Heat Recovery for improving Energy Efficiency of Hydrogen Production by Liquid Hydrocarbon Plasma Decomposition

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Abstract: To improve the energy efficiency for hydrogen production by liquid hydrocarbon plasma decomposition, following two points have been required: (1) supplying vaporized ingredient to the plasma constantly, (2) reusing the plasma heat for ingredient vaporization. In the present study, a prototype to realize the points has been built and hydrogen production has been attempted. As a result, the liquid ingredient was vaporized by heat recovery from the plasma, and the vaporized ingredient has been decomposed by the plasma.

Keywords: Hydrogen, Thermal equilibrium plasma, Heat recovery, Hydrocarbon

1. Introduction

In order to solve the global warming and climate change, it is necessary to expand the use of clean energy that does not emit greenhouse gases such as CO_2 . In particular, hydrogen is an attractive energy. Because hydrogen does not emit CO_2 and has a high energy density. Although hydrogen atoms exist almost inexhaustibly on the earth, most of them are compounds such as water and oil. To obtain H₂ which is a clean energy, it is necessary to decompose those compounds. And energy input is required to induce the decomposition. Namely hydrogen production is a kind of energy conversion, higher energy efficiency (=hydrogen production efficiency: HPE) is important to solve the global warming.

Liquid hydrocarbon plasma decomposition is potentially has very high HPE which is several times grater than that of conventional method such as water electrolysis and natural gas steam reforming. And it does not emit $CO_2[1]$. However, the actual HPE for the plasma method is approximately half of that of water electrolysis. To realize super efficient hydrogen production, some researches has been conducted to improve the efficiency for the plasma method[2]. From those previous studies, causes of efficiency deterioration are following two points:

- (1) The in-liquid plasma extinct repeatedly in conjunction with the generation and detachment of bubbles generated around it, is not stable.
- (2) Most of the energy of the plasma is not used for the reaction and is diffused as heat to the surroundings.

To deal with these causes, the following two measures were devised:

- Keep the surroundings of the plasma are always gas, and this gas is supplied steadily to stabilize the plasma.
- (ii) Insulate the surroundings and recover the heat.

In this study, we built a prototype of a device that implements these two countermeasures, and confirmed whether the countermeasures functioned well.

2. Experimental method

Fig. 1 shows a schematic illustration for the prototype hydrogen production system. A tungsten electrode is inserted into the reactor, and the gap between the electrode and the inner wall of the reactor is 1.7 mm. The electrode is connected to the welder and the reactor is connected to ground. At the beginning of the experiment, the reactor is empty. At first, preheating is conducted. Argon gas flows into the reactor at 5 L/min, and a DC pulse electric current of 25 A, voltage of 40 V, a frequency of 350 Hz, and a duty ratio of 80 % was applied from the welder. By doing so, an argon plasma is generated between the electrode and the reactor. This plasma continues for about 30 s, the reactor is preheated by the plasma. Then the argon gas flow is stopped while maintaining the plasma, and 20 mL of the liquid ingredient is injected into the reactor. As shown in Fig. 1, the liquid level is lower than the plasma, the surroundings of the plasma is kept gas. The injected liquid is heated by the high-temperature reactor and immediately reaches the saturation temperature and starts to vaporize. The vapor is decomposed by the plasma at the flow destination, producing gas containing hydrogen. Also, the heat diffusing from the plasma and generated gas is transferred to the liquid ingredient through a copper reactor



Fig. 1. Schematic illustration for the prototype hydrogen production system.

(thermal conductivity: 390 W/($m \cdot K$)), and the liquid ingredient is continuously vaporized. In this way, (i) the surroundings of the plasma is kept gas, and (ii) the heat diffusing from the plasma can be recovered (Note the reactor is not insulated). The discharge is performed for a while without argon gas and with liquid ingredient, and the argon gas was completely exhausted from the reactor to the atmosphere. Then the produced gas was collected by water replacement. And the gas production rate was obtained by measuring the time it takes to collect 200 mL of gas. In this study, methanol was used as the liquid ingredient for ease. When liquid hydrocarbons are decomposed, there are problems such as clogging of flow paths and obstruction of discharge due to carbon deposition. In contrast, in the case of methanol, the carbon component is exhausted as carbon monoxide, so that almost no carbon is deposited. Also, the saturation temperature is low (65 °C, 1 atm), so the experiment can be conducted in a relatively low temperature.

3. Results and Discussion

As a result of the experiment, it took 3 s to collect 200 mL of produced gas, so the gas generation rate is 67 mL/s. In the present study we could not measure the gas composition, so a rough estimate is made from a possible reaction formula. Formula (1) shows the methanol decomposition reaction formula. The reaction of formula (1) has been well reproduced in the previous study[3]. Although carbon deposition does not occur in the reaction of formula (1), deposition of solid carbon was observed in the present study as shown in Fig. 2. Therefore, the reactions formula (2) and (3) may be also induced. And formula (2) and (3) is summarized to formula (4). Although the frequency of reactions of formula (2), (3) are unclear, considering the possible reaction formulas (1) to (4) and the fact that carbon deposition was observed, the estimated hydrogen content in the produced gas is 67 - 100 %. Multiplying this hydrogen content by the gas generation rate, the hydrogen production rate in the present study is calculated, is 44 - 67 mL-H₂/s. Next, the input power is: $current(A) \times voltage(V) \times duty ratio = 25 \times 40 \times 0.8 = 800$ W. From these, the HPE is (hydrogen production rate)/(input power) = 055 - 0.83 mL-H₂/J, that is 0.20 - 0.30Nm³-H₂/kWh. This value is similar to or slightly lower than that of the previous research with the in-liquid plasma method[3]. In other words, the HPE was not improved in the present study. However, the system in the present study is just a prototype, and conditions have not been optimized. It is well known that the HPE is strongly affected experimental condition such as electrode gap and flow rate of ingredient. Further, the reactor has not been insulated. Therefore, it is quite possible that efficiency exceeding that of the conventional method can be obtained. At present, the achievements are: (1) the surroundings of the plasma can be kept gas, (2) the heat recovery system works.

By the way, if the reaction of formula (2) dominates, the HPE deteriorates (see ΔH_r^{\ominus} of formula (2)). And if it proceeds to formula (4), the hydrogen production

efficiency improves(See ΔH_r^{\ominus} of formula (4)). The progress of these reactions can be controlled by the temperature of the reaction field. So, we will proceed with the analysis of the gas components and try to control the reaction by controlling the temperature.

$CH_3OH \rightarrow 2H_2 + CO$	$\Delta H_r^{\ominus} =$	+129	kJ/mol(1)
$\mathrm{CH_{3}OH} \xrightarrow{} 2\mathrm{H_{2}} + 1/2\mathrm{O_{2}} + \mathrm{C}$	$\Delta H_r^{\ominus} =$	+240	kJ/mol (2)
$2H_2 + 1/2O_2 \rightarrow H_2 + H_2O$	$\Delta H_r^{\ominus} =$	-286	kJ/mol (3)
$CH_{3}OH \rightarrow H_{2} + H_{2}O + C$	$\Delta H_r^{\ominus} =$	-46	kJ/mol (4)



: Carbonized area

Fig. 2. Carbon deposition on the inner wall of the ractor.(a), (b) photo image of inside the reactor before experiment.(c), (d) photo image of inside the reactor after experiment. Black carbonized area is observed.

(e) Schematic showing the position of (c), (d) in the reactor.

4. Conclusion

To improve the HPE of liquid hydrocarbon plasma decomposition, two counter measures: (1) Keep surroundings of plasma is gas, (2) heat recovery, has been realized by the prototype system. Although the HPE has not been improved, the high potential of the system has been confirmed. Optimizing experimental condition and by doing so, realize efficient hydrogen production is the future work.

5. References

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