Hydrogen production by plasma electrolysis reactor of KOH-ethanol solution

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Abstract. Plasma electrolysis has great potential in industrial hydrogen production, chlor-alkali production, and waste water treatment. Plasma electrolysis produces more hydrogen with less energy consumption than hydrocarbon or Faraday electrolysis. This paper investigated the hydrogen production by plasma electrolysis of KOH-ethanol solution at 80 °C and 1 atm. The effects of voltage, KOH solution, ethanol addition, and cathode deep on plasma electrolysis performance were studied. The hydrogen production was analyzed using bubble flow meter and hydrogen analyzer. The electrical energy consumption was measured by a digital multimeter. The effectiveness of plasma electrolysis in terms of hydrogen production was evaluated by comparing it with Faraday Electrolysis. The results showed that hydrogen produced by plasma electrolysis is 149 times higher than the hydrogen produced by Faraday electrolysis. The optimum hydrogen production was 50.71 mmol/min, obtained at 700 V with 0.03 M KOH, 10% vol ethanol and 6.6 cm cathode deep, with energy consumption 1.49 kJ/mmol. The result demonstrates a promising path for hydrogen production by utilizing plasma electrolysis reactor.

1. Introduction
Hydrogen has been considered as a clean energy resource because its high energy density, environmental friendliness and safety. Hydrogen production by steam reforming process can produce pollutant gas. Other than fossil fuel, water electrolysis can also produced hydrogen. However, because of its high electrical energy requirements, producing hydrogen by water electrolysis is a much more expensive process than by using hydrocarbons as feedstock [1].

Plasma electrolysis is another alternative process that can be implemented in hydrogen production. Plasma electrolysis technology consists in an electrolysis conducted in high voltage that produces electrical spark, causing plasma to form in the electrolyte solution. Plasma electrolysis with KOH and Glycerol additive produces hydrogen 8.1 times higher than Faraday electrolysis [2]. Some researches have shown that hydrogen production in plasma electrolysis is affected by some variables such as voltage discharge, electrolyte solution, conductivity, and pH [3-4]. Adding several additives such as acetic acid to the electrolyte solution increased process productivity significantly [5].

This paper describes a reactor design – a scheme of a semi batch reactor for plasma electrolysis that includes a plasma generator that is able to generate voltage up to 700 V (DC). Using KOH as the electrolyte solution, ethanol as an additive, certain cathode configuration, and at high voltage, the reactor was expected to increase the process performance.

2. Experimental
There are three main components in this experiment; electrolysis reactor, coolant system, and purification system which explained as follow.
2.1. Electrolysis Reactor
The scheme of the reactor plasma electrolysis system is shown on Figure 1. The reactor was made of one liter capacity from transparent filter housing with 8 cm of diameter and 25 cm of height. On the top part, an output hole for the hydrogen and the oxygen was set as well as a thermometer and the anode. On the bottom was the cathode. The cathode was made of wolfram, while anode of SS 316G.

Figure 1. Experimental setup: 1. Cooling water basin; 2. Peristaltic Pump; 3. Electrolyte Solution; 4. Hydrogen Outlet; 5. Cathode Room; 6. Acrylic Screen; 7. Cathode; 8. Thermometer; 9. Anode; 10. Hydrogen Outlet; 11. Flow meter; 12. Condenser 1; 13. Condenser 2; 14. Silica Absorber; 15. Hydrogen Analyzer; 16. Power Supply; 17. Slide Regulator; 18. Diode Bridge; 19. Digital Multimeter

2.2. Coolant System
The open circulation cooling system was implemented to reach a suitable reactor temperature, 80 – 85 °C, which is 5 °C lower than previous research [6]. A peristaltic pump inside the coolant water basin pumped to coolant through the anode coil all the way to the reactor. The anode coil inside the reactor was set to form a spiral, in order to extend surface area between electrolyte solution and anode.

2.3. Purification System
The reactor produced water vapor. Two condensers were set to separate the hydrogen and oxygen of the water vapor. Each condenser was made of a one liter capacity housing filter with 8 cm in diameter and 25 cm of height. A silica gel absorbent, 5 cm in diameter and 20 cm in height, was set as the final water vapor absorbent. GNL-400F Hydrogen Analyzer (ChangAi Electronic Science & Technology Co. Ltd China) was used to measure the composition of the hydrogen produced and its volume flow rate was measured by bubble flow meter. The volume of solution fed into the reactor for plasma electrolysis was 1L.

Hydrogen flow rate \( F_{H_2} \) is defined as:

\[
F_{H_2} = \frac{V_{H_2}X_{H_2}}{24.45} \text{ mmol.min}^{-1}
\]

where \( V_{H_2} \) and \( X_{H_2} \) denote hydrogen volume and hydrogen composition at 25°C and 1 atm.
Voltage (DC) and current (DC) were measured by a A830L digital multimeter. \( G(H_2) \) is the mole number of hydrogen divided by the Faraday stipulated yield by passing the given electricity. In our experiments the \( G(H_2) \) calculation has been done by using the equation below [4]:

\[
G(H_2) = \frac{V_{H_2}/22.4}{Q/12F} = \frac{V_{H_2}}{11.2Q} \text{mol}^{-1}
\]

where \( Q, F, V_{H_2} \) denote the electric charge, Faraday constant, and hydrogen volume at 25°C and 1 atm respectively.

\( W_r \) is defined as the power depleted divided by the hydrogen mol. \( W_r \) is calculated by the equation:

\[
W_r = \frac{VQ}{F_{H_2}} \text{kJ} \text{mmol}^{-1}
\]

where \( V, Q, F_{H_2} \) denote the voltage across the circuit, the electric charge and hydrogen flow rate at 25°C and 1 atm respectively.

3. Results and discussion
This research describes the formation of plasma in the electrolyte solution during plasma electrolysis. It also observes the correlations of KOH concentration, ethanol additive percentage, voltage, cathode depth, and electrical energy consumption in the hydrogen production. It compares the effectiveness of plasma electrolysis with the Faraday Electrolysis. The result of this research can be seen in table 1 below.

| Table 1. Result of plasma electrolysis on different variable at 500 V |
|---------------------------------------------------------------|
| KOH Concentration (Molar)* | Ethanol Concentration (% vol)** | Cathode Deep (cm)*** |
| 0.03 | 0.05 | 0.1 | 0 | 5 | 10 | 15 | 0 | 3 | 6.6 |
| H_2 Production (mmol/min) | 15.97 | 37.80 | 35.98 | 2.89 | 29.18 | 35.46 | 33.03 | 18.06 | 35.23 | 44.36 |
| G (mol/mol) | 49.81 | 100.53 | 102.86 | 45.34 | 71.46 | 100.53 | 96.71 | 55.11 | 103.21 | 132.31 |
| Energy (kJ/mmol) | 3.68 | 1.25 | 2.83 | 12.42 | 3.23 | 2.31 | 2.55 | 1.24 | 1.42 | 2.66 |

* 10% ethanol, cathode deep 6.6 cm  
** 0.05 M KOH, cathode deep 6.6 cm  
*** 0.03 M KOH, 10% ethanol.

3.1. The Effect of KOH Concentration in Hydrogen Production
The effect of KOH concentration in hydrogen production can be seen in Table.1. This result were obtained using 10% ethanol as additive at 500 V and with cathode deep 6.6 cm. This research shows hydrogen generation at 0.05 M is higher than 0.03 M and 0.1 M KOH; it was 37.80 mmol/min, 15.97 mmol/min, and 35.98 mmol/min, respectively. Energy consumption showed a similar pattern. The energy consumption at 0.05 M is lower than the energy consumption at 0.03 M and 0.1 M KOH; it was 1.25 kJ/mmol, 3.68 kJ/mmol, and 2.83 kJ/mmol, respectively. At 0.03M and 0.1M KOH, the normal electrolysis appeared to be more dominant, but at 0.05M KOH, plasma electrolysis is more dominant. The normal electrolysis is characterized by high electrical energy consumption and producing less hydrogen, while plasma electrolysis is characterized by low electrical energy consumption and producing more hydrogen.

Higher electrolyte concentration leads to higher conductivity and high conductivity increases hydrogen radicals forming [7-9]. In the course of the gas discharge or plasma electrolysis, the energy is primarily
dissipated in the cathode fall section. When the cathode fall occurred on the solution side, the energy dissipated in the cathode fall section could be consumed primarily in solution vaporization. And then it is easy to get a thicker and bigger volume continuous gas envelope around the discharged electrode. When the thickness of the gas envelope is high, to develop a full glow discharge during plasma electrolysis is difficult and needs higher voltage [4]. Higher voltage in high conductivity solution will produce a large amount of current. This large current destabilizes the plasma formation in the solution. Consequently, normal electrolysis becomes more dominant than plasma electrolysis.

3.2. **The Effect of Ethanol Concentration in Hydrogen Production**

Table 1 also shows the effects of ethanol concentration additive in hydrogen gas production. These results were obtained using 0.05 M KOH at 500 V and with cathode deep 6.6 cm. Table 1 shows that hydrogen production increased from 2.89 mmol/min to 29.18 mmol/min then to 35.46 mmol/min at 0%, 5%, and 10% ethanol, respectively. But at 15% ethanol, the hydrogen production decreased to 33.03 mmol/min. The energy consumption followed the same pattern. It decreased from 12.42 kJ/mmol to 3.23 kJ/mmol then to 2.31 kJ/mmol at 0%, 5%, and 10% ethanol, respectively. But at 15%, the energy consumption value increased to 2.55 kJ/mmol. It showed that at 0%, 5%, and 15% ethanol, normal electrolysis was more dominant, while at 10% ethanol plasma electrolysis was more dominant.

The plasma discharge is generated in the gas envelope between the electrode and the surface of the solution. Because ethanol is easier to vaporize than water, the gas enveloping around the discharged electrode is easier to form. In effect, it tends to be bigger in volume in ethanol solution than in aqueous solutions [4]. The bigger plasma volume, the higher the amount of hydrogen ion in the solution. As mentioned before, full glow discharge during plasma electrolysis in high concentration produces large current and this large current can destabilize plasma formation in solution.

3.3. **The Effect of Cathode Deep in Hydrogen Production**

Cathode Depth is the distance between the tip of cathode with surface of electrolyte solution, as shown on Figure 2. This research was conducted using 0.05 M KOH, 0.05% ethanol, and at 700V discharged voltage. The depths of cathode observed were 0 cm, 3 cm, and 6.6 cm.

![Figure 2. Cathode position at electrolyte solution](image_url)

Figure 3 below shows that plasma emitted purple glow and its brightness was varied for every cathode depth. At a depth of 6.6 cm, the plasma glow that induced is brightest, while at a depth of 0 cm the glow was dimmest.
The effects of cathode deep in hydrogen production are shown in Table 1. Table 1 shown that the deeper the cathode was, the more hydrogen produced. The discharge plasma was generated in the gas envelope between the electrode and the surface of the solution. At the depth of 6.6 cm, more electrolytes were in contact with cathode, allowing more electrons to move freely to the cathode. Electron excitation intensified the plasma generation, thus increased the hydrogen production.

The increasing of cathode deep causes the increasing of energy consumption. Because the movement of electrons in the liquid zone is easier than in the gas zone, the electrical current increases. The formation of the gas sheath is the beginning of plasma formation due to Joule heating levels [10]. With the deeper cathode position, most of the energy was used for creating a continuous gas sheath. However, the presence of hydrostatic pressure hindered the stability of the gas, allowing electric current to flow easily to the cathode. Smaller amount of energy was used for gas formation, due to position of cathode that was close to the solution surface. Consequently, the plasma was formed and stabilized quickly due to the lower influence of hydrostatic pressure. The plasma stability can resist electrons movement effectively [11].

3.4. The Effect of Voltage in Hydrogen Production

This study conducted in 0.03 M KOH with 10% ethanol, and cathode deep 6.6 cm. Various voltage were given into the reactor such as 500 V, 600 V, 700 V. The results can be seen in table 2 below.

| Voltage (V) | H₂ Production (mmol/min) | G (mol/mol) | Wr (kJ/mol) |
|------------|--------------------------|-------------|-------------|
| 500        | 15.71                    | 48.75       | 2.76        |
| 600        | 31.14                    | 95.73       | 1.90        |
| 700        | 50.71                    | 149.68      | 1.49        |

Table 2 shows that the higher the voltage, the more the hydrogen produced. It is due to increase of electron species. The electrons are responsible for creating the active species in plasma, that breaks down the water to produce hydrogen. Plasma in the electrolysis solution will increase the production of hydrogen by forming compounds of hydrogen radicals and hydroxide radicals [4]. High voltage excites the electron to attack OH- ion and H+, forming OH* and H*. The more electrons that attacked the vapour solution and got excited, the greater the plasma volume and the hydrogen produced. As the voltage increased, the amount of energy consumption decreased, as shown in table 2. The decrease in energy consumption is related to the stability of the plasma volume, as already described. At 700 Volt,
hydrogen production is equal to 50.71 mmol/min and energy consumption is 1.49 kJ/mmol. In this condition, hydrogen production is 149 times higher than normal electrolysis.

4. Conclusion
Experiments have been conducted in order to produce hydrogen by plasma electrolysis and to study the influence of the variables during the hydrogen production by plasma electrolysis such as KOH concentration, ethanol additive, depth of the cathode, and the voltage. The result shows that KOH concentration and percentage of ethanol additive influence the level of hydrogen production and electricity consumption during the plasma electrolysis. An increase in the voltage causes a decrease in the electricity consumption and an increase in the hydrogen production. The more in the cathode submerged in electrolyte, the more hydrogen produced, which is characterized by plasma glow, and the greater the amount of electrical energy used. In this study, the optimum level of hydrogen production is 50.71 mmol/min and the optimum energy consumption is 1.49 kJ/mmol. Obtained by plasma electrolysis at 700 Volt, with 0.03 M KOH, 10% ethanol, and cathode 6.6 cm deep, this level of hydrogen production is 149 times higher than the level of hydrogen produced by normal electrolysis.

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