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Study on Gas Hydrates for the Solid Transportation of Natural Gas

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Natural gas hydrate typically contains 85 wt.% water and 15 wt.% natural gas, and commonly belongs to cubic structure I and II. When referred to standard conditions, 1 m^3 solid hydrate contains up to 200 m^3 of natural gas depending on pressure and temperature. Such the large volume of natural gas hydrate can be utilized to store and transport a large quantity of natural gas in a stable condition. In the present investigation, experiments were carried out for the formation of natural gas hydrate governed by pressure, temperature, gas compositions, etc. The results show that the equilibrium pressure of structure II is approximately 65% lower and the solubility is approximately 3 times higher than structure I. It is also found that for the subcooling of structure I and II of more than 9 and 11 K respectively, the hydrates are rapidly being formed. It is noted that utilizing nozzles for spraying water in the form of droplets into the natural gas dramatically reduces the hydrate formation time and increases its solubility at the same time.

Key Words : Gas Hydrates, Natural Gas, Induction Time, Cavity, Subcooling Nucleation

1. Introduction

Gas hydrate is formed by physical binding between water molecule and gas such as methane, ethane, propane, or carbon dioxide, which is captured in the cavities of water molecule under the specific temperature and pressure. The hydrate (Fig. 1) is a solid container similar to ice the crystal structure of which is polyhedron cavity consisting of water molecule by hydrogen bond, and it is expressed as n^m. For example, $5^{12}6^2$ means 14 cavities with 12 pentagons and 2 hexagons. 5^{12}, $5^{12}6^2$, $5^{12}6^4$, $5^{12}6^8$, and $4^35^66^3$ are so far recognized as cavity type. Structure I (Fig. 2) is a combination of 6 polyhedrons ($5^{12}6^2$) containing 14 facets and 2 polyhedrons (5^{12}) containing 12 facets, structure II (Fig. 3) is a combination of 16 polyhedrons (5^{12}) containing 12 facets with 8 polyhedrons ($5^{12}6^4$) conta ining 16 facets, and structure H in Fig. 4 is a combination of 3 polyhedrons (5^{12}) containing 12 facets, 2 polyhedrons ($4^35^66^3$) containing 16 facets and 1

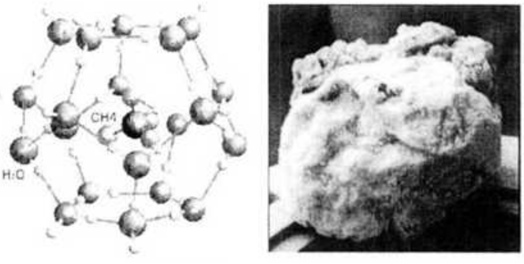

Fig. 1 Natural gas hydrate

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polyhedron ($5^{12}6^8$) containing 20 facets (Sloan, 1998 ; Kim et al., 2000).

Siberian chemical plants in 1930's frequently had a blocking problem in the transportation pipeline of natural gas. The cause of such the problem was attributed to the combination of gas and water in the pipe that produces hydrate adhered an to the inner pipe wall. The natural gas hydrate attracted attention by this discovery (Hammerschmidt, 1934). More than 99% of naturally produced natural gas hydrate consists of methane, and is widely dispersed in the continental slope and continental Shelves of the Pacific, the Atlantic, the Antarctica, etc. The reserve of fossil fuel is 500 billion carbon tons and the reserve of methane is 360 m illion carbon tons. The reserve of gas hydrate is more than 1 trillion carbon tons, which is twice the fossil fuel (Kvenvolden, 1988 ; Chang et al., 2000). Therefore, natural gas hydrate as a kind of gas hydrate is expected to replace fossil fuel as new energy source of 21st century. Also, 1 m^3 hydrate of pure meth ane can be decomposed to the maximum of 216 m^3 methane at standard condition and 1 m^3 hydrate of natural gas can be decomposed to 200 m^3 natural gas at standard condition (Okuda, 1996). If these characteristics of hydrate are reversely utilized, natural gas 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. Especially the transportation cost is known to be 24% less than the liquefied transportation (Gudmundsson et al., 1997).

When the solid hydrate of natural gas is decomposed and extracted in order to commercially utilize, more than 99% of generated natural gas is methane. Since it is a mixed form, its hydrate structure has different forms when its hydrate is changed to solid form and transported. Therefore, the present study focuses on the structure of hydrates with pure methane and natural gas for the comparison of their characteristics. When natural gas hydrate is artificially formed, its reaction time may be too long and the gas

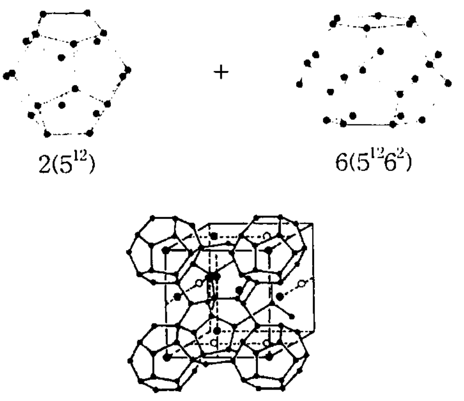


Fig. 2 Crystalline lattice of natural gas hydrate, structure I

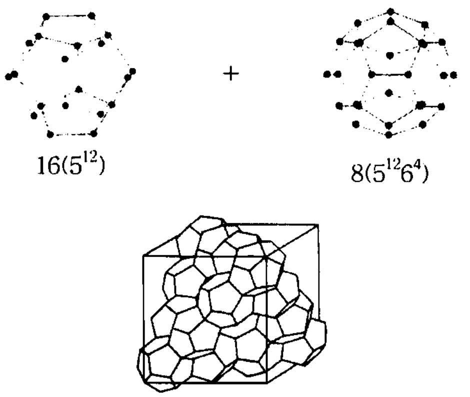


Fig. 3 Crystalline lattice of natural gas hydrate, structure II

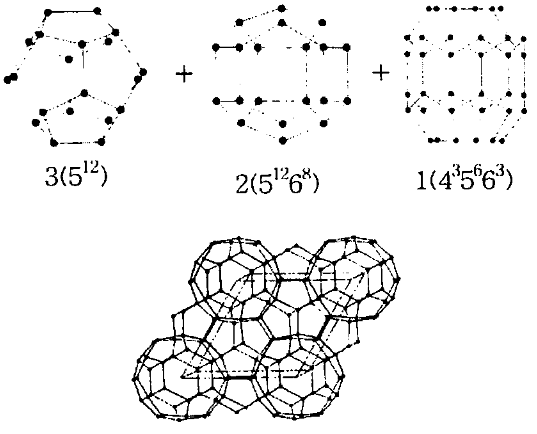


Fig. 4 Crystalline lattice of natural gas hydrate, structure H

consumption in water becomes relatively low because the reaction rate between water and gas is low. Therefore, for the practical purpose in the application, the present investigation focuses on the rapid production of hydrates and the increase of gas consumption by injecting water into gas utilizing nozzle to increase the interfacial area between gas and water. Also, an alternative method to form hydrates more effectively in the need applications is suggested.

2. Experimental Apparatus

Figure 5 shows a schematic diagram for the experimental apparatus. 600 mL reactor (1) and 1.5 L supplemental tanks (24, 27) were manufactured with SUS316 to endure pressure of 30 MPa and salt erosion. Considering high pressure operations in the reactor, a 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 are installed for visualization at front and rear sides of the reactor. A tube (7) of 2 m length is used in order to ensure full heat transfer between gas and water entering the reactor. In the case of masa flow controllers (MFC, Bronkhorst 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 separately installed. For the experimental precision, 97~98% of experimental pressure is controlled by MFC for large gas quantity and then the remaining 2~3% by MFC for small gas quantity to reduce overpressure which may be generated by instantaneous inflow of large quantity. An analog style manometer (19, 0~350 kgf/cm^2, Heise Co.) and a digital gauge (16, Sensys Co.) of error range less than 0.25% in pressure measurement are used. A 1/32 inch T-type heat transmitter (3, OMEGA Co.) and a digital gauge (16, Sensys Co.) are used in the temperature measurement. A chiller (11, 228~403K, Jeio Tech Co.) for the control of reactor temperature, a gas booster (28, 700 kg/cm^2, Schmidt, Kranz & Co Gmbh) for high pressure gas, and a PC (17) for the reading and recording of data such as pressure, temperature, and flow rate are installed. Reactants used in most experimentations are secondary distilled water, 99.99% methane gas (47, Quadren Cryogenic Co.), and Indonesian natural gas (47, Rigas Co.). Table 1 shows the composition of reactant gases.

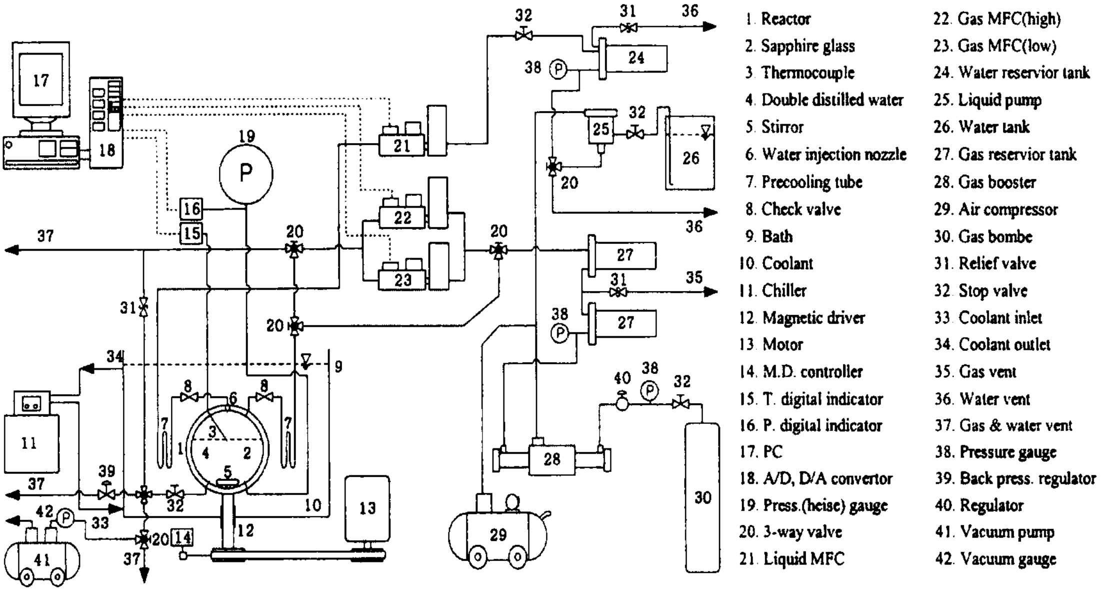


Fig. 5 Schematic diagram of the apparatus

Table 1 Compositions of natural gas

	Certified Concentration (mol/mol)	Uncertainty
Methane (CH_4)	90.8784%	
Ethane (C_2H_6)	5.63%	±2%
Propane (C_3H_8)	2.52%	±2%
iso-Butane (i-C_4H_{10})	0.493%	±2%
n-Butane (n-C_4H_{10})	0.447%	±2%
iso-Pentane (i-C_5H_{12})	102 PPM	±3%
Nitrogen (N_2)	214 PPM	±3%

Table 2 Hydrate crystal structure according to composition ratios based on methane gas

Compositions	Ratios (%)	Structure
Ethane (C_2H_6)	≥10	I (II*)
Propane (C_3H_8)	≥0.0146	II
iso-Butane (i-C_4H_{10})	≥0.01	II
n-Butane (n-C_4H_{10}	≥0.108	II (I*)
iso-Pentane (i-C_5H_{12})	≥0.866	H
n-Pentane (i-C_5H_{12})	>0	No formation
Nitrogen (N_2)	>0	I or II
Carbon dioxide (CO_2)	>0	I

*Apparent character

Table 3 Characteristics of structure I and II

Parameters	Structure I	Structure II
No. of H_2O molecules in the unit cell	46	136
No. of 5^{12}	2	16
No. of $5^{12}6^2$	6	—
No. of $5^{12}6^4$	—	8
Latice parameters at 273 K (nm)	1.2	1.73
Crystal type	Cubic	Cubic

3. Experimental Methods and Results

3.1 Structure of natural gas hydrate

Since natural gas is a mixed gas, its hydrate structure depends on the composition. The structure of natural gas investigated by CSMHYD, a program provided by Colorado School of Mines is shown in Table 2.

The natural gas containing more than 10% ethane forms structure I but has the characteristics of structure II. The mixed gas containing more than 0.108% n-butane forms structure II but has the characteristics of structure I. On the other hand, the natural gas containing more than 0.0146% propane and 0.01% i-butane forms structure II, and the natural gas with more than 0.866% i-pentane forms structure H. Since the natural gas including n-pentane cannot form any hydrates, n-pentane does not affect the structure of hydrate. Carbon dioxide forms structure I regardless of composition ratio, and nitrogen can form structure I or II depeding on the formation temperature and pressure (Kuhs et al., 1997). However, the gas of large molecular weight affects its structure when it forms hydrate of mixed gas. Imported natural gas to Korea has less than 0.05% i-butane which has the largest molecular weight; its hydrate forms structure II, not structure H. In the case of the natural gas hydrate which naturally exists (more than 99% of decomposed gas is methane and the other is carbon dioxide), its hydrate forms structure I. Therefore, reactant methane and natural gas form the structure I and II hydrate, respectively. Table 3 shows their structural characteristics.

3.2 Equilibrium measurement

Hydrate is generally stable under high pressure and low temperature. It is easily decomposed to water and gas out of the stable region. Since the formation and decomposition of hydrate can be visually confirmed, phase equilibrium is performed considering the specialty of experimental apparatus. Model cases are isothermal and isobaric experiments as shown in Fig. 6. In the isothermal experiment, hydrate is formed at arbitrary temperature B (T_{equ}) and pressure A (P_{exp}) that is higher than pressure D (P_{equ}), and pressure gradually decr eased at a constant temperature in the course A → B. In the isobaric experiment, temperature gradually increased at a constant pressure in the course A → C (Englezos, 1987). After performing two experiments in the present study, the isobaric experiment is found to be more convenient than the isothermal experiment. Since the decomposition of hydrate can be

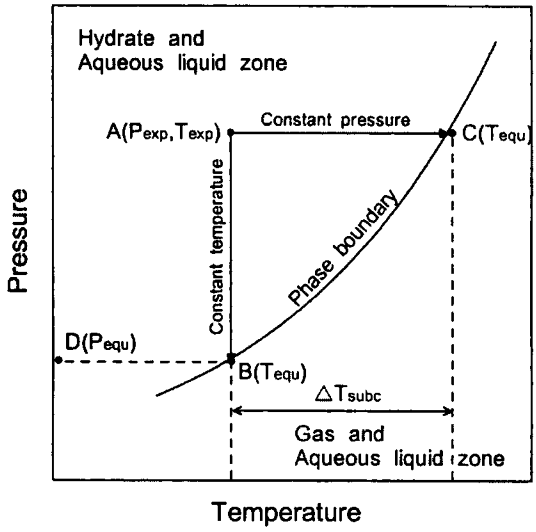
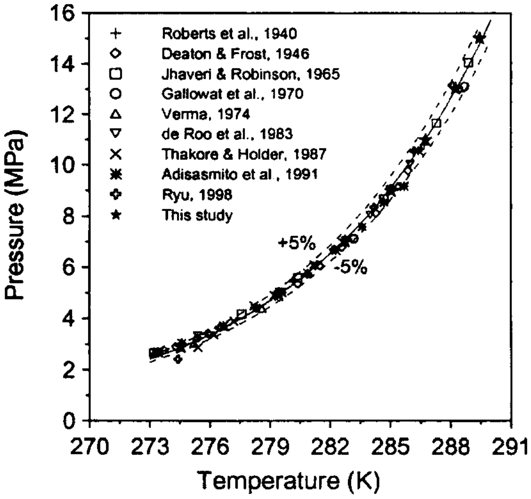


Fig. 6 Experimental method

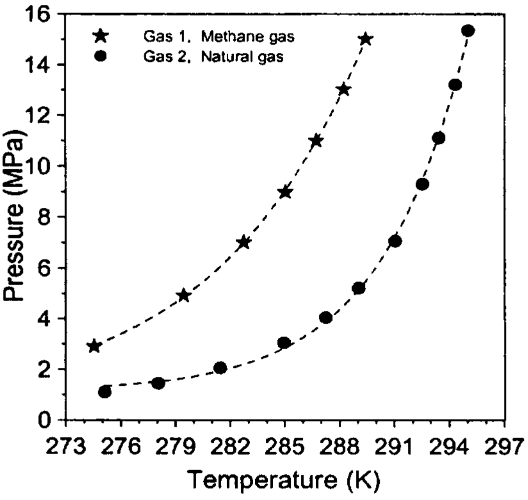
visually observed, the isobaric experiments have been performed as follows.

300 mL distilled water is poured into the reactor using a liquid phase pump and cooled to 274.15 K, and experimental gas under 19 MPa is injected into the reactor at the pressure of 1~15 MPa according to experimental conditions. The experimental conditions A is kept constant for several hours in order to completely grow hydrate. After hydrate is fully grown, reactor temperature is raised by 0.1 K for every two hours (course A → C). The pressure increase due to the decomposition of hydrate is controlled to keep constant by discharging (37) gas within the reactor through the 3-way valve (20) and MFC. Figure 7 shows melting temperatures of the hydrate.

Figure 7(a) shows a good agreement between the earlier results (Sloan, 1998) and equilibrium points of gas 1 from this study. Therefore, the experimental apparatus and method of the present investigation are proven to be adequate. Figure 7(b) shows the equilibrium of gas 2. Hydrate formation pressure in gas 2 is about 65% lower than that in gas 1 at the same temperature and hydrate is formed at relatively higher temperature under the same pressure. Therefore, the formation process of gas 2 is advantageous to that of gas 1. Equation (1) shows the relation between equilibrium temperatures and pressures. Table 4 gives the coefficients for the equation.



(a) Gas 1



(b) Gas 1 and 2

Fig. 7 Equilibrium points

$$P_{equil}=a+b\times e^{cT_{equil}} \tag{1}$$

2.3 Measurements of hydrate nucleation time

As shown in Fig. 6, hydrate formation is accelerated at higher pressure than the equilibrium pressure and at lower temperature than the equilibrium temperature. The subcooling temperature, ΔT_{subc} is defined as the difference

Table 4 Constants for pressure and temperature

	Gas 1	Gas 2
a	5.384E-01	1.111E-00
b	1.023E-14	3.303E-26
c	1.205E-01	2.078E-01

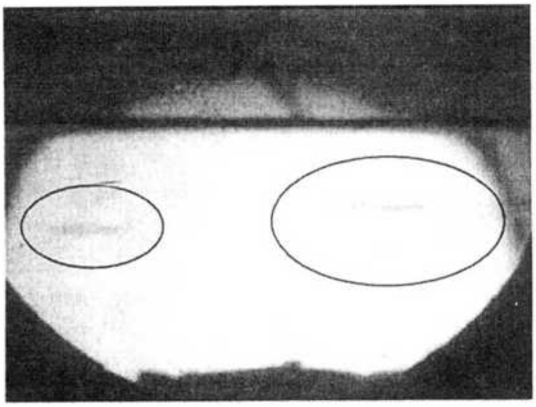


Fig. 8 Photograph of nucleation

Table 5 Constants for induction time (min)

	Gas 1	Gas 2
a	−1.046	−1.654
b	11.273	20.238

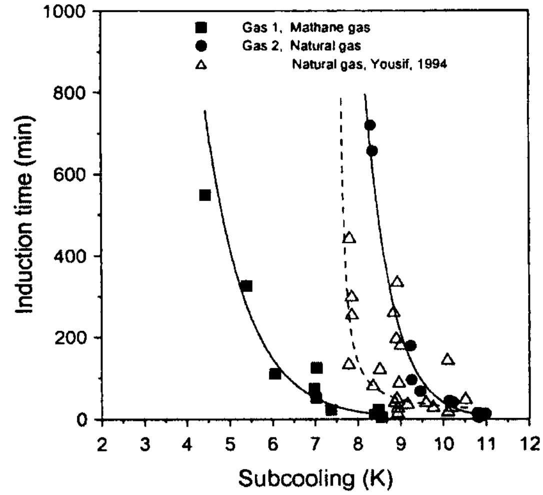


Fig. 9 Induction time of hydrate nucleation

between the experimental and equilibrium temperatures. 300 mL of distilled water is poured into the reactor and cooled to the experimental temperature and then the gas is injected. After reaching the experimental pressure, hydrate nucleus is observed for 24 hours in the circle as shown in Fig. 8.

Figure 9 shows the formation time of hydrate nucleus. As shown in the figure, hydrate formation time increases as the system approaches the equilibrium condition. At the same time, it is found that if subcooling temperature increases, hydrate formation time decreases. At the same subcooling conditions, gas 1 hydrates are formed faster than gas 2. For gas 2, however different results were induced comparing to the results of Yousif (1994) due to different experimental gas, formation rate, and experimental set-up. This is considered to be attributed to the difference between gas components and its composition. However, if subcooling condition is set above 11 K for structure II or 9 K for structure I, hydrates were formed rapidly regardless of gas components and its composition during pressurization. The following equation expresses nucleation time with its coefficients in Table 5.

$$\ln(time) = a \times \Delta T_{subc} + b \qquad (2)$$

3.4 Measurements of gas consumption on subcooling

300 mL distilled water is poured into the reactor and cooled to be 274.15 K 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 constant. Figure 10 shows gas consumption, temperature, and pressure as mean-values between the initial time reached at experimental pressure and the terminal time.

Since subcooling increases as the pressure is raised at a constant temperature, the gas consumption trend can be observed. Gas consumption in gas 2 is three times greater than that in gas 1 at the same pressure because subcooling, number of holes, and the size of unit cell in gas 2 are larger than gas 1, which allows gas 2 to conta in more amount of gas.

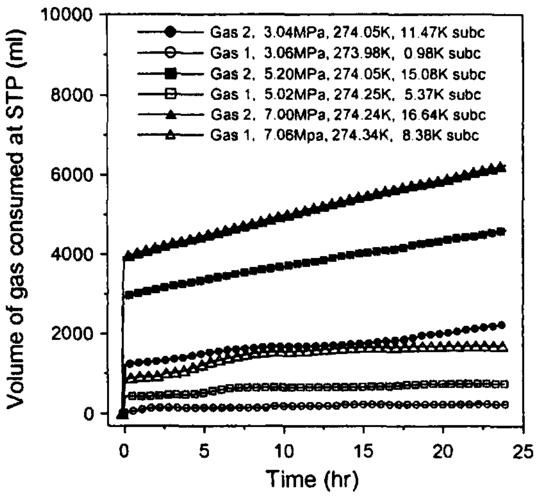


Fig. 10 Gas consumption volume for variable degrees of subcooling

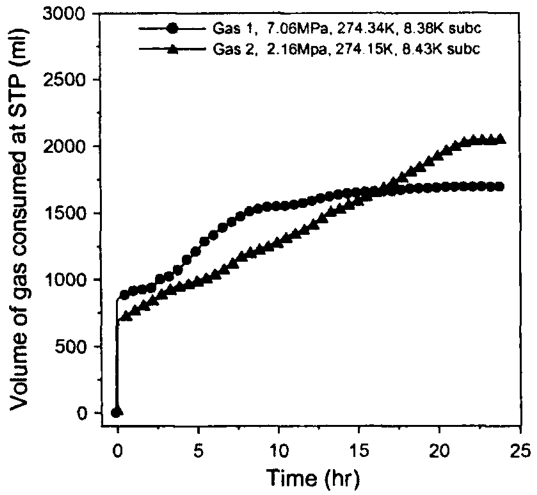


Fig. 11 Gas consumption volume at the same subcooling over the freezing point

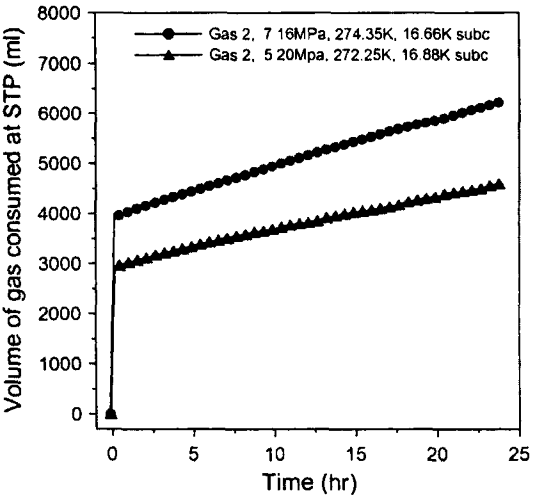


Fig. 12 Gas consumption volume at the same subcooling below the freezing point

Figures 11 and 12 show gas consumption above and below the freezing point at the same subcooling conditions. Figure 11 shows that gas 1 has more gas consumption at the initial stage because hydrate formation time in gas 1 is faster than that in gas 2 as shown in Fig. 9. However, as the time passes in the investigation, the characteristics of gas 2 revitalize and give more gas consumption than gas 1. In Fig. 12, it is also shown that more gas is consumed above the freezing point because the main component of natural gas is methane that is non-polar gas and insoluble to water. This coincides with Henry's law which states solubility in non-polar gas or little polar gas is proportional to pressure. Therefore, the pressure increase is better than the temperature increase in order to increase the gas consumption.

3.5 Measurements of gas consumption with the injection of distilled water

The experiments have been carried out to increase gas consumption by raising the interfacial area between gas and distilled water after pouring gas into the reactor and injecting distilled water. Gas consumption depending on subcooling, as shown in Fig. 13, was measured in 24 hours after poured into the vacuum reactor (A-A') and cooled to 274.15 K (A'-B). After the reactor reached 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 μm dia meter utilizing a nozzle (B-C). After injecting the distilled water, experimental gas is injected to maintain a constant pressure (D) and the gas consumed in hydrate formation is made up using MFC to maintain a constant pressure. The res ults are shown in Figs. 14 and 15 for gas consumption and pressure changes.

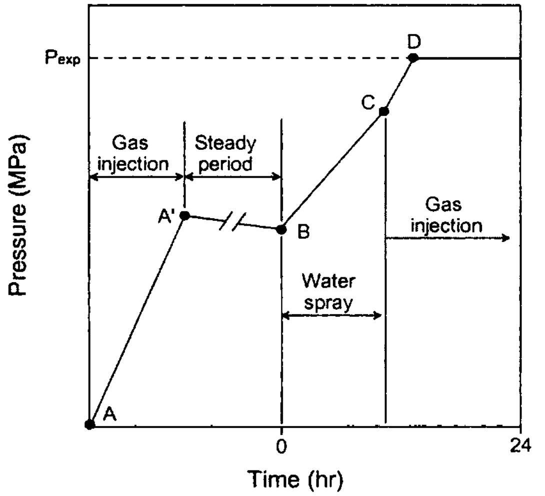


Fig. 13 Water spray test method

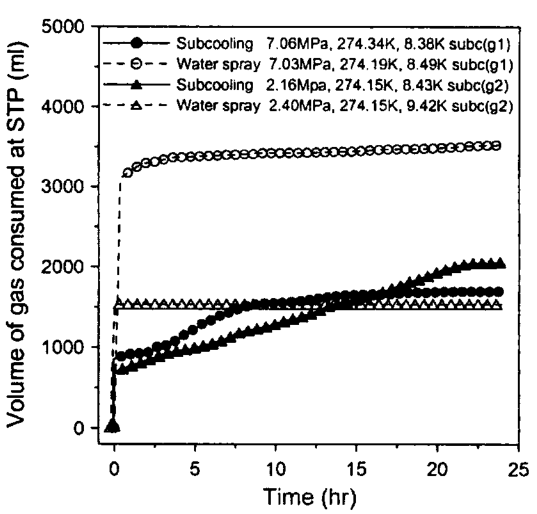
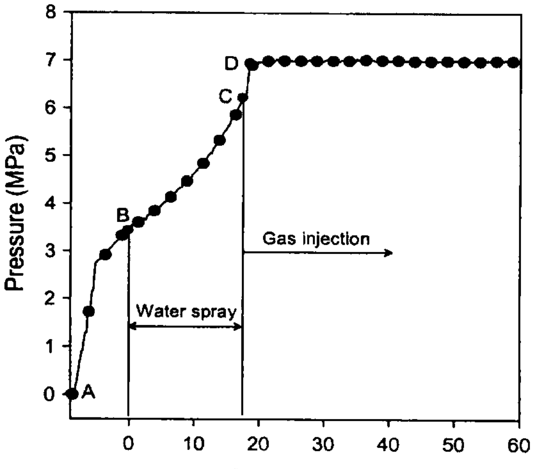
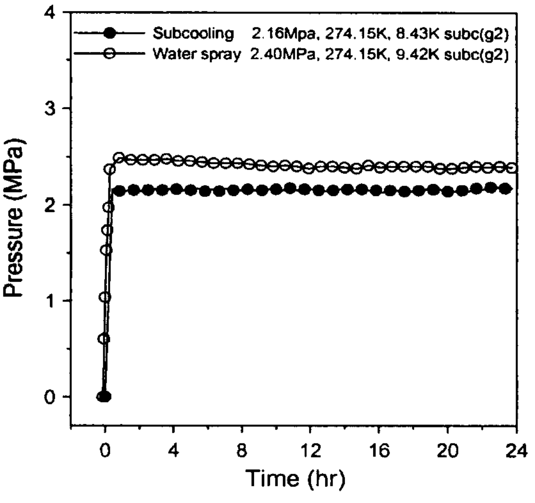


Fig. 14 Gas consumption volume according to subcooling and water spray methods



(a) Gas 1



(b) Gas 2

Fig. 15 Pressure change according to water spray and gas injection

In injecting distilled water using a nozzle as shown in Fig. 14, hydrate formation time in gases 1 and 2 decreases. In Fig. 15(a), gas 1 shows that the pressure after the injection is decreased to be approximately 90% of experimental pressure and gas consumption becomes four times larger in order to maintain the experimental pressure (7 MPa). As a result, gas is additionally injected to compensate the pressure difference of 10%. However, the gas consumption in gas 2 does not show the increase in gas consumption as gas 1. It is explained that the hydrate nucleation time in gas 2 is longer than that of structure I (Table 3) and the hydrate is not completely formed during the water injection because of the large size of unit cell and overpressure is accomplished after the water injection as shown in Fig. 15(b) due to the large hydrate volume.

Gas consumption increases at the time of hydrate formation as shown in Fig. 14. However, the gas consumption after the hydrate formation barely increases. Therefore, the reinjection of distilled water where hydrate is not formed in the

Fig. 16 Combustion of methane hydrate (gas 1)

reactor is more effective. Since water cannot be injected at more than 9 and 11 K subcoolings of gases 1 and 2 in real situations, the hydrate formation using a nozzle must be performed at below 9 and 11 K of subcooling. After the complete reaction of methane with the distilled water at 11 MPa and 274.15 K, the formed hydrates are collected and burned to prove good combustion as shown in Fig. 16.

4. Conclusions

The investigation has been carried out for methane and natural gas hydrates in order to transport large amounts of natural gas in the form of solid. The results are summarized as follows :

(1) Methane hydrate has the structure I in its nature while major natural gas hydrates imported to Korea have the structure II.

(2) In the equilibrium measurement of the gases 1 and 2, hydrate formation pressure in the gas 2 is approximately 65% lower than that of the gas 1.

(3) The hydrate formation rate in the gas 1 is faster than that of the gas 2 at the same subcooling, and the subcooling conditions of the structure I and II must be above 9 and 11 K in order to rapidly form hydrates regardless of the gas components.

(4) The gas consumption in the gas 2 is three times of larger than that of gas 2 since the subcooling, the size, and the number of holes in the gas 2 are larger than those of gas 1 at the same pressure.

(5) Since the main component of the natural gas is methane that is non-polar, the pressure increase is more advantageous than the temperature decrease in order to increase the gas consumption.

(6) The gas consumption of the structure I in water injection using a nozzle is four times larger than that in subcooling.

(7) Because the unit cell size and nucleation time of the gas 2 are larger than those of the gas 1, the hydrate is not completely formed during the water injection and the nozzle effect is not acquired in the gas 2 and the combustion of produced hydrates is proven to be of good quality.

Acknowledgment

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