

HYDROGEN PRODUCTION SYSTEM USING NON-THERMAL PLASMA ELECTROLYSIS IN GLYCEROL-KOH SOLUTION

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ABSTRACT

Hydrogen is one of chemical industry feedstock and automobile fuel, which is commonly produced by electrolysis. Electrolysis, however, has several constraints that are primarily due to its large energy requirement. Plasma electrolysis is a breakthrough method that not only improves hydrogen production but also suppresses energy consumption. This research has been conducted to investigate the effectiveness of plasma electrolysis on hydrogen product quantity and energy consumption by varying the voltage and glycerol concentration. The results of this research showed that an increase in voltage led to increased hydrogen production and energy consumption; the addition of glycerol caused a decrease in hydrogen production but still resulted in an increase in energy consumption. The process effectiveness of plasma electrolysis at 300V and 0.1M KOH was 8.1 times higher than Faraday electrolysis.

Keywords: Hydrogen production; Plasma electrolysis

1. INTRODUCTION

Hydrogen is an important reactant and energy carrier manufactured from a variety of energy sources, such as hydrocarbon-based fuels, through steam reforming or partial oxidation. In areas where natural gas is not available, hydrogen can be produced from water using the process of electrolysis. The cost of producing hydrogen by water electrolysis, however, is much more expensive than the cost of the conventional process of using hydrocarbons as feedstock because of the high electricity requirements of water electrolysis (Holladay et al., 2009). Non-thermal plasma electrolysis is an alternative method that has been developed to reduce electricity use.

Many types of non-thermal plasma-assisted reforming technologies for Hydrogen production have been implemented in recent years. The most notable examples are plasmatron, gliding arc, dielectric barrier discharge (DBD), corona, microwave, and pulsed discharge. Reformed hydrocarbons include methane, diesel, and biofuel. Among the possible innovative reforming options, plasma systems provide original responses to drawbacks of other technologies in terms of reactivity, compactness, and efficiency (Petitpasa et al., 2007). Experiments conducted by Chaffin et al. (2006) presented plasma electrolysis in an aqueous environment as a new plasma technology for hydrogen production.

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Plasma electrolysis technology is similar to the conventional electrolysis process but it runs with high voltage until plasma is formed in the electrolyzed solution. The plasma produces reactive species in large amounts, increasing water bond separation and the formation of hydrogen by up to 8 times when compared to conventional electrolysis (Mizuno et al., 2003). Plasma is known more as an ionized gas flow, and in this research, plasma formed on the liquid medium that had been saturated with hydrogen gas bubbles during the plasma electrolysis process. Plasma formed in the negative pole (cathode), which had been placed adjacent to the anode to reduce the electron route from positive pole to negative pole. Hydrogen formed in the cathode room, where hydrogen did not mix with oxygen that had formed in the anode room. Adding several additives such as methanol and ethanol to the electrolyte solution increased process productivity significantly (Zong-cheng et al., 2006; Zong-cheng et al., 2008; & Zong-cheng et al., 2009).

This research describes a design-scheming of the semibatch reactor for non-thermal plasma electrolysis, which includes a plasma generator that is able to create up to 300 V (DC). The reactor features a coolant and product separation system. Use of KOH as the electrolyte solution and glycerol as an additive are expected to increase process performance.

2. METHODOLOGY

There are three main components in this experiment, include electrolysis reactor, coolant system, and purification system which explained as follow.

2.1. Electrolysis reactor

The scheme for the reactor and experimental set up for the plasma electrolysis system is shown in Figure 1. The reactor is made from transparent filter housing, with a diameter of 8 cm, height of 25 cm, and capacity of 1000 mL. There is an output hole for Hydrogen and Oxygen, and the thermometer and anode are positioned above, while the cathode is positioned below the anode room. Wolfram was used to create electrode material while minimizing corrosion. The reactor was filled with 600 ml of 0.1 M KOH solution and glycerol additive. KOH is a strong electrolyte that is generally used in plasma electrolysis; it is more effective in producing hydrogen than other electrolytes (Zong-cheng et al., 2006). Power supply used was Matsunaga Slide Regulator with 50 Hz frequency and maximum voltage of 500 V. The AC current was converted to a DC current by using a diode-bridge before connecting to the electrode inside the reactor.

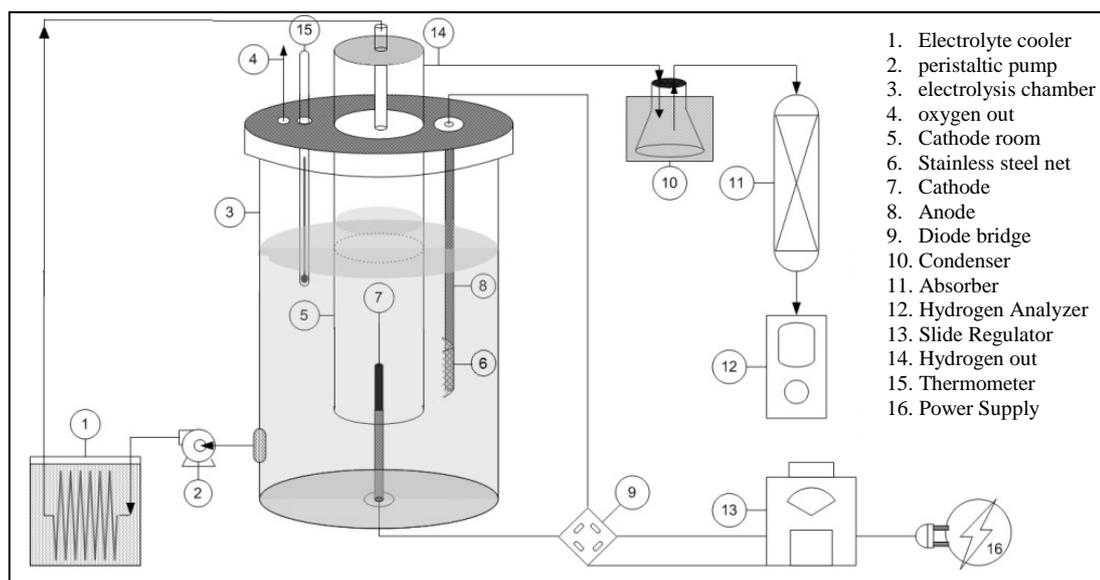


Figure 1 Experimental Set Up

2.2. Coolant system

The KOH electrolyte solution flowed through copper-made cooler coil in the electrolyte cooler using a peristaltic pump in closed circulation. The electrolyte flow rate controlled the reactor temperature. The temperature of the reactor was maintained at 90 °C to optimize performance (Saksono et al., 2010).

2.3. Purification system

Water vapour in the produced hydrogen was separated with a steam trapper in a two-stage condenser. Silica gel was used as the water vapour absorbent; vessel measurements were 5 cm in diameter and 20 cm tall. The composition and the flow rate of hydrogen were measured with a GNL-400F Hydrogen Analyzer (ChangAi Electronic Science & Technology Co. Ltd China). The effectiveness of plasma electrolysis process in this research was measured with the parameter of comparison of hydrogen production in plasma electrolysis versus the Faraday electrolysis process; it is stated as $G(H_2)$. Faraday electrolysis produces the maximum amount of hydrogen conventionally. Process effectiveness, $G(H_2)$, can be formulated in Equation 1, as follows (Zong et al, 2009):

$$G(H_2) = \frac{V_{H_2} / 24}{Q / 2F} = \frac{V_{H_2} \cdot F}{12Q} \text{ mol.mol}^{-1} \quad (1)$$

Q , F , and V_{H_2} are, respectively, the flowing electric charge (Coulomb), the Faraday constant, and the volume of the H_2 product.

3. RESULTS AND DISCUSSION

This research describes plasma formation in the electrolyte solution, and the behaviour of temperature, current, and plasma electrolysis on hydrogen production. Additionally, the influence of voltage and the glycerol additive in hydrogen production, electricity consumption, and process effectiveness of plasma electrolysis, as compared to the Faraday electrolysis process, are discussed.

3.1. Plasma formation phenomenon

The initial stage of plasma electrolysis is the conventional electrolysis process that is marked with hydrogen gas formation on the cathode and oxygen on the anode (Figure 2a and 2b). Figure 2a shows that only a small amount of hydrogen bubbles is initially formed around the cathode; the solution temperature is around 40°C. As the temperature increases, the formation of hydrogen bubbles increases (Figure 2b), causing solution conductivity to decrease and resistance of the solution to increase (Figure 2c). The resistance of the electron current occurring from the cathode and anode due to hydrogen gas in the solution causes the electron to leap towards the anode without going through solution ions. It is marked with the plasma flash, as shown on Figure 2d. Plasma formation in the 0.1M KOH solution occurs at 60°C and 200 V (DC). In this research, the result was consistent with the experimental research of Mizuno et al. (2003).

Figure 3 shows that during the first 220 seconds, the only reaction that occurs is electrolysis, which is characterized by low production of hydrogen. In this study, the temperature reached 60°C and the electric current reached 10 A. The measured electric current increased steadily during the electrolysis process without fluctuation due to the electron transfer mechanism that occurred as it progressed through the conductive solution (electrolysis mechanism). The subsequent formation of plasma was marked by a decrease of the electric current and an increase of H_2 production (marked by thick dashes in Figure 3).

Up to 2000 watts of electric power is needed in the electrolysis process to reduce and oxidize water at the anode and cathode. The reduction reaction equations are written as follows:

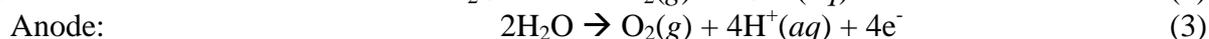


Figure 3 shows that, when the plasma begins to form, the electric current decreases dramatically from 9.5A to an average of 3A, and the power decreases from 1900W to 600W. Zong (2006) identified the phenomenon of decreasing current and the formation of plasma at 220V in 0.02M KOH solution. The measured current when the plasma forms is fluctuating because the electron transfer mechanism is changing as the electron flows through the conductive solution (electrolysis mechanism) and hydrogen gas ionization (plasma). The decreasing electric current that occurs in plasma electrolysis shows that the electric power consumed is also decreasing, because the voltage is maintained at 200V. This phenomenon shows that the plasma electrolysis process is able to run after a electrolysis process. Saturation of the solution by hydrogen gas causes the resistance of the solution to escalate, forcing high-energy electrons to leap from cathode to anode when the gas is ionized (Chaffin et al., 2006).

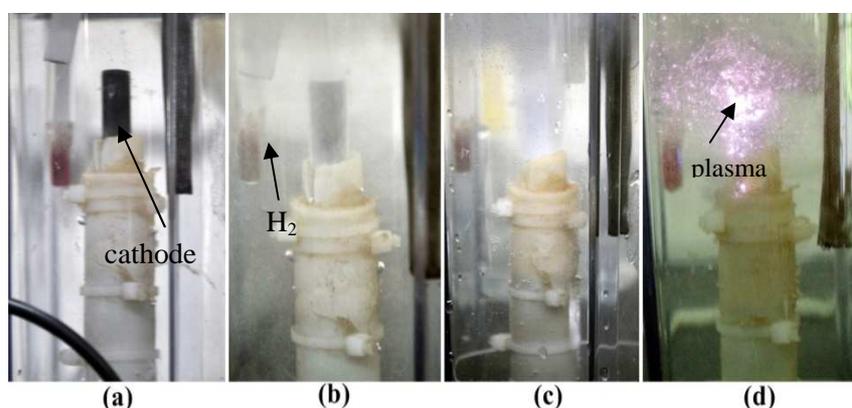


Figure 2 Formation of plasma at 0.1M of KOH solution and 200V (DC)

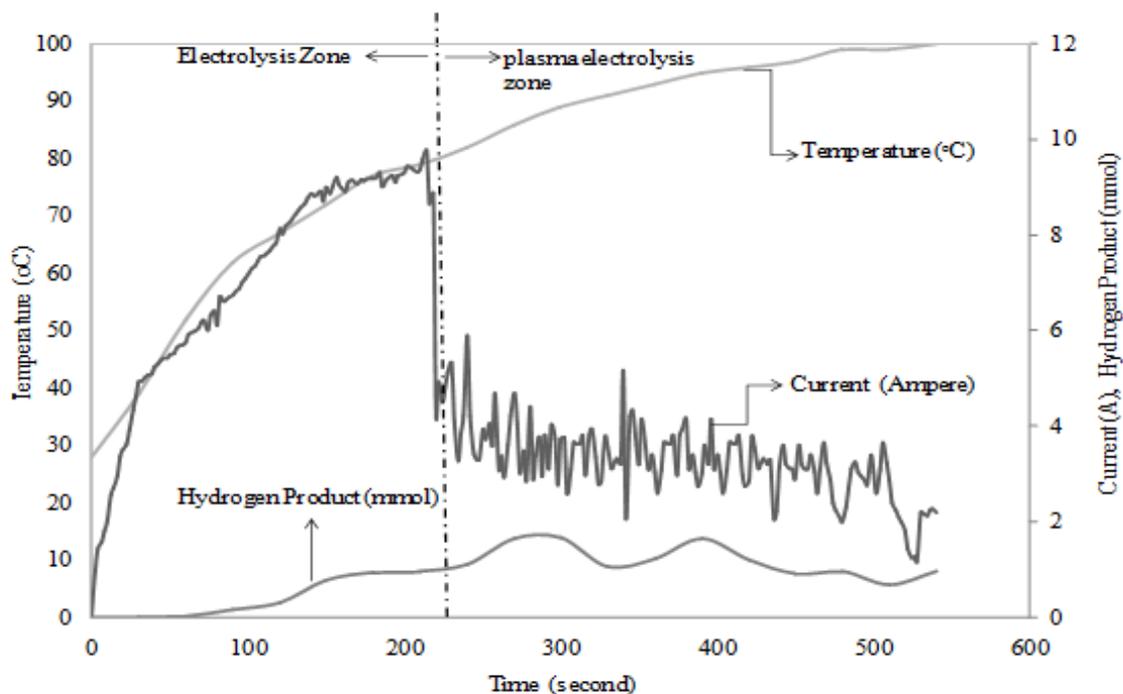
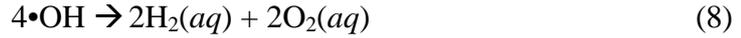


Figure 3 The curve of temperature, electric current, and hydrogen production rate on plasma electrolysis process at 0.1M of KOH solution and 200V

When plasma electrolysis begins, the production rate of H_2 becomes high while the electric current decreases (electric consumption decreases), as shown in Figure 3. Because of the formation of metastable species from H^+ and OH^- to radical $\bullet H$ and $\bullet OH$, H_2 and O_2 are formed. Hence, the total production of H_2 increases. The reaction between these metastable species can be written as follows (Jinzhang et al., 2008):



Equations 7 and 8 show that as many as 4 moles of H_2 from the existing metastable species of $\bullet H$ and $\bullet OH$ in the solution are formed by the plasma mechanism. The decrease in electric current when the plasma is formed is caused by increasing resistance in the conductive solution with the formation of hydrogen bubbles and increasing temperature in the solution. The electrolysis reaction in plasma electrolysis creates a need for more electrical power than the power needed in the general plasma process. The concentration of KOH determines the voltage value needed to initiate plasma electrolysis. Increasing the KOH concentration results in a decrease of voltage needed (Saksono et al., 2010). It should be noted that glycerol is one of the poly-alcohol (triol) molecules with an $-OH$ functional group (hydroxyl) three times more than a water molecule. Plasma induction in hydroxyl groups accelerates the release of metastable $\bullet OH$; hence, it may increase the production of hydrogen.

3.2. Hydrogen production

Figure 4 shows that increased electric voltage results in increased production of hydrogen. Higher electric voltage causes the energy that is contained in the electron rise; hence, escalated levels of leaping electrons are noted. Formed plasma becomes bigger and brighter. The increasing amount of plasma drives the formation of the radical species of $\bullet H$ and $\bullet OH$, leading to the formation of hydrogen and oxygen gas, as shown in Equations 7 and 8. Hydrogen production decreases as the concentration of glycerol increases (Figure 4).

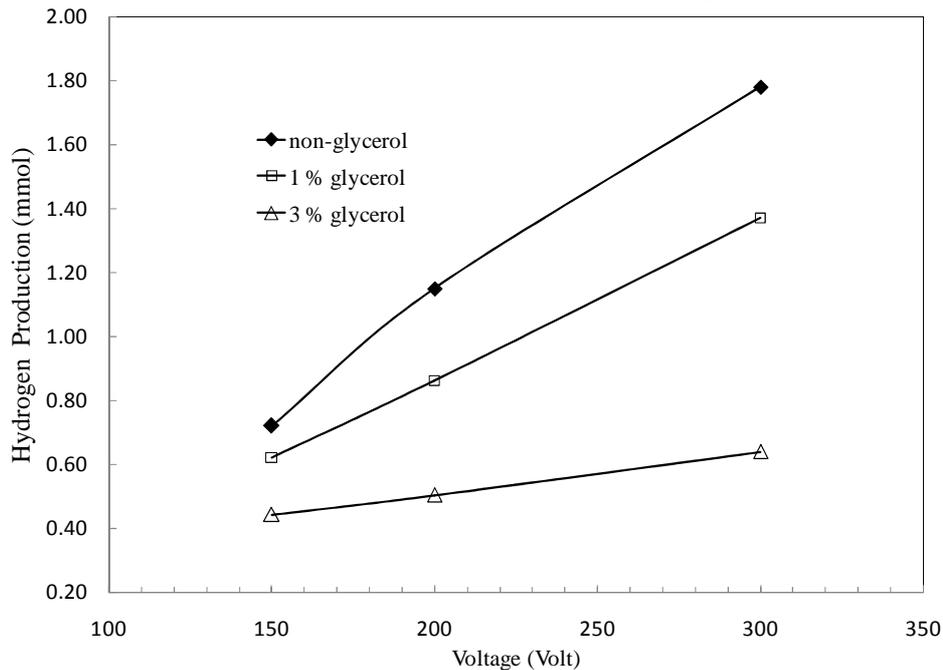
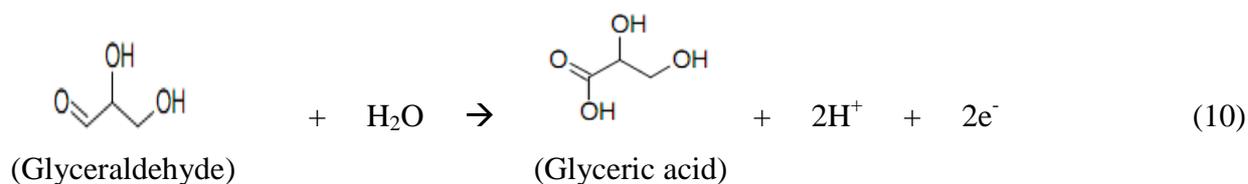
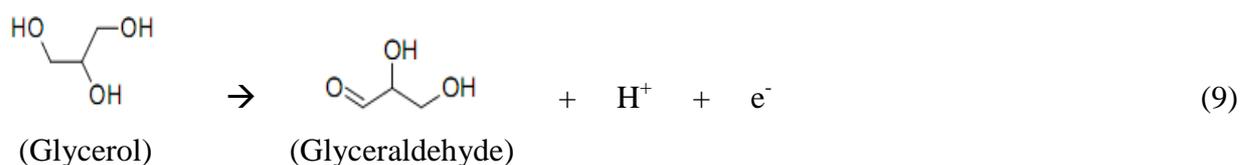
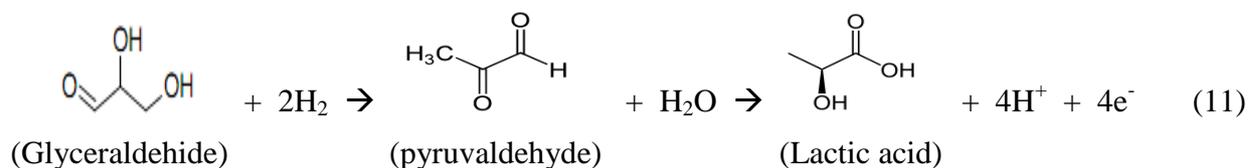


Figure 4 Effect of voltage and glycerol on H_2 production in solution of 0.1M KOH at 90 °C

The decrease in production of hydrogen with the addition of glycerol, as shown in Figure 4, can be caused by the oxidation of glycerol on the anode through a series of reactions to form glyceric acid (Equations 9 and 10), which is difficult to oxidize (Stehring et al., 2009).



The oxidation of Glyceraldehyde during the alkaline solution electrolysis process can also produce lactic acid (Equation 11), which is marked by yellowish changes in the solution (Yuksel et al., 2009).



The yellow colour of the solution produced by the reaction deepened as glycerol concentration and the electrolysis process period increased. The expected decomposition of glycerol into the OH radical group during plasma electrolysis transpired with difficulty due to the lengthy oxidation process and large amount of electrical energy required. The glycerol oxidation process, shown in Equations 11, caused the hydrogen gas is consumed in solution that can lead to reduce hydrogen product.

3.3. Energy consumption

Figure 5 shows that the energy consumption needed to obtain 1 mmol H₂ (W_r) decreased with increasing electric voltage. Increasing voltage was significant on the increasing amount of formed plasma, therefore, hydrogen production increased and W_r decreased. The addition of glycerol 1% vol in 0.1M KOH solution caused an increase in W_r of about 15%, while the addition of glycerol 3% caused an increase of up to 100% in W_r. The data showed that the increase of W_r due to the addition of glycerol was not only caused by a decline in H₂ production, but also because increasing power was needed. The average electric power required for non-glycerol, 1% and 3% glycerol solution, and a voltage of 150 volts, was 846, 1104, and 1320 W, respectively. The increase in power consumption showed that the electrons generated from the electrical current were consumed by oxidation of glycerol, as shown in Equations 9, 10, and 11.

3.4. Energy consumption

Figure 6 shows that the value of process effectiveness [G(H₂)] increases as electric voltage increases. The high value of G(H₂) reflects high hydrogen production. The highest G(H₂) value, 8.1, was obtained by a non-glycerol solution at 300V and 0.1M KOH concentration. The plasma electrolysis reaction under the conditions noted above produced hydrogen at a rate 8.1 times higher than the Faraday electrolysis process.

The addition of glycerol to the KOH electrolyte solution decreased process effectiveness, as shown in Figure 6, because of the decrease in hydrogen production and the increase in electrical energy consumption, which has been explained previously in this paper. The addition of additives from alcohol groups, which can more easily facilitate the formation of OH radicals, such as methanol and ethanol, is an attractive alternative method to research towards improving the effectiveness of plasma electrolysis.

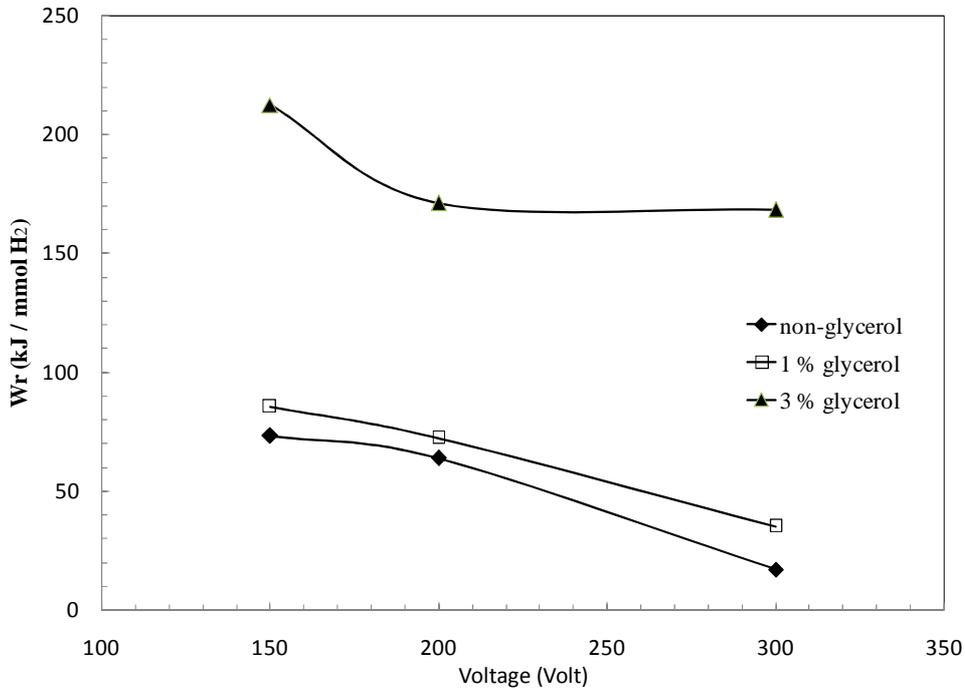


Figure 5 Effect of voltage and glycerol on W_r in solution of 0.1M KOH at 90 °C

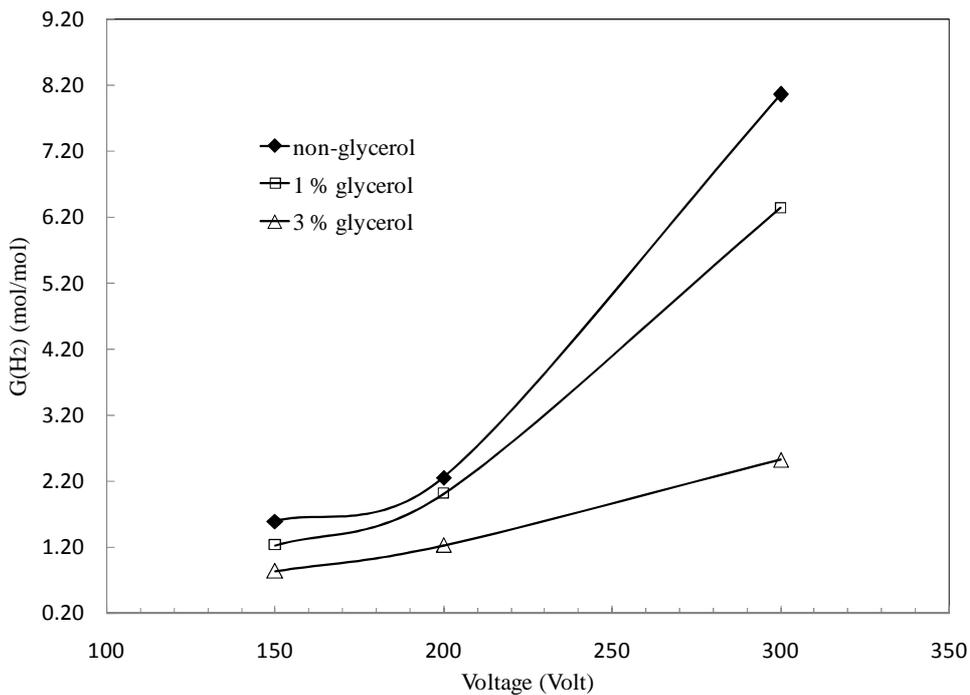


Figure 6 Effect of voltage toward $G(H_2)$ in solution of 0.1M of KOH at 90 °C

4. CONCLUSION

The plasma electrolysis process is able to run after a electrolysis process because the solution saturated by hydrogen gas causes resistance of the solution to become higher. It forces high-energy electrons to leap from cathode to anode through ionized gas media; therefore, the plasma electrolysis phenomenon occurs. Increasing voltage and solution concentration drive a larger formation of plasma, thus increasing hydrogen production and process effectiveness. Further, the addition of glycerol to the KOH solution causes a decrease in hydrogen production and an increase in electricity power consumption.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- Chaffin, J.H., Bobbio, S.M., Inyang, H.I., Kaanagbara, L., 2006. Hydrogen Production by Plasma Electrolysis. *Journal of Energy Engineering*, Volume 132(3), pp. 104–108.
- Holladay, J.D., Hu, J., King, D.L., Wang, Y., 2009. An Overview of Hydrogen Production Technologies. *Catalysis Today*, Volume 139, pp. 244–260.
- Jinzhang, G., Aixiang, W., Yan, F., Jianlin, W., Dongping, M., Xiao, G., Yan, L., Wu, Y., 2008. Analysis of Energetic Species Caused by Contact Glow Discharge Electrolysis in Aqueous Solution. *Plasma Science and Technology*, Volume 10, Number 1.
- Mizuno, T., Akimoto, T., Ohmori, T., 2003. Confirmation of Anomalous Hydrogen Generation by Plasma Electrolysis. In: 4th Meeting of Japan CF Research Society, Iwate, Japan: Iwate University.
- Petitpasa, G., Rolliera, J.D., Darmonb, A., Gonzalez-Aguilara, J., Metkemeijera, R., Fulcheria, L., 2007. A Comparative Study of Non-thermal Plasma Assisted Reforming Technologies. *International Journal of Hydrogen Energy*, Volume 32, pp. 2848–2867.
- Saksono, N., Jainal, A., Setidjo, B., 2010. Hydrogen Production Systems Design through Plasma Non-thermal Electrolysis Process. The 1st International Seminar on Fundamental & Application of Chemical Engineering, Bali, Indonesia.
- Stehring, P., Susanne, L., Thomas, H., Letonja, P., Siebenhofer, M., 2009. Electrochemical Oxidation of Glycerol Combined with Product Adsorption. *AIChE Annual Meeting*, Nashville USA.
- Yuksel, A., Koga, H., Sasaki, M., Goto, M., 2009. Electrolysis of Glycerol in Subcritical Water. *Journal of Renewable and Sustainable Energy I*, 033112.
- Zong-cheng, Y., Li, C., Hong-lin, W., 2006. Experimental Study of Plasma Under-liquid Electrolysis in Hydrogen Generation. *The Chinese Journal of Process Engineering*, Volume 6, Number 3, pp. 396–401.
- Zong-cheng, Y., Li, C., Hong-lin, W., 2008. Hydrogen Generation by Glow Discharge Plasma Electrolysis of Ethanol Solutions. *Journal of Physics, D: Applied Physics.*, Volume 41, 155205.
- Zong-cheng, Y., Li, C., Hong-lin, W., 2009. Hydrogen Generation by Glow Discharge Plasma Electrolysis of Methanol Solutions. *International Journal of Hydrogen Energy*, Volume 34, pp. 48–55.