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Nozzle effect on the formation of Methane hydrate

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Key words : Methane hydrate, Transport, Induction time, Nucleation, Subcooling.

Abstract : When methane hydrate is artificially formed to store and transport large quantity of natural gas, its reaction time may be too long and the gas consumption in water becomes relatively low,the reaction rate between water and methane gas is low. Therefore, the present investigation focuses on the rapid production of hydrates and increases the gas consumption by injecting water into methane gas utilizing nozzle. the hydrate in water injection using a nozzle formed rapidly more than that in gas injection, and the gas consumption of methane hydrate in water injection is about three to four times greater than that in gas injection according to subcooling.

1. Introduction

Methane hydrate (Fig. 1) is formed by physical binding between water molecule and methane gas, which is captured in the cavities of water molecule under the specific temperature and pressure. 1 m^3 hydrate of pure methane can be decomposed up to 180 m^3methane gas. If these characteristics of hydrate are reversely utilized, natural gas consisted of methane gas mainly is fixed into water in the form of hydrate solid. Therefore, the hydrate is considered to be a great way to transport and store natural gas in large quantity [1, 2]. Especially the transportation cost is known to be 24% less than the liquefied transportation. As shown in Figure 2, the Methane hydrate chain consists of three main parts, the production, the marine transportation and the regasification. The production part is assumed to be located on land with loading facilities for large hydrate carriers. The transportation part is by bulk carriers specially designed for dry hydrate, hydrate slurry, and pellet type hydrate. Figure 3 shows schematic diagram for the experimental The regasification part of the frozen hydrate takes place at a receiving terminal located close to markets for natural gas [3-5]. When methane hydrate is artificially formed, its reaction time may be too long and the gas quantity fixed in water becomes relatively low,because the reaction rate between water and methane gas is low. Therefore, the present investigation focuses on the rapid production of methane hydrate and increases the gas volume consumed by injecting water into methane gas utilizing nozzle to increase the interfacial area between the gas and water.

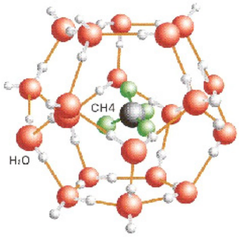

Fig. 1 Natural gas hydrate

2. Experimental Apparatus

Figure 3 shows schematic diagram for the experimental apparatus. apparatus. 600 mL reactor (1) and 1.5 L supplemental tanks (24, 27) are manufactured with SUS316 to endure pressure of 30 MPa and salt erosion. Considering high pressure operations in the reactor, check valve (8) is installed at the rear side of the tube connected to the reactor in order to prevent the back-flow of gas and water. Sapphire glass (2) of diameter 80 mm is installed for visualization at front side and rear side of the reactor. Tube (7) is made of 2 m length in order to ensure full heat transfer between gas and water entering the reactor. In the

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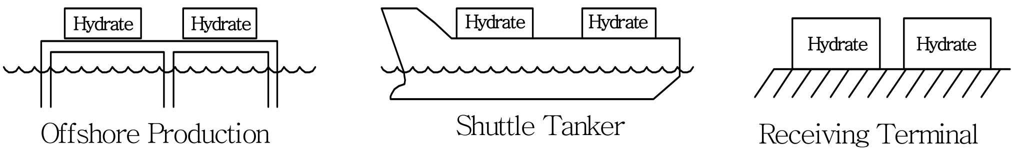


Fig. 2 Hydrate transportation chain

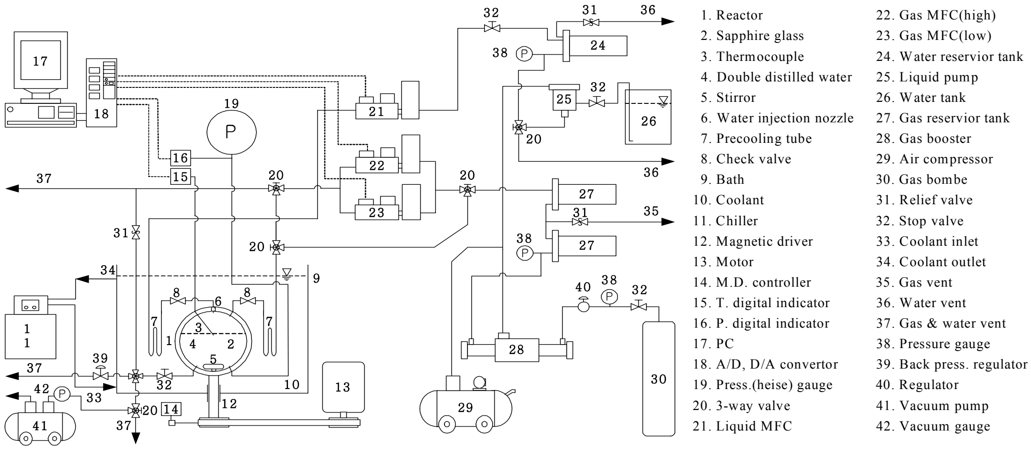


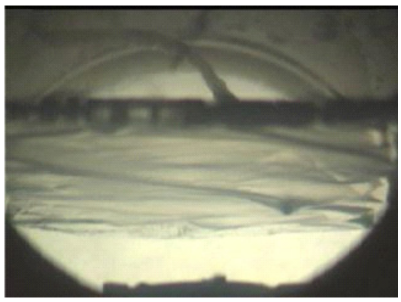
Fig. 3 Schematic diagram of the apparatus

case of MFC(Bronk-horst Hi-tech Co.), MFC (21,0～1000 g/hr) for liquid, MFC (22, 0～60 L/min) for large gas quantity, and MFC (23, 0～1500 mL/min) for small gas quantity are installed separately. For the experimental precision, 97～98% of experimental pressure is controlled by MFC for large gas quantity and the remaining 2～3% by MFC for small gas quantity to reduce over pressure, which may be generated by instantaneous inflow of large quantity. Analog style Heise manometer (19, 0～350 kg$_f$/cm^2, Heise Co.) and digital gauge (16, Sensys Co.), error range within0.25% in pressure measurement is used. 1/32 inch T-type heat transmitter (3, OMEGA Co.) and digital gauge (16, Sensys Co.) are used in the temperature measurement. Chiller (11, 228～403K, Jeio Tech Co.) for the control of reactor temperature, gas booster (28, 700kg/cm^2, Schmidt, Kranz & Co Gmbh) for high pressure gas, and PC (17) for the reading and recording of data such as pressure, temperature, and flow rate etc. are installed. Reactants were used in most experimentations are secondary distilled water and 99.99% methane gas(47, Quadren Cryogenic Co.).

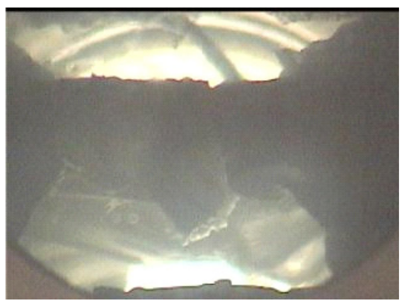
3. Experimental Methods and Results

3.1 Methane gas consumption on gas injection

300 mL distilled water is poured into the reactor and cooled to be 274.15K and the experimental gas is injected at the experimental pressure. Experiments are carried out for 24 hours and its temperature is maintained until the termination of the experimentation. As experimental gas reacts with distilled water to form hydrate, consumed gas is made up by MFC and pressure is maintained at constant. Figure 4 is the photos of methane hydrate growing in the cell according to gas injection, and Also, Figure 5 show the volume of the consumed gas, temperature, and



(a) 8.38K(7.06 MPa, 274.34K)



(b) 15.28K(15.00 MPa, 274.30K)

Fig. 4 Methane hydrate growing after 1hour by gas injection

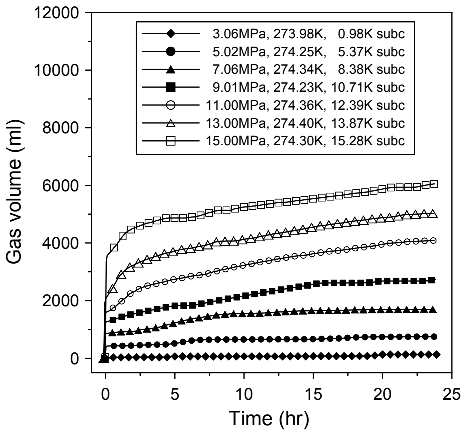


Fig. 5 Volume of methane gas consumed for variable degrees of subcooling

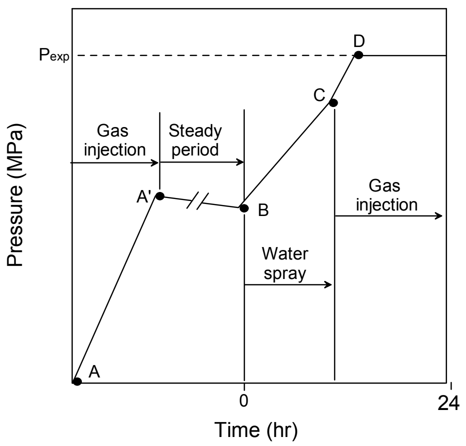
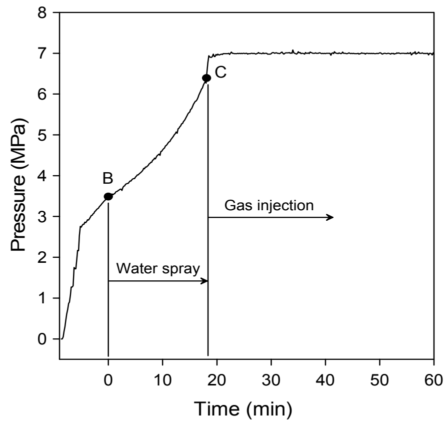
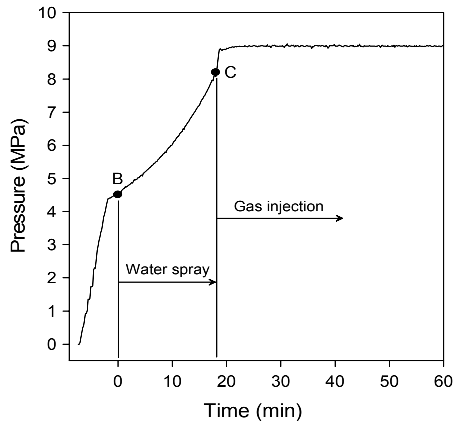


Fig. 6 Water spray test method



(a) 7 Mpa



(b) 9 Mpa

Fig. 7 Pressure change according to water spray and gas injection

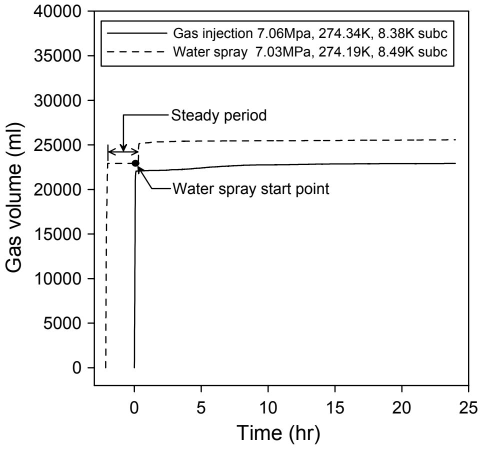
pressure, as mean-values between the initial time reached at experimental pressure and the terminal time. In the figures, since subcooling increases as the pressure is raised at constant temperature, the gas consumption increase can be observed.

3.2 Methane gas consumption on water injection

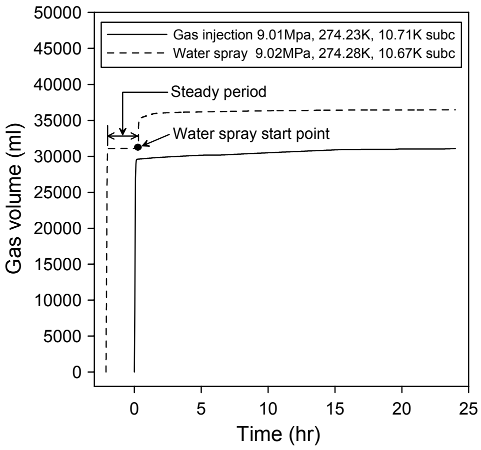
The experiment has been carried out to increase the gas volume consumed by raising the interfacial area between gas and distilled water after pouring gas into the reactor and injecting distilled water. Total volume of the gas fixed in the hydrate on gas injection test, as shown in Figure 11, is poured into the vacuum reactor (A-A') and then cooled to 274.15K (A'-B). After reactor is reached at the experimental temperature, 300 mL distilled water is injected at the rate of 1000 mL/hr for about 17 minutes as liquid droplets with 5-10 ㎛ diameter utilizing a nozzle (B-C). After reactor is reached at the experimental temperature, 300 mL distilled water is injected at the rate of 1000 mL/hr for about 17 minutes as liquid droplets with 5-10 ㎛ diameter utilizing a nozzle (B-C). After the injecting distilled water, experimental gas is injected to maintain constant pressure (D) and the gas consumed in hydrate formation is made up using MFC to maintain constant pressure. Pressure change and total volume of methane gas charged during the test are shown in Figures 7 and 8, and Figure 9 is the photo of methane hydrate growing in a cell with water spray nozzle at 7.03 MPa and 274.19K. Figure 10 shows the volume of methane gas consumed according to water spray and gas injection. As shown in figure 5, since subcooling increases as the pressure is raised at constant temperature, the consumed gas is also increased. And the gas consumption in water injection using a nozzle is three to four times greater according to subcooling than that in gas injection, also, methane hydrate formed immediately after water injecting by a nozzle. Therefore, in this test, it is confirmed the effect of a nozzle, which hydrate formation time can be decreased and the consumed gas quantity is to be increased.

4. Conclusions

The investigation has been carried out for methane hydrate in order to transport of natural gas in the form of solid. The results show that subcooling condition of methane hydrate must be above 9K in order to form hydrate

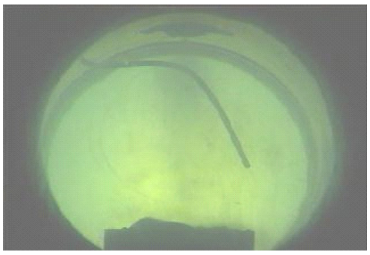


(a) 7 Mpa

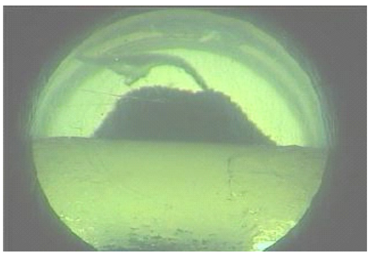


(b) 9 Mpa

Fig. 8 Total volume of methane gas charged during the test



(a) 0 sec



(b) after 17 minutes

Fig. 9 Methane hydrate growing in a cell after water spray

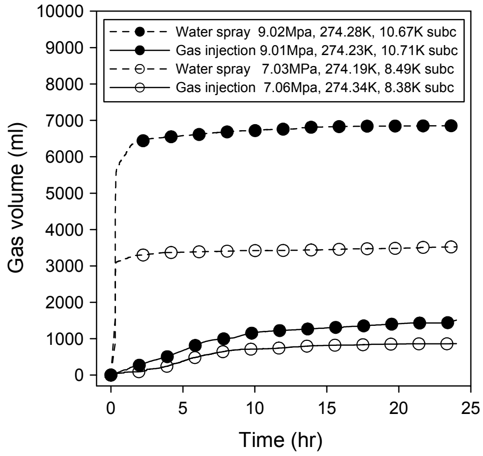


Fig. 10 Volume of methane gas consumed according to the test methods

rapidly, and since subcooling increases as the pressure is raised at constant temperature, the gas consumption increase can be observed both in water injection and in gas injection. Also, the hydrate in water injection formed rapidly more than that in gas injection, the gas volume fixed in methane hydrate in water injection is three to four times according to subcooling greater than that in gas injection, and methane hydrate formed immediately after injection water.

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