Original Paper

Hydrogen Production from *n*-dodecane Using Steam Reforming in-Liquid Plasma Method

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The aim of this study was to investigate the effect of gas flow rate on the gas production rate from *n*-dodecane using steam reforming in-liquid plasma. A steam reforming of *n*-dodecane was carried out within the reactor vessel which was connected to a waveguide, an aluminum rectangular tubes that guides the propagation of electromagnetic waves with minimum loss of energy. The liquid medium used for plasma generation was *n*-dodecane (commercial reagent). The tip of a single electrode was positioned in the bottom center of the reactor vessel for plasma formation. The produced gas flowed through an aspirator and was trapped and collected in a water filled container. The gas production rate was measured and its compositions were analyzed using a gas chromatograph. The gas production rate by plasma with steam feeding was 1.4 times greater than that by plasma without steam feeding. The hydrogen content of the gas produced ranged from 73% to 82%. The maximum energy efficiency, as indicated by the ratio of the enthalpy difference of the chemical reactions to the input energy, was approximately 12%. The maximum hydrogen generation efficiency obtained from experiments was up to 59% higher than the efficiency of hydrogen production from electrolysis of alkaline solutions as reported in literatures. The energy payback ratio of hydrogen (EPR_{H₂}) was also calculated in order to obtain the hydrogen production efficiency.

Key Words

in-liquid plasma, Electrolysis, hydrogen, *n*-dodecane, Steam reforming

1. Introduction

Hydrogen is not a primary energy source like coal, oil, and natural gas, which freely exist in nature. Rather, it is a secondary energy that can only be obtained through various processes involving primary energy source^{1) ~ 3)}. In such process, energy is required to extract and capture hydrogen from the processed materials. Until now, electrolysis of water is the dominant method for manufacturing clean hydrogen^{4) 5)}. However, since water is an extremely stable material, creating hydrogen from

it requires a large amount of energy and the higher cost of hydrogen production through electrolysis is the main disadvantage of electrolysis methods⁶⁾. Catalytic steam reforming of vegetable oils, organic acids, and natural gas is another method for manufacturing large amounts of hydrogen that has seen commercial application^{7) ~ 9)}. However, carbon dioxide, a greenhouse gas, is released in the final stage of the steam reforming reaction such that there is a need for methods to capture and store the carbon dioxide produced from the process^{10) ~ 12)}. If we take into account the energy required for solidifying the carbon, this method may actually be less energy efficient than the electrolysis method^{13) ~ 15)}. In order to make hydrogen energy a viable alternative energy source, the development of a low-cost hydrogen manufacturing method that can minimize or eliminate the formation of carbon dioxide is necessary. While hydrogen production through thermal plasma

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decomposition of methane gas is one method that does not release carbon dioxide, this method is not practical because the amount of energy required for thermal cracking is approximately the same as the amount of energy contained in the resulting hydrogen^{16) 17)}.

In previous research, Toyota, Nomura, and Mukasa developed an experimental apparatus for in-liquid plasma and optimized the size, shape, and number electrodes¹⁸⁾. These authors used the system to decompose *n*-dodecane for hydrogen production and to perform plasma chemical vapor deposition (CVD) for creating diamond film from the vapor of a mixture of methanol and ethanol on the surface of a silicone sheet¹⁸⁾. The results reported by these authors indicated that with a proper design and number of electrodes the amount of energy required to generate 1 mol of hydrogen from *n*-dodecane can be reduced from 640 kJ¹⁹⁾ to 560 kJ¹⁸⁾, a reduction in energy requirement by as much as 12.5%.

Hydrogen production using non-thermal plasma technologies has been thought to be viable alternatives due to their relatively lower energy requirements. In addition, non-thermal plasma technologies have the capability to induce physical and chemical reactions at lower temperatures because of their non-equilibrium properties^{20) ~ 22)}.

In-liquid plasma is created by applying microwaves or high-frequency waves to a liquid medium. The temperature of plasma within the liquid can exceed 3000 K at atmospheric pressure. Under this condition, nearly all waste products can be decomposed and hydrogen molecules contained in the processed material (e.g. hydrocarbons which naturally contain large amount of hydrogen) can be extracted^{23) ~ 27)}. The amount of energy which is actually used to decompose 1 mol of feedstock to produce hydrogen using radio frequency (RF) plasma was approximately 6.3% to 7.3% of 150 W the input power¹⁷⁾ while the actual energy used to decomposed water into hydrogen, oxygen, and hydrogen peroxide is only about 0.4% of the input power²⁵⁾. In addition, by using the in-liquid plasma process, the carbon components can be solidified simultaneously. Therefore, in-liquid plasma technology solves the problems associated with electrolysis and steam reforming. Previous research has indicated that hydrogen with a purity of 66% to 81% can be produced from decomposition of organic solvents and waste oils using plasma^{19) 28)}. This technology can also be applied for the collection of hydrogen from methane hydrates in sea beds^{16) 17) 29)}. In this research, it is proposed that a continuous steam flow, microwave-based in-liquid plasma device could be used as a method for continuously producing hydrogen through the decomposition of *n*-dodecane.

2. Experimental Setup

The apparatus used in the experiment is shown in Fig. 1. About 200 cm³ of *n*-dodecane at 21 °C was placed in the reactor vessel and electric power in the range of 150 W to 300 W was supplied to the microwave for plasma formation. The mass balance was checked by measuring the gas generation rate in a gas jar. The reaction container was made of a 250 cm³ glass pipe placed inside the reactor vessel which was connected to a waveguide, a rectangular aluminum tube was used to guide the propagation of electromagnetic waves with minimum loss of energy. Microwave energy was supplied to the reaction container and concentrated by an electrode placed in the reactor vessel. Plasma was generated by the high intensity electric field at the tip of the electrode as shown in Fig. 2.

The electrode was made of copper tube. The electrode had an outside diameter of 3 mm, an inside diameter of 2 mm and a length of 22 mm. The base of the copper electrode was placed to the bottom of the reactor vessel. After plasma was generated, a three way valve was opened to allow steam to flow from a closed test tube into the reactor vessel through the copper tube electrode. The test tube was immersed in a water bath maintained at a constant temperature. The pressure inside the reactor vessel was reduced to 10 kPa by an aspirator which caused the water in the test tube to vaporize due to pressure difference. It was not possible to adjust the impedance of the reactor vessel when water vapor was introduced into the plasma region. Therefore, in the present experiment, vaporized water (steam) was drawn into the reactor vessel by decompression. The steam feeding rate was calculated from the difference in the weight of the test tube before and after plasma reaction. The temperature of the steam supplied from the test tube can be varied by changing the temperature of the water bath. The gas generated from the plasma was mixed with water stream from the aspirator. This mixture was later separated in a water reservoir tank and the gas produced was collected by water replacement. Measurement of the gas generation rate was carried out by measuring the volume of gas entrapped in the glass jar every minute. The compositions of the gas produced was analyzed using a gas chromatograph (GC-8A, Shimadzu) equipped with a thermal conductivity detector (TCD) and with argon gas as a carrier.

3. Results and Discussion

Experiments were conducted to investigate the effect of steam reforming on in-liquid plasma steam reforming of *n*-dodecane. The following formula shows the decomposition reaction of *n*-dodecane with water vapor :

Fig. 1 Experimental setup for hydrogen production using the steam reforming method

Fig. 2 Reactor vessel with a single electrode for creating plasma placed in the bottom center of reactor: (a) Actual reactor vessel, (b) Single tip electrode

where

$$a = (2n_{H_2} + 4n_{CH_4} + 2n_{C_2H_2} + 4n_{C_2H_4} - 2b)/26 \quad (2)$$

$$b + n_{CO} \quad (3)$$

$$c + 12a - (n_{CO} + n_{CH_4} + 2n_{C_2H_2} + 2n_{C_2H_4}) \quad (4)$$

The compositions ratio of n_{H_2} , n_{CO} , n_{CH_4} , $n_{C_2H_2}$, $n_{C_2H_4}$ are shown in Table 1. The reaction enthalpy for the chemical reaction in Eq. (1) using the law of the conservation of energy (Hess's law) is as follows.

$$\Delta H = -a\Delta H_{C_{12}H_{26}} - b\Delta H_{H_2O} + n_{CO}\Delta H_{CO} + n_{CH_4}\Delta H_{CH_4} + n_{C_2H_2}\Delta H_{C_2H_2} + n_{C_2H_4}\Delta H_{C_2H_4} \quad (5)$$

This equation can be used to find the enthalpy change of the reaction to produce 1 mol of gas in the chemical reaction in Eq. (1). ΔH is shown in Table 1.

The following formula shows energy efficiency, which is the ratio of the energy consumed in the chemical reaction per unit time in relation to the power P input.

$$\varepsilon = \frac{v\Delta H}{VP} \quad (6)$$

where, V is the standard mole volume (22.4 L/mol), v is the gas generation rate by plasma breakdown. The values obtained in this study for ε ranged from 6.8% to 12.2%. For electrolysis of alkaline water, the enthalpy change required

Table 1 Composition gas and component reaction for hydrogen generation using microwave with varying input power

Method	P (W)	v (cm ³ /s)	Contents of produced gas (%)					ΔH (kJ/mol)	ε (-)	η (-)	Q_{H_2} (mm ³ /J)	EPR_{H_2} (-)
			H ₂	CO	CH ₄	C ₂ H ₂	C ₂ H ₄					
Without steam reforming	150	3.2	76.8	0	3.0	16.2	4.0	65.4	6.3	26.5	16.6	21
	175	5.3	73.0	0	2.3	21.1	3.6	76.7	10.3	34.9	21.9	28
	200	6.8	76.6	0	5.3	9.6	8.4	53.1	8.1	41.6	26.1	33
	225	7.9	68.3	0	2.8	24.7	4.3	85.0	13.4	38.4	24.1	31
	250	8.7	79.5	0	3.9	14.0	2.6	30.3	4.7	44.3	27.8	36
	300	10.5	82.5	0	3.1	10.5	3.9	52.5	8.2	46.1	28.9	37
Steam reforming	150	4.4	76.6	10.8	2.5	6.9	3.2	52.3	6.8	35.4	22.2	28
	175	7.4	74.7	8.8	2.3	10.6	3.6	59.6	11.3	50.0	31.6	40
	200	8.3	75.4	13.6	2.1	6.5	2.4	53.2	9.9	50.0	31.4	40
	225	10.5	79.3	4.6	1.7	10.7	3.7	57.0	11.9	59.0	37.0	47
	250	12.5	73.8	12.9	2.5	6.8	3.9	54.5	12.2	58.9	36.9	47
	300	12.5	82.0	6.5	1.5	6.7	3.2	49.0	9.1	54.5	34.2	44

to produce 1 mol of hydrogen from water is approximately 285.8 kJ/mol ($H_2O \rightarrow H_2 + 1/2 O_2$). If we use the common value of 80% for the energy conversion rate for creating hydrogen from electrolysis, the required amount of energy to create 1 mol of hydrogen is approximately 357.3 kJ/mol ($258.8 / 0.8$). Hence, the hydrogen generation efficiency for electric hydrolysis $Q_{H_2,EL}$ becomes 62.7 mm³/J¹⁹⁾, which is obtained by dividing 22.4 L/mol by 357.3 kJ/mol. The values for the hydrogen generation efficiency based on electrolysis η as shown in Table 1 can be calculated using Eq.(7) as follows.

$$\eta = \frac{vn_{H_2}}{Q_{H_2,EL} P} \quad (7)$$

The maximum η obtained in this study was 59% which was affected by the gas production rate and hydrogen content. The hydrogen production efficiency Q_{H_2} can be calculated by multiplying the gas production rate v by the hydrogen content n_{H_2} per input energy as shown in Eq.(8). Therefore, the gas production rate and hydrogen content should be large due to improvement of hydrogen production efficiency.

$$Q_{H_2} = \frac{vn_{H_2}}{P} \quad (8)$$

As indicated previously, the enthalpy change ΔH_{H_2} required to create 1 mol of hydrogen from water is about 286 kJ/mol. This is much larger than the enthalpy change found in this study as shown in Table 1. Therefore, for industrial production of hydrogen from *n*-dodecane, the microwave in-liquid plasma decomposition process is a viable method and must be considered. The energy payback ratio of hydrogen (EPR_{H_2}) which is the ratio between total energy content of the hydrogen produced and the electric energy used by microwave generator is governed by Eq. (9). The maximum EPR_{H_2} for this experiment was approximately 47% which was obtained when the input power reaches 225 W and 250 W and the gas generation rate reaches 10.5 and

12.5 cm³/s respectively.

$$EPR_{H_2} = \frac{v(n_{H_2} \cdot \Delta H_{H_2})}{VP} \quad (9)$$

The gas generated from the experiment using steam method consisted of H₂, CO, CH₄, C₂H₂, and C₂H₄. The compositions of the gas obtained after 5 to 8 minutes reaction time were 82%H₂, 6.51%CO, 1.54%CH₄, 6.71%C₂H₂, and 3.19%C₂H₄ when input power was 300 W (Table 1). The carbon balance was found to be between 40% and 60%.

Fig. 3 shows that the water bath temperature was varied from 40 °C to 80 °C at a constant power supply of 250 W. Here, T is the water temperature, which is the same as the water temperature in the test tube. Water temperature in the test tube was controlled by the water bath. The steam feeding rate was approximately 1×10^{-3} g/s at 40 °C, 1×10^{-3} g/s at 50 °C, 2×10^{-3} g/s at 60 °C, and 6×10^{-3} g/s at 80 °C. The steam feeding rate increased as the water temperature in the water bath increased due to steam pressure difference. The data presented in Fig. 3 shows that the gas generation rate reached 12.5 cm³/s when T = 60 °C. At temperature higher than 60 °C, the

Fig. 3 Effect of temperature on gas generation rate when $P = 250$ W

steam flow to the reaction container became excessive and some of the steam did not involve in reaction and condensed at the bottom of the reaction vessel absorbed microwave energy which then impeded the reaction.

The rate can be increased by increasing the temperature because at the initial stage of filament development as the temperature kept raising as the molecules gained more energy through electron neutral collisions. However, increased temperatures can cause an electric field breakdown that occurs near the center of the electrode. Then, the heat of the n-dodecane was released into the reactor vessel and to the surrounding atmosphere.

In this experiment the input power P was varied from 150 W to 325 W. Fig. 4(a) shows hydrogen production efficiency with and without the supply of steam. The maximum efficiency for the steam reforming method was found at 225 W power input with gas production of $37 \text{ cm}^3/\text{kJ}$. The data shown in Fig. 4(a) also indicate that in the case of steam reforming (steam was supplied into the reaction container), the rate of gas formation increased linearly with

the increase of power from 150 W to 250 W and further increase of power to 300 W resulted in a decrease of the gas generation rate. It can also be seen from the figure that when no steam was supplied into the reaction container, the rate of gas formation also tended to increase linearly as the power input was increased up to 300 W. Fig. 4 (b) and (c) show the compositions of gas produced from the in-liquid plasma; with and without steam supply.

Overall results show that at all power input levels used in this study, the rates of gas generation obtained from steam reforming experiments were about 1.4 times higher than the rates obtained from experiments without steam supply but the hydrogen contents of the gas produced from the two methods were relatively the same and in the range of 76% to 82%. It is important to note, however, that carbon monoxide (CO) and acetylene (C_2H_2) contents in the gas produced from the two methods were significantly different. In the experiments with no steam supplied into the reaction container, there was no CO gas detected but relatively higher concentration C_2H_2 gas was detected (range

Fig. 4 Efficiency and composition of generated gas for hydrogen production using the in-liquid plasma method

9.6%–24.7%; average 16.0%). On the other hand, from the steam reforming experiments, the CO contents of the gas produced ranged from 4.6% to 13.6% (average 9.6%) while acetylene contents ranged from 6.5% to 10.7% (average 8.0%). Methane (CH_4) and ethylene (C_2H_4) contents in the gas produced from the experiments without steam supply were slightly higher compared to those from the steam reforming experiments. The reduction in the hydrocarbons contained in the gas produced from the steam reforming method was likely caused by the reaction between oxygen atoms in the steam and carbon atoms in the n-dodecane which reduce the number of carbon atoms available for formation of hydrocarbon gases.

3. Conclusion

A single electrode positioned in the bottom center of a reactor vessel was utilized to generate plasma at its tip. The volume of the gas produced was measured and the composition of the gas was analyzed. The rate of gas production using plasma steam injection was about 1.4 times the rate without using steam. Hydrogen production was dominant in the experimental results and amounted to 73% to 82% of the gas produced from experiments with steam injection. The maximum hydrogen production efficiency determined by the ratio of the enthalpy difference of the chemical reactions to the input energy was approximately 12%. The optimal EPR_{H_2} is found to be 47% when gas generation reaches $10.5 \text{ cm}^3/\text{s}$ input power of 225 W and gas generation rate of $12.5 \text{ cm}^3/\text{s}$ at 250 W power input. The hydrogen production efficiency using 2.45 GHz microwave plasma can provide an improvement of 59% over that by alkaline water electrolysis for the same power consumption.

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Nomenclature

EPR_{H_2}	energy payback ratio of hydrogen [-]
ΔH	change enthalpy for all gas [J/mol]
n_{CH_4}	methane content [-]
$n_{\text{C}_2\text{H}_2}$	acetylene content [-]
$n_{\text{C}_2\text{H}_4}$	ethylene content [-]
n_{CO}	carbon monoxide content [-]
n_{H_2}	hydrogen content [-]
P	input power [W]
Q_{H_2}	hydrogen production efficiency [m^3/J]
$Q_{\text{H}_2,\text{EL}}$	hydrogen production efficiency for electrolysis [m^3/J]
T	temperature [$^{\circ}\text{C}$]

v	gas production rate [m^3/s]
V	standard mole volume [m^3/mol]
ε	energy efficiency [-]
η	hydrogen generation efficiency [-]

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