



## Study on methane hydrate formation using ultrasonic waves

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### ABSTRACT

Methane hydrate is a kind of gas hydrate and has the crystal structure I.  $1 \text{ m}^3$  of methane hydrate can be decomposed to a maximum of  $172 \text{ m}^3$  of methane gas in standard conditions. If this characteristic of methane hydrate is reversely utilized, natural gas, which mainly consists of methane gas, is fixed into water in the form of hydrate solid. However, when methane hydrate is formed artificially by simply reversing its process of natural generation, the amount of methane gas consumed owing to hydrate formation is fairly low, which would be problematic for its massive synthesis and application. In this study, experiments are carried out with the goal of increasing the amount of gas consumed by using ultrasonic waves. The power for maximum gas consumption was observed at 150 W, and the amount of gas consumed was four times higher than that at 0 W at the subcooling temperature of 0.5 K. The ultrasonic waves are more effective at the subcooling temperature of 5.7 K than at the subcooling temperature of 0.5 K, and are another effective method for enhancing methane hydrate formation and reducing the hydrate formation time.

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### 1. Introduction

A Siberian chemical plant in the 1930s had frequent blocking problems in the transportation pipeline of natural gas. The cause was attributed the combination of gas and water in the pipe that produce hydrate, which adhered to the inner pipe wall. Methane hydrate drew attention by this discovery [1]. More than 99% of naturally produced methane hydrate consists of methane, and is widely dispersed in the continental slope and continental shelf of the Pacific and the Atlantic, Antarctica, and other places. The reserve of fossil fuel is 500 billion carbon tons, and the reserve of methane is 360 million carbon tons. The reserve of methane hydrate is more than 1 trillion carbon tons, which is twice the amount of fossil fuel [2,3]. Methane hydrate is expected to replace fossil fuel as a new energy source of the 21st century. Methane hydrate is a kind of gas hydrate, and has the crystal structure I. Also,  $1 \text{ m}^3$  of pure methane hydrate can be decomposed to a maximum of  $172 \text{ m}^3$  of methane gas and  $0.8 \text{ m}^3$  of water at standard conditions [4]. If this characteristic of methane hydrate is reversely utilized, natural gas, which mainly consists of methane gas, is fixed into water in the form of hydrate solid. The hydrate is considered to be a great way to transport and store natural gas in large quantity. In particular, the transportation cost

of natural gas is expected to be 18–24% lower than that of liquefied natural gas [5,6].

However, when methane hydrate is formed artificially, the quantity of gas fixed in water may be relatively low and the hydrate formation time is late due to the slow reaction between water and methane gas. To solve these problems, extensive work has been carried out to promote the hydrate formation rate for the transport and storage of natural gas through agitation, using a magnetic driver or a nozzle to increase the gas and water contact area, adding surfactants, and so on. Lin et al. experimentally investigated the effects of the anionic surfactant sodium dodecyl sulfate (SDS) on the methane hydrate storage capacity, and showed that the presence of SDS can enhance the formation of methane hydrate [7]. Cho and Lee reported that the hydrate formation rate increased with increasing concentration of sodium dodecyl benzene sulfonic acid (DBS) [8]. Seo et al. and Ryu et al. examined the active roles of porous silica gels and nano sized materials when used as natural gas storage media [9,10]. Zang et al. reported that the existence of 3A molecular sieve promoted THF hydrate formation [11,12]. Kim et al. and Kim and Kim investigated the influence of multi-walled carbon nanotubes, a magnetic driver, and a nozzle [13,14]. Zhong and Rogers reported that the crystallization could also be induced abruptly from the super-cooled solution with a 5 s pulse of 100 W ultrasonic energy [15]. Sun and Fan and Sun et al. studied the effect of ultrasonic on natural gas hydrate, and reported that the nucleation of hydrate occurs almost simultaneously when ultrasonic was employed and less depends on the supercooling [16,17]. There is also reported

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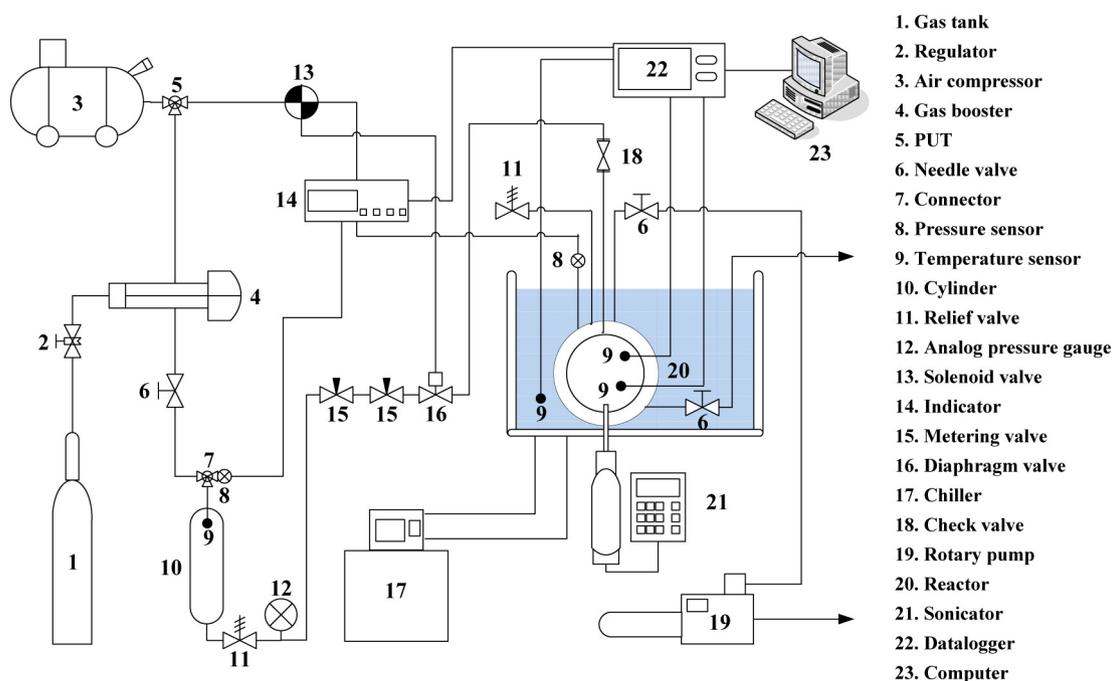


Fig. 1. Schematic diagram of the experimental apparatus.

that the induction time decreased with the increase of ultrasonic power or reaction pressure [18–20].

Therefore, in the present study, we carried out experiment with hydrate formation by using ultrasonic waves. Additionally, we focused on the ultrasonic power level indicated optimal performance, amount of gas consumed, and hydrate formation time as a function of subcooling temperature, and compared and analyzed for the rapid production of methane hydrate and the increase of gas consumption.

## 2. Experimental apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus used in this study. A 350-mL reactor (20) and 100-mL supply vessel (10) were manufactured with SUS316 to endure a pressure > 10 MPa and salt erosion. The reactor was immersed in a constant-temperature bath (water + ethylene glycol). Two copper-constant thermocouples (9) were used to measure the temperatures of the gas and liquid in the reactor, and one pressure gauge (8) was installed to check the internal pressure in the reactor. One thermocouple (9) and one pressure sensor (8) were inserted in the supply vessel to calculate the number of moles of gas consumed in the hydrate phase. Considering the high-pressure operations in the reactor, a check valve (18) was installed at the rear side of the tube connected to the reactor to prevent the back-flow of gas. Quartz glass with a diameter of 30 mm was installed at the front and rear sides of the reactor (20) to allow observations of the reaction. When methane hydrate was formed on the surface between distilled water and methane gas using an ultrasonicator (21), a diaphragm valve (16) was installed to supply the gases in order to maintain a constant pressure in the reactor. For high-precision measurements, two metering valves were installed between the supply vessel (10) and the diaphragm valve (16) to control the flow rate. As the gas in the reactor is consumed to form hydrates, additional gas is supplied automatically from the supply vessel while the pressure in the reactor is kept constant using the diaphragm valve. During the experiment, a data logger (22) acquisition system was used to scan the pressure and temperature readings every second and to record their average values every 10 s.

## 3. Experimental results and discussion

### 3.1. Phase equilibrium

Hydrates are generally stable at high pressures and low temperatures but can decompose easily into water and gas outside the stable region. Since the formation and decomposition of the hydrate can be confirmed visually, phase equilibrium is achieved while observing the specificity of the experimental conditions. According to the method reported by Englezos et al. [21], 150 mL of distilled water was injected into the reactor through an injector and cooled to 274.15 K, and the reactor was pressured with methane gas to 3–9 MPa according to the experimental conditions.

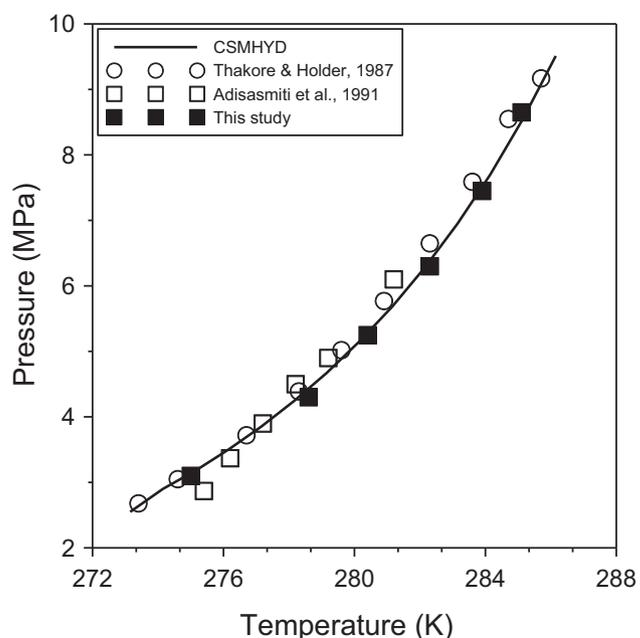


Fig. 2. Gas consumption volume with variable degrees of electric power.

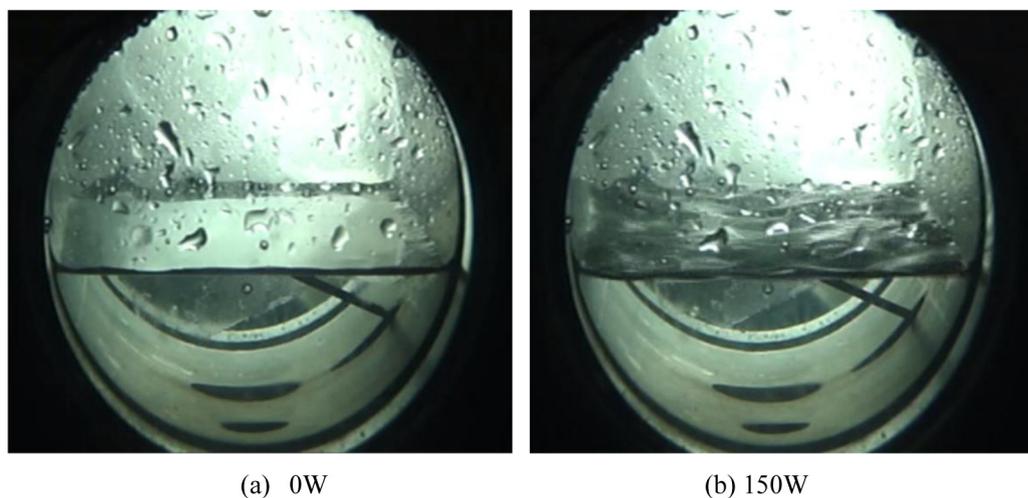


Fig. 3. Surface photograph of the distilled water.

The experimental conditions were kept constant for several hours to allow the complete formation of hydrates. Once the formation of hydrates was complete, the reactor temperature was increased by 0.1 K every 2 h. Fig. 2 graphically compares the methane hydrate phase equilibrium of distilled water where its measured values in the present study are plotted against the reference symbols from Thakore & Holder, Adisasmiti et al. and a CSMHYD program [22]. Specially, it shows a very good agreement where the measured and reference values lie within a 1% margin of error in comparison with the CSMHYD program data.

### 3.2. Measurements of gas consumption

150 mL of distilled water was poured into the reactor and cooled to 274.15 K, and methane gas was injected at the experimental pressure. The experiment was carried out for 6 h and the temperature was kept constant until the termination of the experiment. As methane gas reacts with the solution to form hydrates, it is constantly replenished by the diaphragm and metering valves to maintain a constant pressure. At any instant, the number of moles of the gas consumed up to that point is equal

to the difference between the number of moles of the gas at time  $t = 0$  and the number of moles of the gas at time  $t$  present in the supply vessel. The following equation was used to calculate the number of moles of captured methane gas, which was calculated using Pitzer's correlations [23].

$$\Delta n = V_{sv} \left( \frac{P}{zRT} \right)_0 - V_{sv} \left( \frac{P}{zRT} \right)_t$$

where  $V_{sv}$  is the volume of supply vessels, and  $z$  is the compressibility factor calculated from the following equation:

$$z = 1 + \left\{ \left( 0.083 - \frac{0.422}{T_r^{1.6}} \right) + \omega \left( 0.139 - \frac{0.172}{T_r^{4.2}} \right) \right\} \frac{P_r}{T_r}$$

By definition,

$$\omega \equiv -1.0 - \log(P_r^{sat})_{T_r=0.7}, \quad T_r \equiv \frac{T}{T_c}, \quad P_r \equiv \frac{P}{P_c}$$

where  $\omega$  is the acentric factor,  $P_r^{sat}$  is the reduced vapor pressure,  $T_r$  and  $T_c$  are the reduced temperature and the critical temperature,

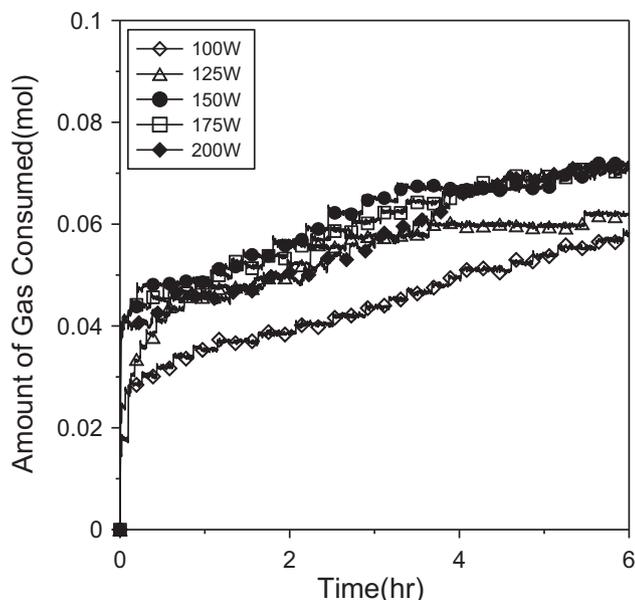


Fig. 4. Gas consumption volume with variable degrees of electric power at the subcooling temperature of 0.5 K.

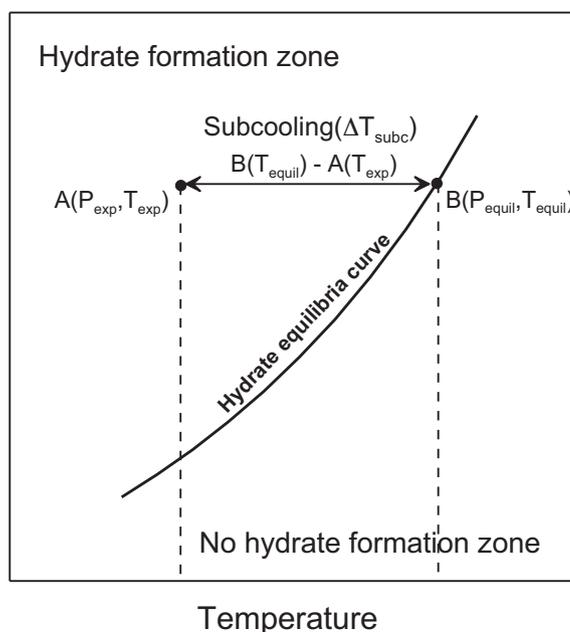


Fig. 5. Subcooling temperature.

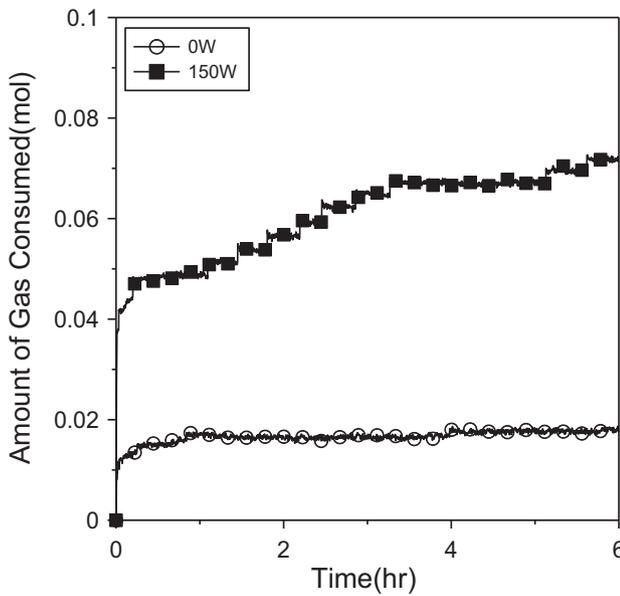


Fig. 6. Gas consumption volume in case of 0 W and 150 W at a subcooling temperature of 0.5 K.

and  $P_r$  and  $P_c$  are the reduced pressure and the critical pressure, respectively.

As shown in Fig. 3, the sonicator creates waves on the surface of the distilled water. If the electric power is strong, because the strong power makes larger waves, the interfacial area between methane gas and water becomes wider. Fig. 4 shows the amount of captured methane gas with variable degrees of electric power at a subcooling temperature of 0.5 K. Here, as shown in Fig. 5, the subcooling temperature,  $\Delta T_{subc}$ , is defined as the difference between the experimental and equilibrium temperatures. In Fig. 4, the amount of methane gas consumed by methane hydrate formation was proportional to the electric power until 150 W. This means that the ultrasonic waves enhanced the reaction of the distilled water and methane gas. However, when more than 150 W was used, the amount of gas consumed decreased due to the excessively rapid formation and the excessively thick layer of methane hydrates on the surface area between the methane gas and distilled water. This means that using more than 150 W prohibits methane hydrate from being formed.

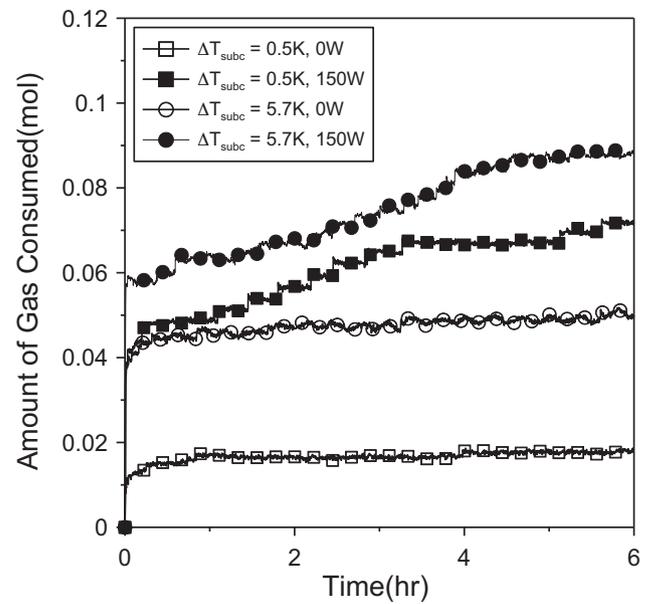


Fig. 7. Comparison of gas consumption as a function of subcooling temperature at 0 W and 150 W.

Therefore, it is necessary to use 150 W to increase the amount of gas consumption.

Fig. 6 shows the comparison of the amount of gas consumed with electric powers of 0 W and 150 W at a subcooling temperature of 0.5 K. As shown in the figure, it was confirmed that at 0 W and 150 W, the amount of gas consumed was 0.0178 mol and 0.0715 mol, respectively. Specifically, in case of 150 W, the amount of gas consumed is approximately four times higher than that in distilled water in 6 h when the ultrasonic waves were used. This is due to the increase in the interfacial area between the methane gas and the distilled water by agitating the distilled water, meaning that the ultrasonic waves can be used to enhance methane hydrate formation. In Fig. 7, the amounts of gas consumed with various subcooling temperatures are presented at 0 W and 150 W. As shown in the figure, the amount of gas consumed at the subcooling temperature of 5.7 K increased more than that at the subcooling temperature of 0.5 K. This means that ultrasonic waves are more effective at a high subcooling temperature than at low subcooling temperature.

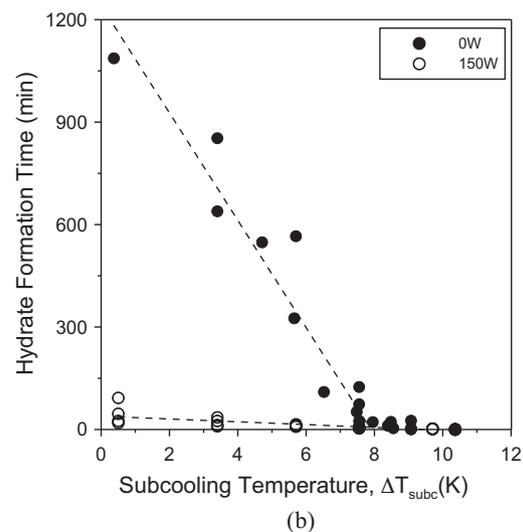
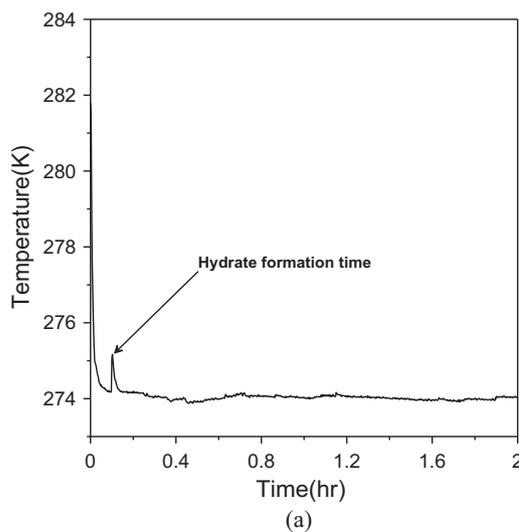


Fig. 8. Hydrate formation time.

### 3.3. Hydrate formation time

The distilled water was injected into the reactor, cooled to the experimental temperature, and then gas was sprayed. When the hydrate crystals formed on the interfacial area between the methane gas and distilled water, the temperature of the distilled water increased slightly, as shown in Fig. 8(a). The hydrate formation time means the time from the start point (0) to the pick point in Fig. 8(a). The results are plotted in Fig. 8(b). As shown in the figure, methane hydrate formed rapidly as soon as the experiment started when the subcooling temperature was 7 K or greater, but the hydrate formation time increased with increasing subcooling temperature below 7 K. However, when ultrasonic waves were used, methane hydrate formed much faster at low subcooling temperatures (<7 K). This suggests that using the ultrasonic waves is an effective method for reducing the hydrate formation time and promotion of the nucleation and growth of methane hydrate.

### 4. Conclusions

Ultrasonic waves were used on distilled water as a promoter of methane hydrate formation. The maximum power of gas consumption was observed at 150 W of electric power, and the amount of gas consumed was four times higher than that at 0 W of electric power at the subcooling temperature of 0.5 K. Therefore, the ultrasonic waves are an effective method for enhancing methane hydrate formation and reducing the hydrate formation time.

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