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Plasma Decomposition of Clathrate Hydrates by 2.45 GHz Mircowave Irradiation at Atmospheric Pressure

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The purpose of this research is to develop a process to use the plasma decomposition of clathrate hydrates to produce fuel gas. An ordinary microwave (MW) oven is used as the source of 2.45 GHz MW radiation under atmospheric-pressure. The plasma decomposition of the hydrates could pave the way for a new utilization of atmospheric pressure plasma. Cyclopentane (CP) hydrate formed at atmospheric pressure was decomposed by plasma in a MW oven generating gases with a content of 65% hydrogen, 12% CO, and 8% CO_2. About 7% of the MW input power was consumed to decompose the hydrates.

In Japan, a country which has scarce energy resources, methane hydrate is an important research topic as a next-generation fuel resource to replace petroleum and natural gas. It is estimated that there are substantial amounts of methane hydrate distributed in the seas near Japan at depths of about 500 m, where, under low-temperature and high-pressure conditions it exists in a stable form. The government of Japan has already targeted the establishment of mass production technology; however, there are many issues that must be overcome before utilizing methane hydrate becomes feasible. For example, the costs involved in excavating methane hydrate are huge, and if methane gas be released into the atmosphere, it would have a major affect on global warming.[1–4] Currently natural gas production from hydrates is being researched using thermal stimulation methods such as down-hole combustion,[5] hot water injection,[6] and depressurization.[7]

We succeeded in creating plasma within air bubbles in a liquid by irradiation with microwave (MW) and high-frequency radio waves in 2003.[8] Up to then, discharge phenomena in liquids had been researched from the viewpoint of electrical insulation engineering using arc discharge and pulse discharge.[9,10] Plasma within a liquid can create high-temperature chemical reaction sites that reach local temperatures of several 1000 K within air bubbles in the liquid.[11,12] Utilizing in-liquid plasma for the decomposition of waste oil or other such organic liquids can generate hydrogen gas and carbon at purities of 70 to 80%.[13,14] There has also been considerable interest in the utilization of MW plasma operated at atmospheric pressure for other practical applications.[15–17]

Through the application of in-liquid plasma, the methane hydrate that exists stably under low-temperature and high-pressure conditions can be decomposed by the plasma, harvesting only the hydrogen gas while leaving the remnant carbon compounds solidified in the sea. As a result, zero-emission hydrogen generation technology could become possible. Because only hydrogen gas would be recovered from the methane hydrate without any methane gas, the problems of releasing greenhouse gasses and reformation of methane hydrate in subsea pipeline[18] are surmountable. Moreover, it might become possible to reduce the exhaust of carbon dioxide, a major cause of global warming, to theoretically zero. Although deep ocean disposal of CO_2 has been researched, in the present method, any CO_2 or other carbon components produced will be directly fixed under the ocean when the methane gas is harvested by plasma decomposition of the hydrates.

In preliminary research towards achieving these goals, an ordinary MW oven is used as an inexpensive source of MW radiation to generate an in-liquid plasma under atmospheric pressure. The MW plasma could be generated in the ocean using transmission cables and the magnetron such as that installed in a conventional MW oven could be powered by natural energy sources like sunlight or wind power. The objective of this research is to recover hydrogen gas as a fuel gas by using MW plasma to decompose clathrate hydrate. In the present study, cyclopentane (CP) hydrate, classified as a structure II of clathrate hydrate, was used, as it can be formed at atmospheric pressure.

A simplified illustration of the experimental apparatus is shown in Fig. 1. Most of the equipment, except for the tubing for gas exhaust in the upper section, has the same structure as a commercial MW oven. Atmospheric pressure plasma can be produced using such a common device through a special modification of the receiver antenna for the MWs. A magnetron on the right side of the equipment irradiates the reaction chamber with 2.45 GHz MWs. The MWs are received by antennas in the reaction vessel and plasma is generated at the tips of the antennas. Items within the reaction vessel platform, tubing, etc., and the reaction vessel itself are made from heat-resistant materials such as teflon and pyrex glass to prevent the absorption of MW energy. The power consumed by the MW oven is 1260 W, of which 750 W is consumed by the MW output of magnetron in the oven.

The receiving antenna configuration is also illustrated in Fig. 1. The antennas are arranged on a copper plate that rests on a Teflon platform. One antenna is mounted in the center of the plate. Six other antennas are arranged at equal intervals in a circle concentric to the central antenna with a diameter 1/4 of the wavelength. The antennas are 20 mm long. This apparatus is nearly identical to the device described in ref. 14. The lengths of the antennas are equivalent to approximately 1/4 the wavelength of the MWs when the reaction solution is CP. Experimentation was conducted after completely replacing the gas in the reaction vessel with argon gas.

Generation of plasma becomes easy when the tip of the antenna is approximately the position for the antinode of a standing wave of the MW. In addition, since the copper plate that supports the antenna is also a conductor, when two antennas are being used, it is desirable that the distance between them be $\lambda/2$. However, since the electric field pattern

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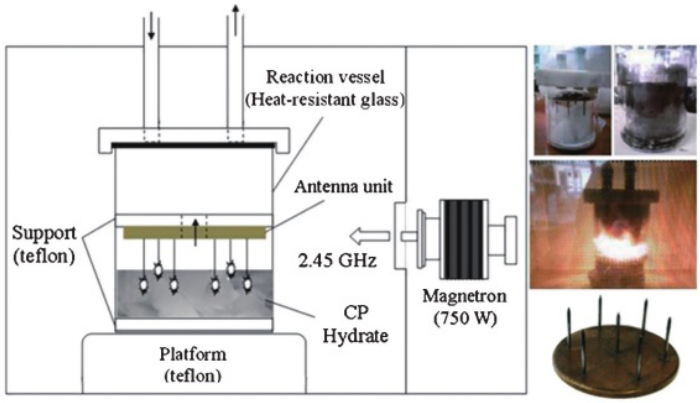

Fig. 1. Decomposition of cyclopentane hydrates using a MW oven. Exhaust gas is collected through downward displacement by water.

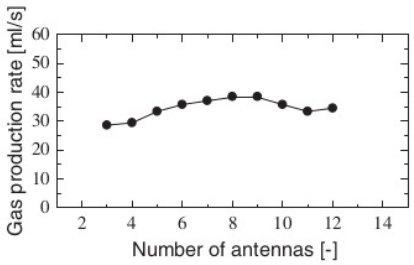

Fig. 2. Number of antennas and gas production rate by MW plasma. Here, one antenna was placed on a copper plate and the other antennas were positioned evenly around circumference.

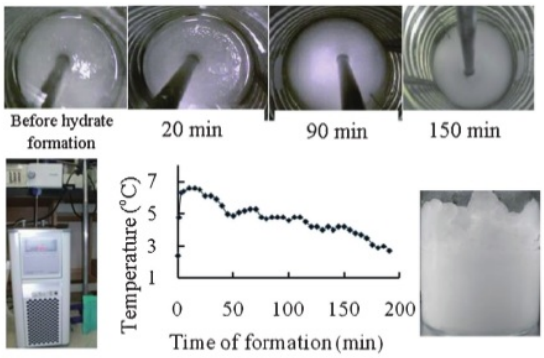

Fig. 3. Hydrate formation processes.

inside the MW oven including a reaction furnace and the hydrate is unknown, experiments were conducted in which the number of antennas was changed from 3 to 12 and the distance among them was changed around so that plasma could be generated at any position in a MW oven. As a result, it was determined that an antenna array comprised of 7 to 10 antennas provided approximately the same values of gas generated by plasma as shown in Fig. 2, therefore, an antenna array of seven antennas was selected for use in the experiment. The arrangement of the antennas can be seen in Fig. 1. The experiment was started with only 3 mm of the tip of the antenna inserted into the hydrate so that there would be no problem with the dielectric constant being the value of the air.

The generated gas was collected from the exhaust tube connected to the reaction vessel by displacement of the gas above the liquid. The gas used for analysis was collected after sufficient time had passed for any gas remaining in the vessel and the tubing. The gas composition was analyzed by gas chromatography (GC). The rate of gas generation and the amount of time that passed after generation of plasma was measured until 1 L of gas had been generated.

The plasma decomposition is conducted using a hydrate composed of CP and pure water. The composition of the CP hydrate is 79.7% pure water, 18.3% CP, and 2.0% surfactant. The CP hydrate formation procedure in this study was essentially the same as that used by Nakajima *et al.*[19] After dispersing the CP in the water, adding a surfactant, and mixing, the solution was cooled with an ethanol cooling medium to about 2 °C at which the temperature was maintained at atmospheric pressure. The solution was then agitated at 120 rpm. CP crystal grains were added into solution when the solution temperature reached approximately 2 °C.[19] CP hydrate begins to form after adding CP crystal grains, which is marked by the solution temperature rising to about 7 °C, as shown in Fig. 3.

The photograph in Fig. 1 shows the CP hydrate placed below the tips of the antennas. The CP:water:surfactant (Noigen) proportions of the hydrate are $C_5H_{10}\cdot 17H_2O$. A piece of hydrate 3 cm thick and 7 cm in diameter (50 g) was placed on the bottom of the reaction vessel, the antennas were inserted from above, and the vessel was irradiated with MWs. After 30 s of irradiation, the hydrate began to melt from the heat generated by the antennas. Then, the plasma ignited and the hydrate was vaporized in the liquid. The subsequent process was the same as the plasma decomposition process of an organic solvent as described in ref. 14.

At the end of the experiment, the hydrate had almost melted into a liquid state, and the surface of the liquid had dropped to approximately the 2 mm position from the tip of the antenna. Moreover, the antenna was completely exposed at the area above the liquid. Though plasma is initially ignited in the hydrate, over the passage of time, the plasma comes to be generated on the surface of the liquid as the

Table I. Contents of gas generated by MW in-liquid plasma from $C_5H_{10}\cdot17H_2O$.

Contents of gas (%)								Collected time (s)
H_2	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2	C_5H_{10}(g)	1000 ml of gas
65	12	8	3	2	2	1	1	54

hydrate melts and the surface of the liquid drops. It has already been reported previously that once the plasma is generated, the temperature of the gas will quickly reach several thousand kelvin,[12,20] and it is almost certain that the ratio of the main decomposed gases, H_2, CO, and CO_2, is not dependent on the duration of plasma generation. However, since it is assumed that when the plasma-generation state is maintained for a long period of time and the liquid level drops sufficiently, the antenna itself will be melted by the heat of the plasma. Therefore, it is desirable to always keep the antenna immersed in the hydrate when used for long periods of time.

GC analysis showed that a gas composed of about 65% H_2, 12% CO, 8% CO_2, and 9% other fuel gases was produced. At this time, 1% O_2 and 3% N_2, which were not produced from CP hydrate decomposition, were also found to be included in the gas composition. Unidentified gasses made up the remaining 6% of the composition. It is supposed that this portion includes the argon gas used as the injection gas.

The chemical reaction formula for 50 g of $C_5H_{10}\cdot17H_2O$(s) based on the contents of gas in Table I is shown below:

$$0.124\ (C_5H_{10}\cdot17H_2O) \rightarrow 0.124C_5H_{10}(l) + 2.108H_2O(l)$$
$$\Delta H = 10.21\,\text{kJ}, \quad (1)$$

where

$$C_5H_{10}\cdot17H_2O \rightarrow C_5H_{10}(l) + 17H_2O(l)$$
$$\Delta H = 82.3\,\text{kJ/mol}.^{21}$$
$$0.124C_5H_{10}(l) + 0.31H_2O(l) \rightarrow 0.68H_2 + 0.13CO + 0.03CH_4 + 0.03C_2H_6 + 0.09CO_2 + 0.02C_2H_4 + 0.01C_2H_2 + 0.01C_5H_{10} + 0.2C(s) \quad (2)$$

CO and CO_2 formation in eq. (2) are shown in the following reactions:

$$0.044C_5H_{10}(l) + 0.22H_2O(l) \rightarrow 0.22CO + 0.44H_2$$
$$\Delta H = 43.21\,\text{kJ} \quad (3)$$
$$0.09H_2O(l) \rightarrow 0.09H_2O(v)$$
$$\Delta H = -3.96\,\text{kJ} \quad (4)$$
$$0.09CO + 0.09H_2O(v) \rightarrow 0.09CO_2 + 0.09H_2$$
$$\Delta H = -3.70\,\text{kJ} \quad (5)$$

Hence, the enthalpy of formation CO and CO_2 is given by

$$0.044C_5H_{10}(l) + 0.31H_2O(l) \rightarrow 0.13CO + 0.09CO_2 + 0.53H_2 \quad \Delta H = 43.47\,\text{kJ}, \quad (6)$$

whereas the formation of CH_4, C_2H_6, C_5H_{10}(g) and carbide in eq. (2) is

$$0.08C_5H_{10}(l) \rightarrow 0.15H_2 + 0.2C(s) + 0.03CH_4 + 0.03C_2H_6 + 0.02C_2H_4 + 0.01C_2H_2 + 0.01C_5H_{10}(g) \quad \Delta H = 6.23\,\text{kJ}. \quad (7)$$

The enthalpy of formation per 1 mol of gas in this reaction is 59.91 kJ/mol or 2.67 kJ/L. The actual power consumption required to collect 1 L of gas during the 54 s of this reaction processes is 49.5 W. Accordingly, the net amount of energy used for the decomposition of the hydrate is approximately 7% of the input power of 750 W. It is assumed that most of the input energy is being used to raise the water temperature of the hydrate.

The results of the experiment into this method raise the possibility of its use for the extraction of hydrogen from methane hydrate rather than from methane gas, with solid carbon remaining as the residue. When used in the actual environment, the produced CO_2 could be separated from the generated gas and sequestered to form carbon dioxide hydrate in the subsea, thus preventing its release into the atmosphere.[22] Nevertheless, the reduction of CO gas and the separation of CO_2 from the generated gas are problems that remain to be addressed in future research. On practical application of plasma generation in hydrate, the antenna electrodes do not need to be deeply inserted into hydrate layer in ocean sediments so it is easy to move the electrodes to another hydrate location. In the future, the common magnetron from a conventional microwave oven may come to be considered as an option for the decomposition of hydrates, even in sea water or at high pressures.

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