Comparison of Hydrogen Production Through In-liquid Plasma Methods

Ryoya SHIRAISHI※1†, Shinfuku NOMURA※2, and Hiromichi TOYOTA※2

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In this study, hydrogen production by the in-liquid plasma methods reported thus far was compared, to find the optimal method and condition. Because the in-liquid plasma is a type of plasma generated within bubbles in a liquid, an ingredient with a small evaporation enthalpy (EE) is found to be more advantageous. In addition, it is necessary to select an ingredient with a high thermodynamic ideal efficiency (IE), as calculated using the enthalpy of the formation. The actual hydrogen production efficiency (HPE) of water (IE, 0.28 Nm3-H2/kWh; EE, 44 kJ/mol), methanol (IE, 1.26 Nm3-H2/kWh; EE, 38 kJ/mol), n-dodecane (IE, 2.99 Nm3-H2/kWh; EE, 62 kJ/mol), were found to be 0.02, 0.28, and 0.13 Nm3-H2/kWh, respectively. The highest HPE was obtained for the methanol decomposition, indicating that ingredients with low EE and high IE are advantageous for hydrogen production. Moreover, the HPE reduced because most of the energy of the plasma diffused to the surroundings. Therefore, it is essential to develop efficient heat recovery methods and heat insulation systems.

Key Words
In-liquid plasma, Hydrogen, Heat diffusion

1. Introduction

Hydrogen has a high energy density (143 kJ/g) and does not emit any greenhouse gases when burned. These features have enabled hydrogen to be potentially the next-generation clean energy source. Many studies have evaluated the hydrogen production by the in-liquid plasma. As the name suggests, the in-liquid plasma is a technique that generates a plasma in a liquid, and most of the liquids can be decomposed and gasified by plasma to produce hydrogen. This means that the in-liquid plasma method can be applied for a wide selection of ingredients. In fact, it has been reported that hydrogen can be produced from various substances such as water1), methanol 1), n-dodecane 2) ~ 4), methane hydrate 5), and cellulose 6) by the in-liquid plasma method. Moreover, the in-liquid plasma method is a simple process that discharges in a liquid. Therefore, unlike, e.g., the natural gas steam reforming method, the high temperature-reactor and the catalyst are not necessarily required in this case. Because the associated apparatus is simple and inexpensive, it is optimal to be used as a distributed hydrogen production device. Furthermore, when hydrocarbons (CmHn) are decomposed, the carbon component remains in the reactor as the solid carbon, which does not emit CO2. Studies on improving hydrogen production efficiency (HPE) have been conducted to enable the practical application of this method. When the in-liquid
plasma has been first developed, the HPE of \( n \)-dodecane decomposition is 0.13 Nm\(^3\)-H\(_2\)/kWh\(^2\), but as for 2019, the value 0.28 Nm\(^3\)-H\(_2\)/kWh\(^4\) can be obtained. The purpose of this study is to review the studies on the improvement of HPE so far and to obtain knowledge for further efficiency improvements.

2. Results reported

Fig. 1 shows the image of a typical in-liquid plasma. As shown in Fig. 1, in-liquid plasma is a type of plasma that is generated and maintained in a bubble generated at the tip of an electrode that is installed in a liquid. Therefore, if this bubble is enlarged and maintained stably, the plasma is stabilized, and the HPE can be improved. We installed a bubble retention plate at the optimum position, 3.5 mm above the electrode and verified its effect by examining the HPE of the methanol decomposition\(^1\). As a result, the HPE was increased by 2.5 times when the bubble retention plate was installed. In this case, a 0.28 Nm\(^3\)-H\(_2\)/kWh of HPE was obtained. The importance of maintaining bubbles in the in-liquid plasma method is demonstrated in this study.

In the study by Mochtar, A. A. \textit{et al.}, \( n \)-dodecane was decomposed in a reduced pressure condition at 10 kPa\(^3\). The boiling point of \( n \)-dodecane is 216 °C under the atmospheric pressure, and its evaporation enthalpy is 2 kJ/mol at 25 °C, which requires a large amount of energy for generating bubbles. For this reason, it is difficult to maintain the plasma even at an input power of 500 W under the atmospheric pressure. In contrast, the plasma can be maintained even with an input power of 150 W in a reduced pressure condition of 10 kPa. Naturally, this is because the generation of bubbles is facilitated by reducing the pressure. However, the HPE, in this case, was 0.10 Nm\(^3\)-H\(_2\)/kWh, which is only slightly smaller than that obtained by \( n \)-dodecane decomposition (0.13 Nm\(^3\)-H\(_2\)/kWh) at atmospheric pressure.

The cause of the efficiency deterioration in the in-liquid plasma method can be attributed to the fact that the energy of the plasma was not used for the reaction but rather, it diffused into the surrounding liquid. According to Mukasa, S. \textit{et al.}, the energy diffused to the surroundings can reach 90 % of the input power\(^7\). To improve the HPE, it is necessary to recover this energy and to use it for the reaction. For this purpose, the method, by introducing a steam reforming reaction into the in-liquid plasma reaction field, has been attempted. Because the steam reforming reaction occurs at a lower temperature than that of the direct decomposition by the plasma, it is expected for the reaction to be caused by the heat that is diffused from the plasma. According to Mochtar, A. A. \textit{et al.}\(^3\), when steam was introduced into the \( n \)-dodecane decomposition reaction field at a reduced pressure of 10 kPa, the HPE was improved by 1.4 times to 0.14 Nm\(^3\)-H\(_2\)/kWh. However, this result is close to 0.13 Nm\(^3\)-H\(_2\)/kWh, as obtained by \( n \)-dodecane decomposition with the pure in-liquid plasma method performed at the atmospheric pressure\(^2\). In the study conducted by Mochtar, A. A. \textit{et al.}, the steam was directly injected into the plasma reaction field through a cylindrical electrode. In this case, although the steam reforming reaction occurred, the direct decomposition of water by plasma has also occurred. The HPE of water plasma decomposition was approximately 0.02 Nm\(^3\)-H\(_2\)/kWh\(^1\), which led to a decreased HPE. Moreover, this method cannot be efficiently used to recover the heat that is diffused from the plasma. As a countermeasure, we installed a thin steam pipe above the plasma electrode with room temperature water flowing through\(^4\). Because the pipe was very thin, it can be completely enveloped in one of the bubbles, insulating it from the surrounding liquid, which can also cause it to reach a very high temperature. Water can then be vaporized when entering the pipe at this temperature. The generated high-temperature steam was

![Fig. 1 Image of a typical in-liquid plasma. (a); photo image, (b); schematic image](image-url)
supplied to \( n \)-dodecane molecules in a bubble and the steam reforming reaction was induced. In this method, the pipe can efficiently recover the thermal energy emitted from the plasma. Moreover, because the plasma and the water are separated by a pipe without any direct contact, the plasma decomposition of water is suppressed. In this study, a 0.28 \( \text{Nm}^3\text{-H}_2/\text{kWh} \) of HPE was obtained at atmospheric pressure. This study has proved the importance of heat recovery. Moreover, in the study for the bubble retention plate mentioned above \(^1\), a 0.37 \( \text{Nm}^3\text{-H}_2/\text{kWh} \) of HEP was obtained by using a catalytic electrode and a plate. The electrode and plate were given the catalytic active temperature and acted as the catalyst by absorbing the heat diffused from the plasma. Therefore, this method can also be considered as a heat recovery method.

### 3. Discussion

For the above-mentioned studies, the experimental method, condition, ingredient, and HPE are summarized in Table 1. Table 1 also shows the reaction formulas for the hydrogen production reaction, the ideal HPE calculated from the reaction enthalpy, energy efficiency, and evaporation enthalpy in each study. The ideal HPE is calculated by dividing the reaction enthalpy of the decomposition reaction at standard condition by the number of moles of hydrogen produced in the one reaction. For example, in the case of methanol, reaction enthalpy is 67 \( \text{kJ/mol} \cdot \text{H}_2 \) and 2 moles of hydrogen are produced in one reaction. Therefore, an HPE of 38.5 \( \text{kJ/mol} \cdot \text{H}_2 \) can be obtained. Then, the unit \( \text{kJ/mol} \cdot \text{H}_2 \) is converted to \( \text{Nm}^3\text{-H}_2/\text{kWh} \), and the HPE of 1.26 \( \text{Nm}^3\text{-H}_2/\text{kWh} \) is obtained. Energy efficiency is obtained by dividing the actual HPE by the ideal HPE. This energy efficiency is used to represent the percentage of the input power that is used in the hydrogen production reaction.

Focusing on the ideal HPE, the direct decomposition of \( n \)-dodecane by plasma is found to be the most efficient, with an HPE of 2.99 \( \text{Nm}^3\text{-H}_2/\text{kWh} \). However, the actual HPE is in the range of 0.10-0.14 \( \text{Nm}^3\text{-H}_2/\text{kWh} \), with the energy efficiency ranging within 3-4%. As demonstrated in Table 1, methanol has the highest actual HPE (0.28 \( \text{Nm}^3\text{-H}_2/\text{kWh} \)) among all the listed ingredients with an energy efficiency of 22%. The ideal HPE of water is 0.28 \( \text{Nm}^3\text{-H}_2/\text{kWh} \), which is considerably lower than that of methanol and \( n \)-dodecane. As a result, its actual HPE is very low at 0.02 \( \text{Nm}^3\text{-H}_2/\text{kWh} \), whereas the energy efficiency is 7%, which is higher than that of \( n \)-dodecane. Recall that the in-liquid plasma is the type of plasma that is generated in a bubble in the liquid. If the evaporation enthalpy of the ingredient is small, less energy is required for the generation of the bubble. Consequently, the plasma becomes stabilized as the size of the bubble grows. In contrast, if the evaporation enthalpy is high, a large amount of energy is required for bubble generation and the generated bubble can quickly collapse or disengage, resulting in poor plasma stability. In fact, in Table 1, energy efficiency is higher for ingredients with lower evaporation enthalpy. Therefore, to obtain higher actual HPE, it is necessary to select the ingredient that has higher ideal HPE (lower reaction enthalpy) and lower evaporation enthalpy.

Developing better heat recovery methods is also an important aspect. The obtained evaporation enthalpy is not sufficient enough to explain the fact that the actual HPE of \( n \)-dodecane is of very low value. It is therefore considered the HPE can be substantially reduced by the thermal energy that is diffused from the plasma to the surrounding liquid. For the ideal efficiency, when the steam reforming reaction is introduced, the water decomposition reaction is produced which reduces the HPE. As shown in Table 1, assuming that the direct decomposition of \( n \)-dodecane and the steam reforming reaction occur at a ratio of 1:1, the ideal HPE is reduced to 1.09 \( \text{Nm}^3\text{-H}_2/\text{kWh} \). Nevertheless, with the heat recovery method by steam reforming, the HPE and the energy efficiency can be improved to 0.28 \( \text{Nm}^3\text{-H}_2/\text{kWh} \) and 26%, respectively. This means that a

| Method                     | Pressure [kPa] | Ingredient | Reaction for H\textsubscript{2} production | Ideal HPE [Nm\textsuperscript{3}/kWh] | Actual HPE [Nm\textsuperscript{3}/kWh] | Energy efficiency [%] | Evaporation Enthalpy [kJ/mol] | Reference |
|----------------------------|---------------|------------|---------------------------------------------|--------------------------------------|----------------------------------------|------------------------|-------------------------------|-----------|
| In-liquid plasma            | 101.3         | Water      | \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \) | 0.28                                 | 0.02                                   | 7                      | 44                            | \(^1\)     |
|                            | 101.3         | Methanol   | \( \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} \) | 1.26                                 | 0.28                                   | 22                     | 38                            | \(^2\)     |
|                            | 101.3         | \( n \)-dodecane | \( \text{C}_\text{12}\text{H}_{26} \rightarrow 13\text{H}_2 + 12\text{C} \) | 2.99                                 | 0.13                                   | 4                      | 62                            | \(^3\)     |
| In-liquid plasma with steam reforming | 10.0       | \( n \)-dodecane | \( \text{C}_\text{12}\text{H}_{26} \rightarrow 13\text{H}_2 + 12\text{C} \) | 1.09                                 | 0.14                                   | 13                     | 62                            | \(^4\)     |
|                            | 101.3         | \( n \)-dodecane | \( \text{C}_\text{12}\text{H}_{26} + 12\text{H}_2\text{O} \rightarrow 25\text{H}_2 + 12\text{CO} \) | 1.09                                 | 0.28                                   | 26                     | 38                            | \(^1\)     |
| In-liquid plasma with catalyst | 101.3       | Methanol   | \( \text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO} \) | 1.26                                 | 0.37                                   | 29                     | 38                            | \(^1\)     |
more robust heat recovery method is more likely to improve the HPE than selecting the ingredient with high ideal HPE. Furthermore, large amounts of heat diffusion from the plasma should be prevented, which can be done by covering the plasma with a thin heat-insulating pipe.

4. Conclusions

To find the optimal method and condition for the in-liquid plasma method, we conducted a comparison study on the in-liquid plasma hydrogen production reported to date. To enable high-efficiency hydrogen production, it is important to first select an ingredient, for which the reaction enthalpy is low (high ideal HPE). However, only a low reaction enthalpy is not sufficient for obtaining a high HPE. Because in-liquid plasma is a plasma generated in a bubble in a liquid, the ease of bubble generation and bubble stability can considerably affect its efficiency. Therefore, the evaporation enthalpy is also considered as a vital factor. In addition, the heat diffusion from the plasma to surroundings can reduce significantly the HPE. Although the ideal HPE is decreased considerably, the actual efficiency was improved by more than twice with the heat recovery method by using the steam reforming reaction. In a future study, it is essential to develop more efficient heat recovery methods and heat insulation systems that prevent the heat diffusion that results in plasma formation.

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