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Research paper

Decomposition of methane hydrate for hydrogen production using microwave and radio frequency in-liquid plasma methods

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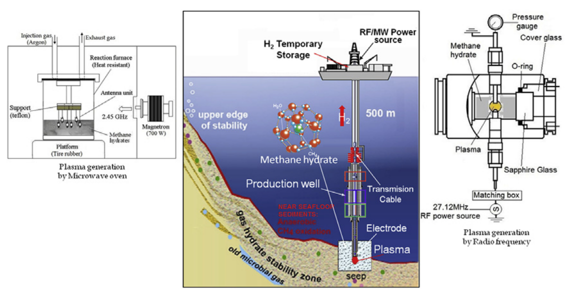
HIGHLIGHTS

- The decomposition of methane hydrate is proposed using plasma in-liquid method.
- Synthetic methane hydrate is used as the sample for decomposition in plasma.
- Hydrogen can be produced from decomposition of methane hydrate.
- Hydrogen purity is higher when using radio frequency stimulation.

GRAPHICAL ABSTRACT



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ABSTRACT

This research involves two in-liquid plasma methods of methane hydrate decomposition, one using radio frequency wave (RF) irradiation and the other microwave radiation (MW). The ultimate goal of this research is to develop a practical process for decomposition of methane hydrate directly at the subsea site for fuel gas production. The mechanism for methane hydrate decomposition begins with the dissociation process of methane hydrate formed by CH_4 and water. The process continues with the simultaneously occurring steam methane reforming process and methane cracking reaction, during which the methane hydrate is decomposed releasing CH_4 into H_2, CO and other by-products. It was found that methane hydrate can be decomposed with a faster rate of CH_4 release using microwave irradiation over that using radio frequency irradiation. However, the radio frequency plasma method produces hydrogen with a purity of 63.1% and a CH conversion ratio of 99.1%, which is higher than using microwave plasma method which produces hydrogen with a purity of 42.1% and CH_4 conversion ratio of 85.5%.

1. Introduction

Hydrogen seems to be one of the more promising energy sources since it is both environmentally friendly and highly energy efficient. The total of energy yield of hydrogen combustion is greater than that of any other fuel [1,2]. Consequently, intense research has been conducted on hydrogen production as an energy source with a variety of methods being proposed such as water electrolysis [3], steam reforming for fossil fuels [3,4], ethanol and methanol reforming [2,5], clathrate hydrate reforming [6], multi-generation energy production system [4,7], conversion of hydrocarbons by microwave plasma or conventional microwave oven [8–10], radio frequency plasma stimulation [11], just to name a few.

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Furthermore, Methane hydrate is increasingly becoming one of the more promising energy resources due to its abundance [12], and potential role in mitigating global climate change [13,14]. It is formed by its constituent CH_4 molecules held within the lattice cavities of water crystals occurring via an exothermic reaction under the proper combination of pressure and temperature [15]. Methane hydrate is an untapped source of hydrocarbon energy [16], which is believed to be both plentiful and stable on the seabed and in permafrost at high pressure and low temperature [10,12,17]. The amount of energy held in methane hydrate beneath the sea could possibly be as much or even more than twice that of the entire energy reserves of the various fossil fuels on Earth [12]. Its considerable C: H ratio and availability make it an attractive energy source for producing hydrogen and could be preferable to the currently most commonly used mode of hydrogen production, steam methane reforming (SMR), which in commercial application supplies from 80 to 85% of the world's hydrogen [14].

Interest in methane hydrate has increased over the last several years, with many governments including those of the USA, Canada, Russia, India, and Japan becoming intrigued by the possibilities of methane hydrate [12,13]. In the process of investigating methane hydrate as an alternative potential source of hydrogen energy, a significant number of methods for extracting hydrogen through methane hydrate decomposition have been recommended and developed. Methane hydrate has a pressure phase equilibrium of 2.3 MPa at 0 °C and consists of an ice/liquid water hydrate [12,16]. It has been exploited for natural gas production through the dissociation process. One hydrate dissociation process involves heating hydrate fields through thermal stimulation to a temperature above the hydrate equilibrium temperature. The thermal stimulation method typically employs injecting hot water (steam and hot brine) into the hydrate field. Unfortunately, the production cost of this method is quite high due to the high energy loss during injection of the hot water [16]. On the other hand, the use of high-frequency waves irradiated directly into the hydrate field can prove to be a more rapid and effective method than the hot-water injection [10].

Moreover, the radio frequency wave and microwave in-liquid plasma method use a technology in which plasma is generated inside bubbles within a liquid creating a high-temperature chemical reaction field [2,18–20]. The temperatures of the in-liquid plasma exceed 3000 K at atmospheric pressure [18]. In-liquid plasma has been employed in the decomposition of waste oils or hydrocarbon liquids during which the useful by-products, hydrogen gas and carbon particles are generated simultaneously [9]. MW plasma, which can be generated using commercial microwave ovens, is commonly used in diamond depositions and IC manufacturing and has the advantages of simple and low-priced operation, high plasma density and high electron mean energy [2,21]. When 2.45 GHz of microwave plasma is generated in a hydrocarbon liquid, hydrogen gas with a purity of 66%–80% can be produced, which means that the energy efficiency of hydrogen production with this method is estimated to be 56% over that by electrolysis of alkaline water for the same power consumption [9,22]. On the other hand, radio frequency (RF) plasma irradiation could easily be used to generate plasma in water under high pressure [18] with the energy consumption required to produce hydrogen, oxygen, and hydrogen peroxide from water under atmospheric pressure being 0.4% of the 150 W of radio frequency input power [11]. This means that RF plasma could be generated at a lower power than microwave plasma in water. Therefore, it is feasible to use RF irradiation for methane hydrate decomposition from hydrate fields as a foreseeable method of hydrogen production by plasma stimulation.

In the present study, decomposition of methane hydrate at atmospheric pressure by radio frequency wave (RF) and microwave (MW) plasma is conducted to compare the attributes of these two methods. This becomes a first step in the process with the ultimate goal of producing hydrogen from hydrate fields using an in-liquid plasma method as shown in Fig. 1.

The in-liquid plasma method generates a high localized temperature at high pressure with the plasma remaining mostly around the tip of the electrode [6]. This makes the method proposed ideal for this purpose. During the initial process of plasma generation in methane hydrate, the hydrate would melt and pass from a solid phase into a liquid phase, hence, the plasma generated in methane hydrate can be considered as the in-liquid plasma.

2. Experiment apparatus & procedure

2.1. Methane hydrate formation

The apparatus for formation of methane hydrate is shown in Fig. 2. The apparatus consists of a cooling bath, temperature control device, magnetic stirrer, methane gas supply, thermocouple and pressure measurement unit. Methane hydrate was formed by injecting pressurized methane gas into shaved ice in the cooling bath.

The inner diameter and height of the cooling bath are 60 mm and 140 mm, respectively, giving it a volume of 400 ml. The maximum pressure is 15 MPa, and temperature of the cooling bath is maintained using ethylene glycol as a cooling medium. A magnetic stirrer with a diameter of 40 mm along with a methane injection tube is positioned 30 mm from the bottom of the cooling bath. 100 g of shaved ice were put into the cooling bath which has been washed by water. The temperature of cooling bath was maintained constant at 0 °C, the methane was pressurized to about 7 MPa and the magnetic stirrer rotated at 500 rpm to agitate the solution of methane gas and shaved ice. The temperature of methane hydrate formation was recorded by a thermocouple located 30 mm from the bottom of the cooling bath, while pressure change was recorded by a camera connected to a computer unit. Pressure and temperature throughout the procedure were recorded every 15 min.

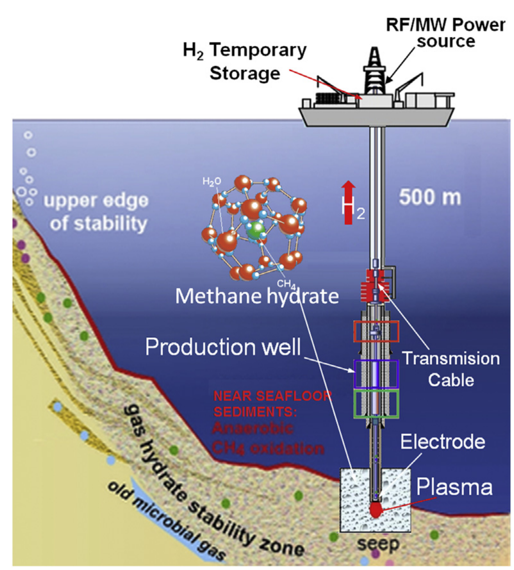

Fig. 1. Process for hydrogen production from hydrate fields in subsea sites using the in-liquid plasma method.