteristic curve can determine the value of voltage and current on the plasma formation (V_B and I_B) and its energy consumption (E_B). While the effectiveness of the process in this experiment was seen from the amount of $^{\cdot}OH$ generated compared to its energy consumption. The generation of $^{\cdot}OH$ is derived from water molecules that dissociated, ionized and excited by vibration/rotation[12] according to the following equations:

$$\text{Dissociation: } H_2O+e\rightarrow{}^{\bullet}OH+{}^{\bullet}H+e \quad (1)$$

$$\text{Ionization: } H_2O+e\rightarrow 2e+H_2O^+ \quad (2)$$

$$H_2O^++H_2O\rightarrow{}^{\bullet}OH+H_3O^+ \quad (3)$$

Excitation by vibration/rotation:

$$H_2O+e\rightarrow H_2O^*+e \quad (4)$$

$$H_2O^*+H_2O\rightarrow H_2O+{}^{\bullet}OH+{}^{\bullet}H \quad (5)$$

$$H_2O^*+H_2O\rightarrow H_2+{}^{\bullet}O+H_2O \quad (6)$$

$$H_2O^*+H_2O\rightarrow 2{}^{\bullet}H+{}^{\bullet}O+H_2O \quad (7)$$

Equation 5-7 showed that the presence of vibration/rotation causes the excited water molecules (H_2O^*) to transform into lower energy molecules by forming some active radicals ($^{\bullet}OH$, $^{\bullet}H$ and $^{\bullet}O$). De-excitation of free radicals, which have high energy, to a more stable state at lower energy causes the generation of emission from ultraviolet radiation[7]. The hydroxyl radical has a very short life-time (3.7×10^{-9} sec)[13] and is very easy to recombine into H_2O_2. Therefore, the amount of OH was calculated based on the amount of H_2O_2 formed by titration permanganometric method (redox titration) using potassium permanganate[14].

This research observed the effects of anode depth and air injection on various phenomena like energy consumption, $^{\bullet}OH$ production and process effectiveness. The air was injected directly to the anode plasma through a glass pipe that covered the anode. A comparison was made between air injected and non-air injected discharge at different anode depth positions and air injection rates. Some tests were performed to determine the plasma energy consumption and generation of the $^{\bullet}OH$ on variable of the anode depth position (5, 15, 25, 45 and 65 mm) and air injection rates (0, 2, 4 and 6 L min^{-1}).

Statistical analysis: To identify the strength of the effect that the independent variable(s) have on a dependent variable were explained using the linear regression method. The value of coefficient of determination (R^2) can be used to predict the contribution of the influence of independent variables on the dependent variable.

RESULTS AND DISCUSSION

The data in Fig. 3 showed the energy consumption of plasma forming became lower due to the addition of air injection compared to process without the air injection. The higher the rate of air injection, the plasma forming energy consumption found lower. The presence of gases in solution can decrease the energy required in plasma formation since the gas has lower dielectric constant than water[6]. The higher airflow rate injected directly to the plasma had caused the ionization process during the formation of plasma required less energy. The addition of air caused an increase in the amount of oxygen in the solution where oxygen has a low ionization potential[7] of 13.61 eV.

The anode depth variation showed that the deeper the anode in the solution, the greater energy of plasma formation required. Several previous studies have shown similar results[1,5] but there are differences on the contact area of the anode. In the previous experiment, the contact area of the anode increased with the deeper the anode in the solution. Therefore, the energy consumption for the sheath formation became larger. In this experiment, the area of contact was made fixed by installing the glass sheath on the anode. Thus the increase in energy in the addition of depth occurred due to the hydrostatic pressure. The deeper the anode position, the greater the hydrostatic pressure, so the higher energy (E_B) required to form the plasma sheath.

As Fig. 4 showed that by adding air injection, the $^{\bullet}OH$ generated became less compared to the plasma electrolysis process without the air injection. The higher the airflow rate was injected, the amount of $^{\bullet}OH$ generated also decreased. Previous experiments showed that the addition of air or other gases (O_2, N_2, Ar, He) into the plasma electrolysis processes

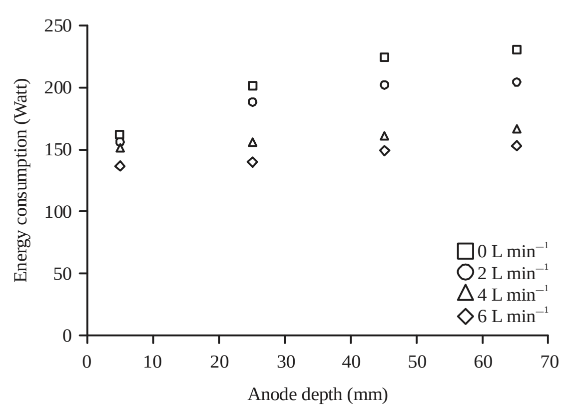

Fig. 3: Energy consumption of plasma formation (E_B) at temperature 55°C

could increase the amount of OH[7,15-17]. In contrast to previous experiments, in this research, the gas injection performed directly on the plasma region. Direct air injection with a high flow rate can disrupt the process of plasma formation. The addition of air injection can reduce energy consumption. Nevertheless the decreasing in the amount of energy required in plasma formation affects the amount of ·OH generated. Based on visual observations, the plasma formed without air injection looked quite large with the bright light of the discharge. Whereas by adding air injection in the anode, the higher the airflow rate was injected, the discharge of plasma looked smaller and the light was dimmer. So it can be concluded that the amount of ·OH generated from the plasma electrolysis process is influenced by the discharge of the plasma. Furthermore, there was a relationship between the plasma formed during the plasma electrolysis process and its energy consumption. The greater the energy during the process, the larger the plasma was formed[1]. As Fig. 5 showed the relationship between energy and the amount of ·OH generated. With linear regression method, the R^2 value close to 1. It can be concluded that the energy consumption during plasma electrolysis process was directly proportional to the production of ·OH. The energy consumption of the plasma electrolysis process is related to Joule heating or the energy of plasma sheath formation around the anode[1]. The gas sheath formed can be observed visually from the size of the plasma discharge where the higher the flow rate of air injection, the smaller the plasma was formed. When the energy consumption becomes smaller, the gas sheath formed becomes insufficiently stable, so the discharge of plasma will be smaller with dimmer light. Meanwhile, the plasma intensity formed affects the formation of ·OH where the smaller the plasma is formed, the process of dissociating of ·OH formation will also decrease.

Although the addition of air injection causes the amount of ·OH generated to decrease, the addition of air injection may increase the effectiveness of the process, where the ratio of the amount of ·OH generated to the energy consumption was

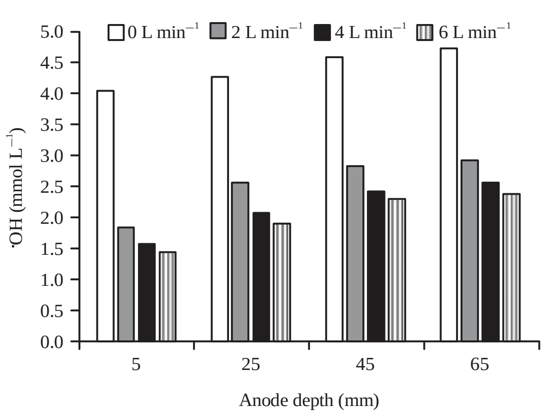

Fig. 4: Amount of ·OH generated at temperature 55°C

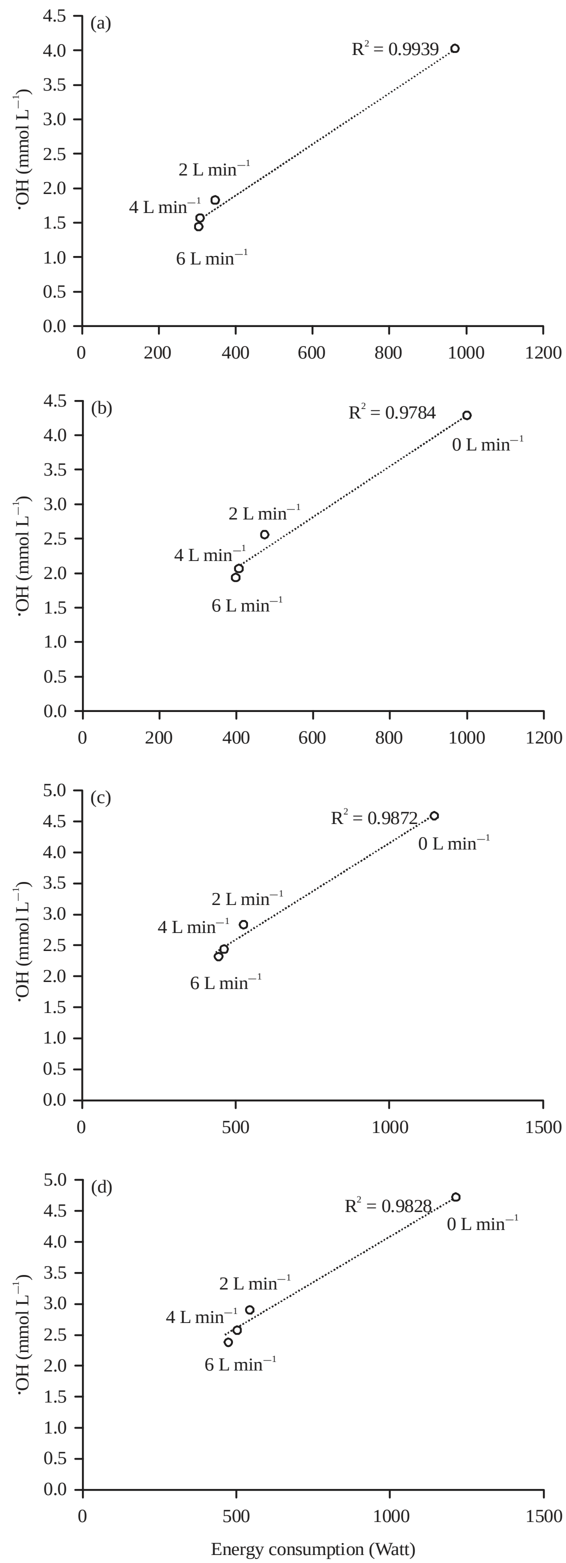

Fig. 5(a-d): Energy consumption in plasma electrolysis with ·OH generated

Table 1: Energy consumption and ·OH formed for various rate of air injection

Rate of air injection (L min^{-1})	Voltage (volt)	Current (ampere)	Energy (watt)	·OH (mmol L^{-1})
0	500	1.31214	656.072	1.6576
2	700	0.77143	540.000	2.9120
4	700	0.71364	499.545	2.5536
6	700	0.67293	471.053	2.3744

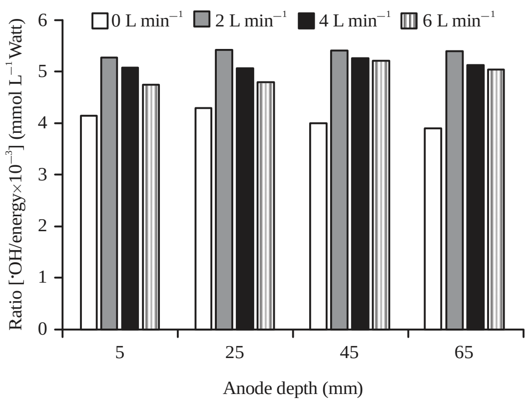

Fig. 6: Energy effectiveness at 55°C

seen to increase (Fig. 6). Moreover, if the production of ·OH was compared to similar energy consumption, the amount of ·OH production in the plasma electrolysis process with air injection is higher than the process without air injections (Table 1).

CONCLUSION AND FUTURE RECOMMENDATIONS

It can be concluded that the amount of ·OH produced is affected by energy consumption during plasma electrolysis. However, the addition of air injection results in an increased ratio of the amount of ·OH generated to the energy required during the process. At the same amount of energy consumption, the production of ·OH along the process with air injection becomes greater than the process without air injection.

Finally, it is clear that anode depth position and air injection are important parameters in plasma electrolysis method to reduce energy consumption and improve process efficiency. The addition of air injection during the plasma electrolysis process can decrease the energy consumption for plasma formation. However, the decrease of energy during plasma electrolysis process influences the production of OH where the resulting OH becomes less. So it is necessary to determine the optimum conditions on pre-research to obtain low energy consumption and also high process effectiveness.

SIGNIFICANCE STATEMENT

This research was conducted to optimize the operating conditions that affect the energy consumption and production of ·OH such as changing the depth of anode and adding the gas bubbles to the reactor. The addition of air injection results in increased ratio of the amount of ·OH generated to the energy required during the process in all variation of anode depth. Moreover, at the same amount of energy consumption, the production of ·OH in the process with air injection becomes greater than the process without air injection.

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