

# A Novel Method for Producing Hydrogen from a Hydrocarbon Liquid Using Microwave In-liquid Plasma

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**Abstract:** The in-liquid plasma method is a technology in which plasma of several thousand degrees Kelvin is generated within bubbles in a liquid. The purpose of this study is to enhance the hydrogen production rate from waste oils by using in-liquid plasma. Two types of microwave in-liquid plasma apparatus are adopted for hydrogen production. One is a conventional MW (microwave) oven, the other is a microwave generator with a waveguide to apply the in-liquid plasma steam reforming method in *n*-dodecane. The produced gas is 58%-90% hydrogen in these methods. The hydrogen production rate is improved by stabilization of the bubble growth. The gas production rate by plasma feeding steam in *n*-dodecane is 1.4 times higher than that without feeding steam.

**Key words:** In-liquid plasma, hydrogen, microwave, *n*-dodecane, steam reforming, waste oils.

## 1. Introduction

In recent years, energy consumption driven by economic growth has increased dramatically, resulting in degradation to the environment. Therefore, sources of clean energy are becoming increasingly important, in order to protect the environment while maintaining an ample energy supply. Recycling of waste from organic and non-organic materials such as household garbage, waste oil, or plastics can protect the environment by reducing the amount of waste and mitigating the effects of greenhouse gasses. Processing organic and non-organic materials to produce hydrogen gas is a challenging task and has been studied by several researchers [1-3]. The main reason that hydrogen used as fuel is water could be its source, and hydrogen has enormous potential energy per unit mass than any other fuel [4, 5].

However, hydrogen is not a primary energy source like coal, oil and natural gas, which exist in nature. Rather, it is a secondary energy source that is obtained by processing a primary energy source. Accordingly, a relatively large amount of energy is needed to extract and capture hydrogen [6-8].

Electrolysis of water is the dominant method for manufacturing clean hydrogen. However, since water is an extremely stable material, creating hydrogen from this material would be required tremendous amount of energy. Steam reforming of natural gas is another method that has been commercially used for generating large amounts of hydrogen [9-11]. However, in the steam reforming method, carbon dioxide is released in the final stage of the reaction, so provisions for capturing and storing the CO<sub>2</sub> are required [12, 13].

One method for extracting and capturing hydrogen from waste materials that has been studied in recent years is the in-liquid plasma process [14-17]. This process can produce hydrogen gas and solidified

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carbon simultaneously without emitting CO<sub>2</sub> [18-21]. However, this method is only focus on hydrogen production, which is not as productive as other methods.

Based on the previous study [19], a conventional MW (microwave) oven is used to irradiate at 2.45 GHz with the ability to circulate the liquid. The power output of the conventional MW oven is 1,260 W with the magnetron using 750 W to generate plasma from the total power of MW oven. The microwaves were irradiated and received at the tip of each antennas used to generate plasma inside the bubbles. Six antennas were arranged on a copper plate and placed on a Teflon platform. The device could be applied as a method for continuous production. The configuration includes an effective bubble control plate [19, 22-24] which is selected based on gas production rate.

Additionally, in-liquid plasma steam reforming, which is plasma fed by steam created in hydrocarbon liquid. The power supplied into the vessel reactor for each experiment was varied from 150 W to 330 W. The microwaves were irradiated through a waveguide in order to prevent loss of energy to the reactor vessel. This method is investigated to accelerate the in-liquid plasma reaction [25-28]. The chemical reactions of discharge in water are used for purification of polluted water [29-31]. In general, the process of discharge in a liquid is a more complicated phenomenon than that in a gas, because discharges in a liquid are unstable and involve phase transitions. When discharge occurs in a liquid, in most cases, bubbles appear. There have been many reports which focused on bubbles in relation to the generation of plasma in a liquid by a variety of methods [32-35]. The behavior of bubbles and plasma generated by high frequency waves and microwaves is observed using a high speed camera [36-39]. Microwave plasma is generated when the electrode is heated to the saturation temperature of *n*-dodecane [33, 40].

The main reason for conducting this study is to

compare the hydrogen gas production efficiency of the in-liquid plasma steam reforming method, when using a MW oven and microwave generator with a waveguide as the power supply and *n*-dodecane as the source material. It is expected to offer the most efficient hydrogen production rate with a method that is both simple and environmentally friendly.

## **2. Plasma Decomposition Experiment in Conventional MW Oven**

Fig. 1 shows the schematic diagram of a conventional MW oven used in this experiment. Not only can the MW oven easily generate microwaves, but also it becomes commonplace in most households, so there is much anticipation that they will be able to be used as a distributed-type hydrogen generator.

Fig. 2a shows a curve-shaped antenna unit. By applying the curved antenna, the tips of the electrodes are closer to each other and it appears that, the generation of plasma usually occurs near the center of the antenna, which makes the volume of the generated plasma larger. While the reason for this cannot be confirmed at this time, with the curved antenna, since the tips of the electrodes are closer to each other, the electric field breakdown occurs near the center of the antenna, which makes for an increased volume of the generated plasma [38].

Experiments were conducted to investigate the optimal shape of the curve-shaped antenna unit, by changing the length of the antenna  $L$  and distance between the tips of the electrodes  $d$  and measuring the decomposition gas rate. The length of the antenna is adjusted according to the type of liquid in order to optimize the generation of gas. The length of the antenna is approximately one-fourth of the microwave wave length ( $\lambda$ ) [33, 41]. The optimal value of gas rate was 33 mL/s when  $d$  was 8-12 mm. It was determined that, the optimal antenna shape is comprised of  $L = 21$  mm and  $d = 10$  mm. In order to generate plasma, a 550 mL heat-resistant glass container was placed in a MW oven to be used as a cracking furnace.

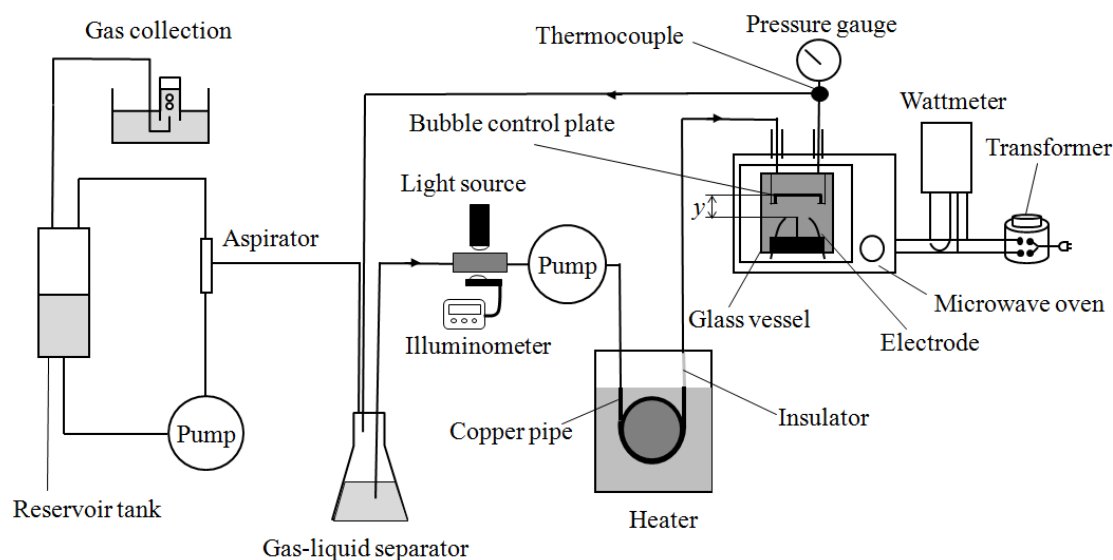


Fig. 1 Experimental setup of hydrogen production using a conventional MW oven.

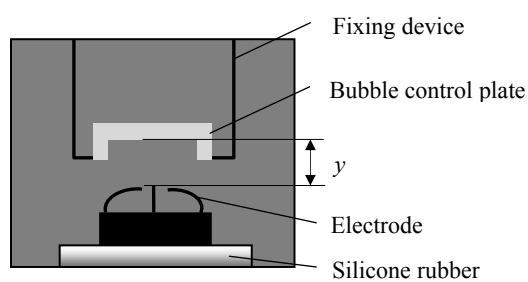
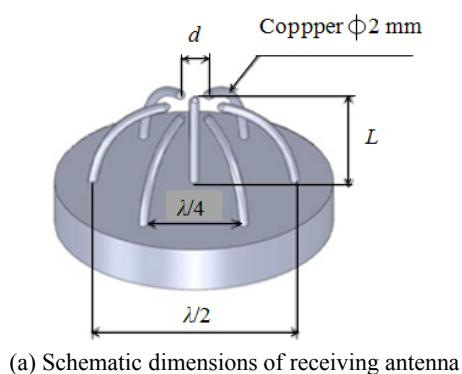


Fig. 2 Position tip of receiving antenna for microwave.

Fig. 2b shows the reactor platform and piping that were made of heat-resistant glass and silicone rubber, to avoid energy absorption from any internal energy reaction. The decomposition furnace was connected to an aspirator. A bubble plate is introduced because use of the plate enhances continuous generation of the plasma [27, 36].

A pressure gauge was setup from the reactor pipe in order to control the air pressure from the MW oven. Experiments were carried out by depressurizing the reactor using an aspirator. The liquid was circulated by a pump from a reservoir tank. The liquid was heated before being introduced to the reaction field, with the liquid temperature set at 80 °C in heating case, and at 25 °C for that without heating. Prior to generating the plasma and collecting gas, the air inside the device was replaced with argon or helium gas, which was then exchanged by the gas generated by the plasma. A thermal conductivity detector was used as the detector for the gas chromatography for analyzing the generated gas. Helium was used as the carrier gas. For the analysis of the gas composition, a gas chromatograph (GC-8A, Shimadzu) equipped with TCD (thermal conductivity detector) was utilized and argon gas was used as a carrier.

With *n*-dodecane, there is ratio of 58%-90% hydrogen in the gas generated by plasma decomposition. Low-grade flammable hydrocarbon gases, such as C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> were also generated. Simultaneously, a large quantity of graphite is synthesized in the vessel.

Fig. 3 shows the effect of the concentration of graphite generated by plasma on the hydrogen yield.

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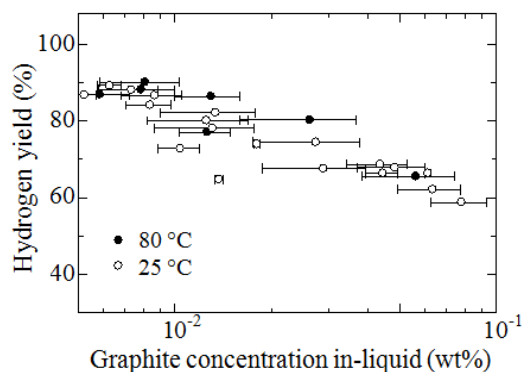


Fig. 3 Hydrogen yield of produced gas.

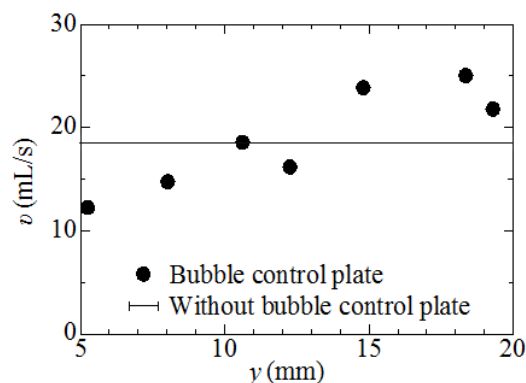


Fig. 4 Effect of the bubble control bubble plate.

The hydrogen concentration in the production gas decreases as the graphite concentration increases in the liquid, with the effect of the liquid temperature becoming negligible. It is highly probable that, a reaction of  $H_2$  with the graphite is promoted as graphite density increases leading to the production of the hydrocarbons such as  $C_2H_2$ .

Fig. 4 shows the experimental results for using a bubble control plate. By using the bubble control plate, the gas production rate can be increased up to 1.3 times. Vapor filled the gap replacing the gas due to the plate, so the gas production rate improves. However, when the gap is increased, the bubble continuously changed in shape in the gap, eventually making the plate ineffective.

### 3. In-liquid Plasma Steam Reforming

Fig. 5 shows the schematic diagram for the steam reforming method, including the gas flow that would be reacted in the vessel reactor. The experiment was

conducted under predetermined conditions in which the pressure was at 101.3 kPa. The water was heated to approximately 60 °C and then the steam was supplied into the vessel through the control valve. A reaction container made of a glass pipe of 250 mL was set up in a wave guide. The microwave irradiation was supplied from a microwave generator to the antenna in the reaction container, with the plasma then generated at the antenna tip where the electric field concentrates.

The antenna was made of a copper material with an outside diameter of 3 mm and inside diameter of 2 mm. After plasma was generated, the valve was opened and steam began to flow into the reaction container from the water tank through the electrode. The steam temperature was varied by changing the temperature  $T$  of the thermostatic bath. The pressure in the reaction container was depressed by an aspirator. The mixture of the gas generated and the water flowing through the aspirator was then separated at a water reservoir tank. Measurement of gas generation rate  $v$  and analysis of the compositions of the gas generated was conducted.

Fig. 6 shows the rate gas generation for that with steam and without steam using MW. Fig. 6 also shows that, by using steam, the gas production rate was increased 1.4 times over that without using steam. In steam reforming, the alkaline water temperature was kept constant at 60 °C in order to produce steam while plasma was generated. The input  $P$  power was varied between 100 W and 325 W. The higher the input power supplied, the greater the rate of generated gas. However, in order to avoid the excessive steam pressure in the reactor, the optimal input power was limited to 325 W.

Fig. 7 shows the gas yield using steam and without steam. At input power of 300 W, the gas yield from decomposition of  $n$ -dodecane with steam reforming was  $H_2$  (82.0%), CO (6.5%),  $CH_4$  (1.5%),  $C_2H_2$  (6.7%) and  $C_2H_4$  (3.2%). On the other hand, the gas yield from decomposition of  $n$ -dodecane without steam reforming was  $H_2$  (82.5%),  $CH_4$  (3.1%),  $C_2H_2$

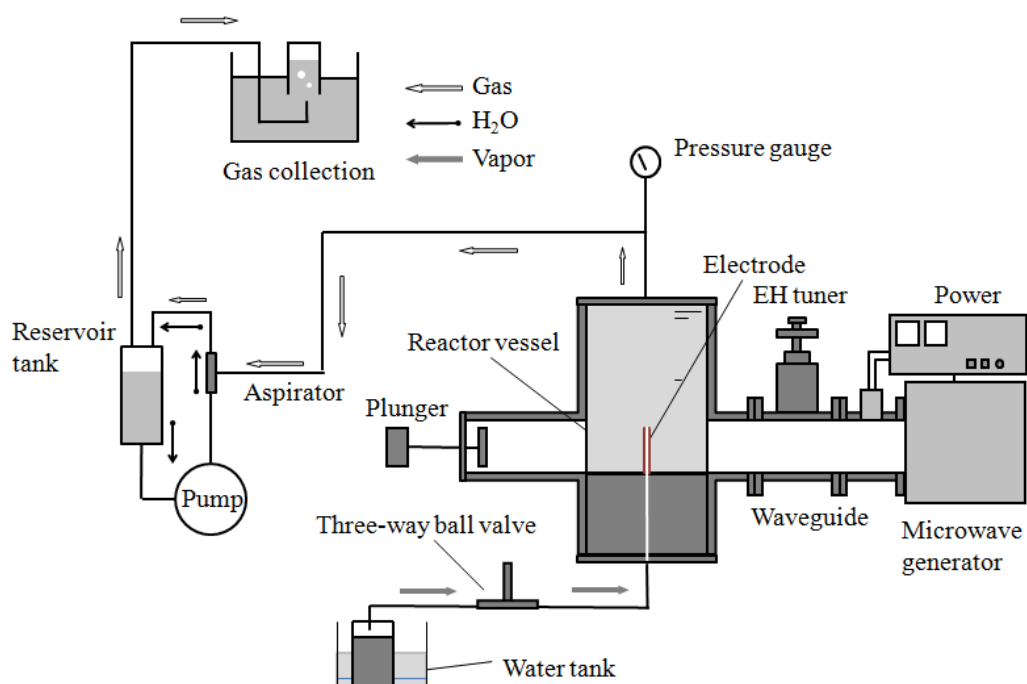


Fig. 5 Schematic of hydrogen production in-liquid plasma using the steam reforming method.

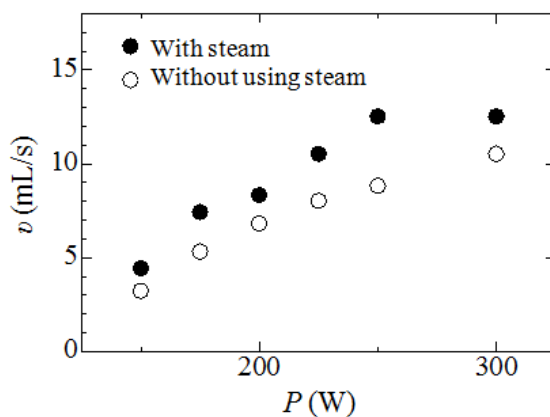


Fig. 6 Rate of generated gas between steam and without steam in the MW reforming method.

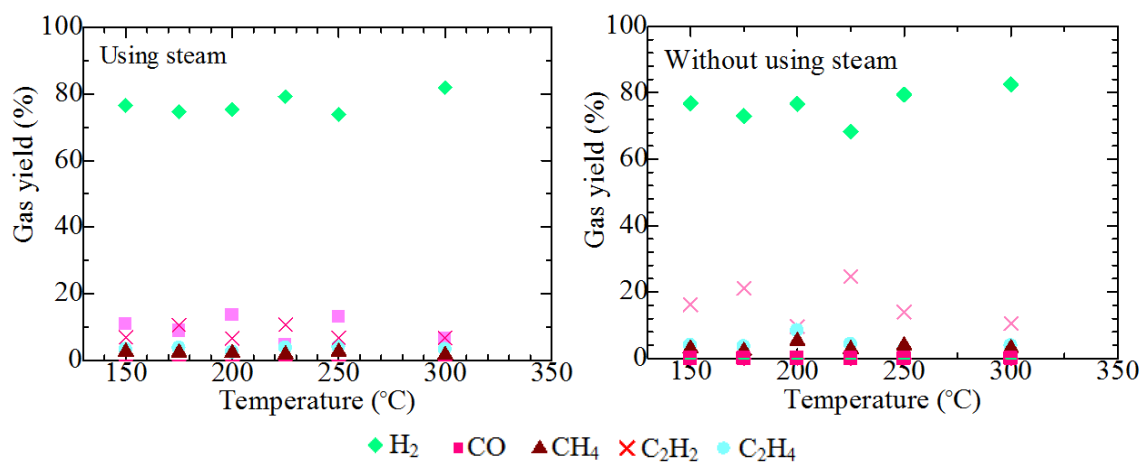


Fig. 7 Gas yield for hydrogen production in MW steam reforming.

(10.5%) and C<sub>2</sub>H<sub>4</sub> (3.9%). The obtained results obviously show that, the steam supplied into the process caused production of CO (carbon monoxide) and reduced other hydrocarbon gases yields. The reduction of hydrocarbon gases yield was suggested due to the reaction of oxygen atoms from steam with carbon atoms from *n*-dodecane for production of carbon monoxide.

#### 4. Conclusions

Plasma was generated within the bubble in-liquid. Two types of microwave in-liquid plasma apparatus are adopted for hydrogen production. One is a conventional MW oven, the other is a microwave generator with a waveguide to apply the in-liquid plasma steam reforming method in *n*-dodecane. A conventional MW oven is used to irradiate at 2.45 GHz within liquid. The conventional MW oven has an output of 1,260 W with only 750 W being used by the magnetron to generate plasma. Furthermore, in a separated system, 150-330 W of energy power was used by the steaming reforming method to generate plasma in the vessel reactor. For the experimental results of the MW oven, the hydrogen proportion of the generated gas was affected by the graphite concentration. Hydrogen was dominant in the gas produced, with the ratio around 58%-90% of the total gas. By using a bubble control plate, the gas production rate could be increased up to 1.3 times. The gas production rate using steam reforming could be increased up to 1.4 times over that without using steam reforming. This indicates that, steam reforming method was effective in producing hydrogen gas since the rate of hydrogen gas production is higher than that of using a conventional MW oven.

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