Decomposition of Methane Hydrate by Argon Plasma Jet at Higher Pressures

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Abstract

The purpose of this study is to decompose methane hydrate into hydrogen gas by the in-liquid plasma method under conditions similar to those on the seabed. In previous studies, an experiment using the radio frequency (RF) in-liquid plasma jet method generated stable plasma at low temperature and high pressure, which has also had satisfactory results in decomposition of methane hydrate under severe conditions. In the present study, by performing the experiment under higher pressures, there is an improvement in the mechanism for the electrode to withstand increased pressure changes and to generate more stable plasma. At the present, this electrode can generate stable plasma under pressures ranging from 0.1MPa to 5MPa. In addition, as part of the ultimate goal, mixed gases of argon and CO_2 were used to generate a plasma jet that is generated stably at higher pressure levels. This would enable the conversion of methane hydrate into CO_2 hydrate under specific conditions such as those found at extremely low temperatures and high pressures. This suggests that this method could be used to solidify CO_2 or other carbon components on the ocean floor.

1. Introduction

Currently, severe environmental problems are felt throughout the world, with the issue of energy resources being perhaps the most serious problem facing us. Recently, attention is being paid to alternative energy sources such biomass, solar energy, tidal power and geothermal power, all of which are natural energy resources that would help to reduce our dependence on fossil fuels. As one alternative energy resource, our team investigated methane hydrate (MH) found on the bottom of the sea. There are several methods of harvesting MH that have been proposed, however these methods suffer from the problems involving harvesting costs and re-hydration. This report proposes obtaining hydrogen from MH decomposition using radio frequency (RF) in liquid plasma as a solution to these problems. In the past four or five years of research into this methodology, it has been found to be difficult to irradiate the plasma stably under the low temperature and high pressure environment found at the bottom of the sea. In this study, an Ar jet mechanism for the electrode was utilized to solve this problem. Furthermore, in the present study, the mechanism of the electrode has been modified to improve its tolerance to high pressure.

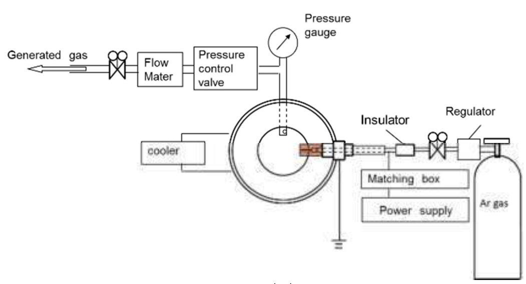
2 Experimental Procedure

2-1 MH decomposition experiment using the previous RF Ar jet plasma method

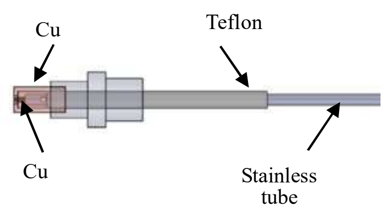
The diagram of the experimental apparatus and the details of the electrode parts are shown in Fig. 1 (a) and (b), respectively. The reaction apparatus is a cylindrical vessel made of stainless steel with a capacity of 10mL able to withstand a pressure 60 MPa and heat-resistant to temperatures of up to 100 degrees Celsius. Windows are opened at both ends of the apparatus to allow observation of the interior. A liquid coolant flows through a copper pipe wound around the apparatus to maintain the temperature of the apparatus at 0 degrees Celsius. The plasma is generated while raising the output of the 27.12MHz RF power supply to 250 W while performing impedance matching to make the reflection power 50W. Seven grams of MH is placed in the apparatus.

Plasma occurs at the tip of the copper electrode with a diameter of φ 1.5 installed in the center of a stainless steel pipe with a diameter of φ 3.2. A copper pipe is attached as a facing electrode. A hole for gas infusion is provided on the side of the stainless steel pipe. Plasma jet occurs at the counter electrode by injecting Ar gas from a cavity 2.0mm in diameter opened into the stainless steel pipe. Ar gas inflow is 200ml/min which is considered to be the most suitable value through experimentation at atmospheric pressure.

Pressure in the experimental apparatus is kept at target pressure using a pressure control valve. The plasma irradiation time is the time required to melt the MH (20 to 60sec). After plasma occurs, the product gas is collected by the water substitution method and ingredient analysis performed using gas chromatography.



(a)



(b)

Fig. 1 Experimental device for decomposition of MH using the previous Ar jet mechanism.

2-2 MH decomposition experiment using the RF Ar jet plasma method in this study

The details of the electrode parts are shown in Fig. 2. The experimental apparatus and procedure to the plasma generation is the same as 2-1. The main change is the thickness of the Teflon and the addition of threaded components for the electrode. Increasing the Teflon wall thickness allows the reactor to withstand additional pressure increase. Also, by adding threaded parts in the electrodes, the distance between them is maintained resulting in an observed improvement in the stability of the plasma over the previous electrode configuration. Since the generation of plasma are given priority, Ar gas inflow is not taken into consideration. In addition, the excitation temperature in the plasma was measured by Boltzmann plots method to clarify the basic properties of the RF Ar jet plasma.

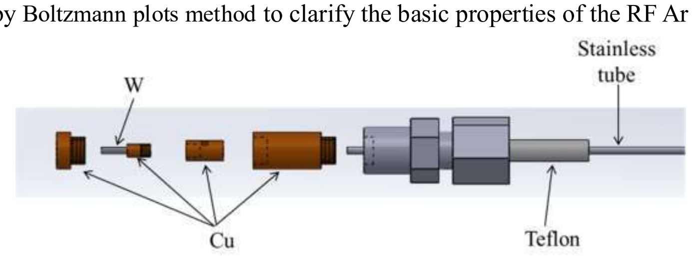


Fig. 2 the details of the electrode parts

3. Results and Discussion

The experimental results for decomposing MH by the RF plasma jet method are shown in Table 1. The ratio of methane increases with an increase in pressure. This is because with Ar gas flowing in the apparatus, a larger amount of methane can be collected before decomposition occurs. The ratios of CO and CO2 decrease with an increase in pressure. This is because the Teflon coating is resistant to thermolysis at high as indicated by the minimal damage to the Teflon coating.

The ratios of hydrogen in the product gas at each pressure are shown in Fig. 3. The ratio of hydrogen is 8.4 percent in 0.1MPa, which then decreases as the pressure is increased to 4.0MPa. However, it regains a high value at 5.0MPa. It is considered that only the decomposition by the plasma without the melting of the MH occurs has been performed by experimental conditions of the MH decomposition experiment satisfies the stability condition of the MH. In order to increase the production ratio of the hydrogen in the product gas under high pressure, it is necessary to consider a flow rate optimum for such not recovered before the methane is decomposed by the Ar gas inflow.

Table 1 Gas yield

	Contents of producted gas (%)				
(MPa)	H2	CH4	CO	CO2	others
0.1	8.4	78.8	10.4	2.1	0.3
0.5	4.1	91.9	3.4	0.5	0.1
1.0	3.4	95.5	1.0	0.0	0.2
1.5	0.5	91.7	0.0	7.8	0.1
2.0	1.3	98.6	0.0	0.0	0.1
2.5	0.2	98.1	0.0	1.4	0.2
3.0	1.8	98.2	0.0	0.0	0.0
4.0	1.5	98.5	0.0	0.0	0.0
5.0	3.9	96.1	0.0	0.0	0.0

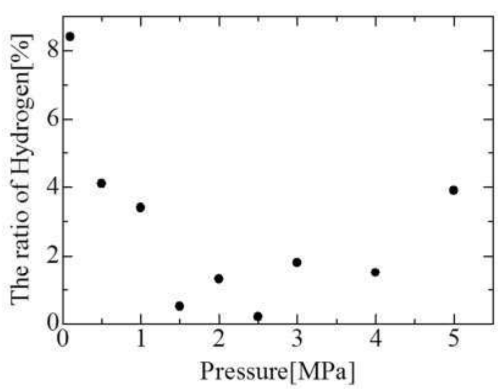


Fig. 3 The ratio of hydrogen in the product gas in each of the pressure

The excitation temperature and pressure in the plasma was estimated by Boltzmann plots method to clarify the basic properties of the RF Ar jet plasma. The excitation temperatures obtained at different gas pressures are summarized in Fig. 4. It is reveals that the excitation temperatures increases with the increasing of gas pressure. It can be referred to a higher frequency of electron collisions with the increase of pressure that affects to the excitation temperature enhancement. The highest excitation temperature is obtained at 10MPa. However, any further increases in pressure consequence in raised excitation temperature. In practical condition, generating plasma under high pressure will give result to the increase of input power. But in the current study, by applying argon plasma jet, plasma can generate under higher pressure with lower input power. In addition, this study became the first time in observing the characteristic of argon plasma jet under very high pressure (10 MPa) particularly in the decomposition of methane hydrate.

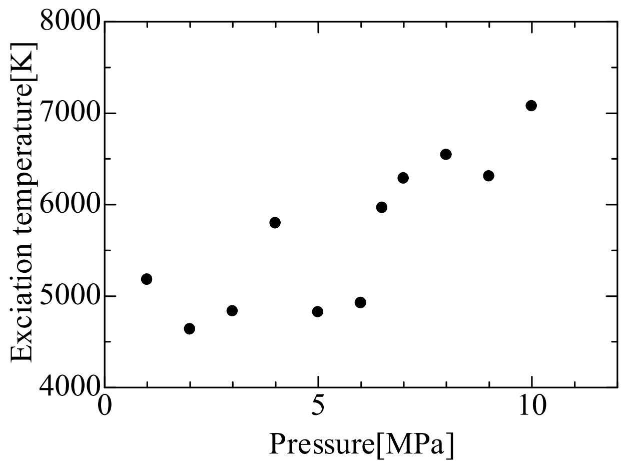


Fig. 4 Measuring excitation temperature in Ar jet plasma

4. Conclusion

MH decomposition experimentation using the RF plasma jet method was performed . It was possible to generate plasma more stably at higher pressures. The ratio of hydrogen in the product gas reaches 8.4 percent in 0.1MPa, which then decreased as the pressure increased to 4.0MPa. However, it had a high value at 5.0MPa. The excitation temperature increases from 3000 - 7000K along with an increase of gas pressure.

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