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Study of a Power Generation System for Distributed Power Supplies that Utilizes the High-Pressure Dissociation Characteristics and the Small Difference in the Temperature of CO_2 Hydrate*

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Abstract

When the mixed fluid of gas and water is pressurized and cooled to a given pressure and temperature, the generation of a gas-hydrate occurs. By heating, a very high pressure is obtained from the dissociated gas from the gas-hydrate. The purpose of this study is to investigate the operation of a high-pressure gas engine generator for distributed power supplies using the high pressure obtained though the dissociation of a gas-hydrate. A gas-hydrate functions as a working fluid and as a form of energy storage. However, until now, an actuator that uses the dissociation inflation characteristics of a gas-hydrate has not been examined. Therefore, the generation rate of CO_2 hydrate and the quantity to be stored from the dissociation expansion energy of CO_2 hydrate were investigated. As a result, when 1 m^3 of water was used to generate CO_2 hydrate for 480 minutes, the result was that electric power corresponding to approximately 45% of the daily power consumption (4.5 kWh of generator outputs) of an individual house can be stored.

Key words: CO_2 Hydrate, Energy Storage, Power Generation, Distributed Power System, High-Pressure Gas Engine, Low-Temperature Exhaust Utilization

1. Introduction

The pressure-temperature characteristics of a gas-hydrate include a large differential pressure that is obtained from a small difference in temperature. Therefore, a clean power generation system could potentially be constructed by using the low-temperature exhaust heat of a factory, the difference in temperature between day and night, the green energy created by the hydrate generation cycle. A gas-hydrate holds a gas molecule with a clathrate compound.

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The generation rate of a gas-hydrate is influenced by the solubility of the gas. When generating a hydrate using a gas with a high solubility in water, it is thought that a clathrate is formed after the gas fully dissolves in water. The pressure-temperature characteristics of the gas-hydrate change greatly with the types of gas[1]. For example, in the case of CO_2 hydrate, a pressure differential (difference in the highest pressure of the gas dissociation and the minimum pressure of the hydrate generation) of approximately 3 MPa can be obtained on the phase equilibrium curve of generation and dissociation for an approximately 10 °C difference in temperature. Moreover, when the temperature of a methane hydrate is changed from 0 °C to 10 °C, a pressure differential of 4 MPa or more will occur on the phase equilibrium curve. Therefore, we were examining the operation of a high-pressure gas engine generator according to the differential pressure obtained from the difference in temperature and the gas-hydrate. In this paper, the basic technology of an engine generator operated by a high-pressure gas for distributed power supplies is investigated. Until now, gas hydrates have been examined in many fields, such as the transportation of fuel gas and the undersea storage of CO_2[2-4]. However, the application of CO_2 hydrate in the working fluid of an actuator has not yet been studied.

Production of the gas-hydrate by green energy and exhaust heat means clean energy storage. However, the energy density of the energy storage, the energy storage velocity, the energy release velocity, etc., of CO_2 hydrate has not been fully investigated. Therefore, in this paper, the generation rate of CO_2 hydrate and the quantity of the dissociation expansion energy to be stored are clarified by tests and numerical analysis.

2. Characteristics of CO_2 Hydrate and Application to a Distributed Power Supply

Figure 1 is a phase diagram of CO_2 hydrate[1]. Generally, the difference in the minimum pressure of the generation time and the highest pressure at the time of gas dissociation of the gas-hydrate can be obtained for a narrow temperature change. For example, when CO_2 hydrate at 0 °C is heated to 10 °C, a differential pressure of approximately 3 MPa can be obtained, as shown in Fig. 1. A high-pressure gas engine generator can be operated using this differential pressure. Cold and warm states can be created from green energy, such as the difference in temperature between the day and the night, low temperature exhaust heat, the sunlight, and wind power generation in a cold region. When an engine generator using the expansion characteristics of the dissociation of CO_2 hydrate proposed in this study (CH engine generator) is realized, a new, clean, distributed power generation system can be constructed. Furthermore, although CO_2 hydrate can provide energy storage, because the generation rate of the hydrate is slow, it is expected that the energy density of a CH engine

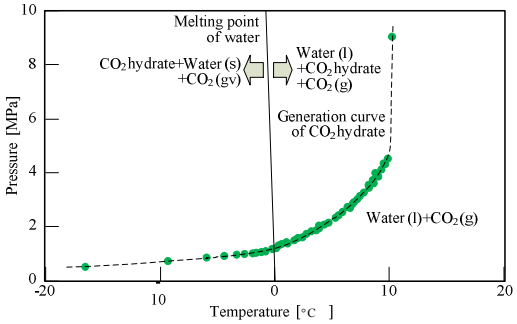


Fig. 1 Phase diagram of CO_2 hydrate

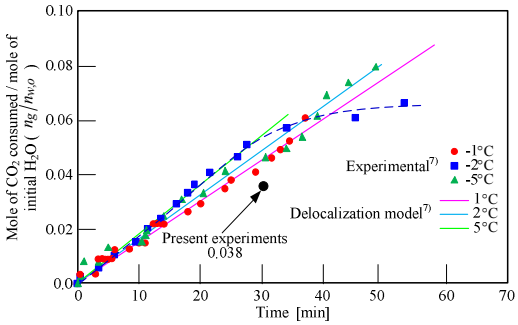


Fig. 2 Experimental and analytic results in the early period of CO_2 hydrate growth

generator will be low. Until now, because there are no examples of using CO_2 hydrate as the working fluid of an actuator, the possibility of the practical use of a CH engine generator is not known. In this paper, the generation rate of CO_2 hydrate and the quantity of the dissociation expansion energy of the hydrate to be stored are investigated, and the energy density of a CH engine generator is clarified.

3. Numerical Analysis

3.1 Generation of CO_2 Hydrate

The dissolved amount of CO_2 in water is large, and the amount of CO_2 contained in 100 cm^3 of water at 25 °C and 100 kPa is 0.145 g. For these conditions, the value of the consumed CO_2 in moles divided by the moles of water ($n_g/n_{w,o}$) in Fig. 2 is 0.000593 (described later). The amount of CO_2 hydrate grows by keeping CO_2 fully dissolved in water under the generation condition of a hydrate. Moreover, it is known from many hydrate generation experiments that a gas-hydrate has a memory effect[5]. The generating time is short when the water is used in the generation and the dissociation of the hydrate is maintained under the generation conditions of the hydrate. The physical phenomenon described above is called the memory effect of a hydrate. It is thought that the memory effect occurs because the next nucleation becomes easier through the survival of part of the hydrate structure in the liquid water phase[6]. Moreover, it was reported by Kawamura et al. in 2002 that the generation rate of CO_2 hydrate at an icy melting point can be compared with the generation rate at other temperature and pressure conditions[7]. Fig. 2 shows the results of the experiments and the analysis of the generation rate of CO_2 hydrate at an icy melting point reported by Kawamura et al.

3.2 Generation Rate of CO_2 Hydrate

The following equations are the generation reaction equation of CO_2 hydrate.

$$CO_2(gas) + Hn \cdot H_2O(liquid) \rightarrow CO_2 \cdot Hn \cdot H_2O(hydrate) \quad (1)$$

Here, Hn is a theoretical hydration number and Hn =5.75 for a filling factor of 1. However, the filling factor is normally 7 to 8[8-13]. Moreover, the specific gravity of CO_2 hydrate is 1.1, which is greater than seawater[14, 15].

The Englezos-Bishnoi model[16] is introduced into the calculation of the growth rate of a hydrate[17]. The fugacity difference is assumed to be the driving force in the Englezos-Bishnoi model. Equation (2) is a computation expression for the CO_2 gas volume consumed with the growth of the hydrate. $n_g(t)$ is proportional to the amount of water (the number of moles), $n_w(t)$, in the container, and the gas-liquid contact area is proportional to amount of water, as assumed in Eq. (2).

$$\frac{dn_g(t)}{dt} = K' \cdot \left(f_{ex} - f_{eq} \right) \cdot n_w(t) = K' \cdot \left(f_{ex} - f_{eq} \right) \cdot \left\{ n_{w,o} - Hn \cdot n_g(t) \right\} \quad (2)$$

Fugacity is defined as the pressure of an ideal gas with the same chemical potential as a certain real gas. Here, when it is assumed that $K' \cdot \left(f_{ex} - f_{eq} \right)$ and Hn are constant, the following formula can be obtained by integrating the above equation.

$$\frac{n_g}{n_{w,o}} = \frac{1}{H_n} \cdot \left[1 - \exp\left\{ - Hn \cdot K' \cdot \left(f_{ex} - f_{eq} \right) \cdot t \right\} \right] \tag{3}$$

Although the generation process of a hydrate is investigated here, as shown in Eq. (4), it is necessary to adjust Eq. (3) for the amount of CO_2 dissolved before the hydrate is generated.

$$\frac{n_g}{n_{w,o}} = \frac{1}{hn} \left[1 - \exp\left\{ - hn \cdot K' \cdot \left(f_{ex} - f_{eq} \right) \cdot t \right\} \right] + \frac{n_{gf}}{n_{w,o}} \tag{4}$$

Here, n_{gf} is the number of moles of CO_2 dissolved in water and hn is the hydration number at the time of generation of the hydrate obtained from the following equation:

$$hn = \frac{1}{\left(q_1 - q_2 \right) \cdot n_{w,o}} \tag{5}$$

Here, q_1 is the number of moles of CO_2 contained in 1 mol of water after hydrate completion, and q_2 is the number of moles of CO_2 included in 1 mol of water at the time of generation. The hydration number, Hn, is 8.13, which is confirmed by the experiment of Haneda et al.[13]. Although hn is 11, it differs based on the conditions.

3.3 External Work of a High-Pressure Fluid

(1) CO_2 gas

The computation expression of the heat insulation work shown in Eq. (6) is introduced into the energy conversion of the gas expansion by an actuator.

$$P_{co_2} \cdot V_{co_2}^{\kappa} = \text{constant} \tag{6}$$

Here, P_{co_2}, V_{co_2}, and κ are the pressure of the CO_2 gas, the volume, and the ratio of the specific heat, respectively. When the CO_2 gas arrives at the exit (condition (P_b, V_b)) from the inlet port (condition (P_a, V_a)) of an actuator, the gas is assumed to be experiencing adiabatic expansion. In this case, the CO_2 gas at P_a and T_a works adiabatically to P_b. The temperature in the actuator exit of the CO_2 gas is calculated from the following equation:

$$T_b = T_a \cdot \left(\frac{P_b}{P_a} \right)^{(\kappa - 1)/\kappa} \tag{7}$$

The work, L_{co_2}, obtained by the expansion of the CO_2 gas is determined using the following equation, where R_{CO_2} is a gas constant of CO_2:

$$L_{CO_2} = G_{CO_2} \cdot \frac{R_{CO_2}}{\kappa - 1} \cdot \left(T_a - T_b \right) \tag{8}$$

The work (L_{vp}) of the steam, as well as the calculation method described above, is obtained.

(2) Liquid water

The high-pressure water under the conditions (P_a , T_a) can be used to calculate the work, L_{H2O} , at the time the conditions change to (P_b , T_b) by the following equation:

$$L_w = V_w \cdot \Delta P_{a-b} \tag{9}$$

Here, V_w is a mass flow rate of water and ΔP_{a-b} is the pressure differential of the operating points a and b.

The work, L_{chd} , obtained from the pressure increase of each gas and the water from the dissociation of CO_2 hydrate in an enclosed space is a combination of Eqs. (8) and (9), where L_{vp} on the right-hand side of Eq. (10) is the heat insulation work done by the steam.

$$L_{chp} = L_{CO_2} + L_{vp} + L_w \tag{10}$$

The mechanical efficiency of the actuator, except for the generator, and the efficiency of the generator are set to η_a and η_e , respectively. The power output, W , from the actuator (engine generator) is calculable by the following equation:

$$W = L_{chp} \cdot \eta_a \cdot \eta_e \tag{11}$$

3.4 Heating Value of Dissociation and Generation of CO_2 Hydrate

The latent heat, h_{ch} , of CO_2 hydrate is approximately 500 kJ/kg[18]. The heat of dissociation, $H_{d,t}$, and the heat of formation, $H_{re,t}$, of CO_2 hydrate during a sampling time, t , are obtained from the following equations, respectively. Here, ΔT_{d-ost} is the difference in temperature between the dissociation temperature of CO_2 hydrate and the outside air temperature, and ΔT_{ost-r} is the difference in the outside air temperature and the generation temperature of CO_2 hydrate. The calculation of the heating value in Eqs. (12) and (13) is based on the outside air temperature.

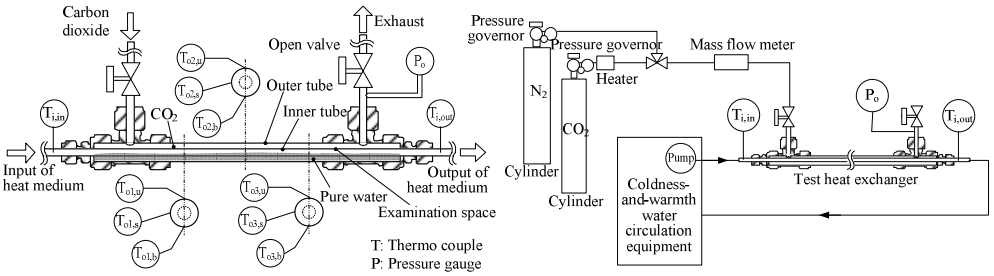
$$\begin{aligned} H_{d,t} &= \left(H_{w,s,t} + H_{CO_2,s,t}\right) \cdot \Delta T_{d-ost} + H_{ch,l,t} \\ &= \left(G_w \cdot h_{w,s} + G_{CO_2} \cdot h_{CO_2}\right) \cdot \Delta T_{d-ost} + G_{CO_2} \cdot h_{ch} \end{aligned} \tag{12}$$

$$\begin{aligned} H_{r,t} &= \left(H_{w,s,t} + H_{CO_2,s,t}\right) \cdot \Delta T_{ost-r} + H_{ch,l,t} \\ &= \left(G_w \cdot h_{w,s} + G_{CO_2} \cdot h_{CO_2}\right) \cdot \Delta T_{ost-r} + G_{CO_2} \cdot h_{ch} \end{aligned} \tag{13}$$

4. Generation and Dissociation Experiments of CO_2 Hydrate

4.1 Experimental Device

Figure 3 shows the outline of an experimental device used for the investigation of the dissociation and the generation of CO_2 hydrate. As shown in Fig. 3 (a), this experiment device consists of double pipe heat exchangers and supplied a heat-exchanger fluid for cooling and heating the inner pipe. The space between the outside pipe and the inner pipe was filled with pure water and CO_2 (this space is described as an examination space below). The volume of this examination space was approximately 100 cm^3. The outside diameter and bore of the outside pipe were 25.4 mm and 21.2 mm, and the outside diameter and bore of the inner pipe were 12.8 mm and 10.2 mm. Moreover, the outside pipe shown in Fig. 3 (a) was approximately 450 mm in length. As shown in Fig. 3 (b), N_2 for the replacement of



(a) Test heat exchanger (b) Test equipment

Fig. 3 Generation and dissociation test equipment of CO_2 hydrate

the examination space could be supplied to the experimental device. A temperature sensor (T-type covering thermocouple) was installed in the outer wall of the outside pipe, and was used to measure the input/output of the heating medium. The pressure in the examination space was measured using a pressure sensor (Fig. (a)). Because the pressure in the examination space was 3 MPa or more, the temperatures of the water, the CO_2, and the CO_2 gas-hydrate in the examination space were not measured directly in this experiment.

4.2 Experimental Method

Because the solubility of CO_2 is large, the test equipment filled up with CO_2 is placed 30 minutes or more. The pressure of the examination space before each test is adjusted to 3 MPa. The examination space was filled with CO_2 and 50 cm^3 of pure water. Furthermore, an improvement in the generation speed of the hydrate as the result of the memory effect was expected, and the generation and dissociation steps were repeated several times in the experiment. Moreover, the heat of generation and dissociation of CO_2 hydrate was fully supplied in this experiment.

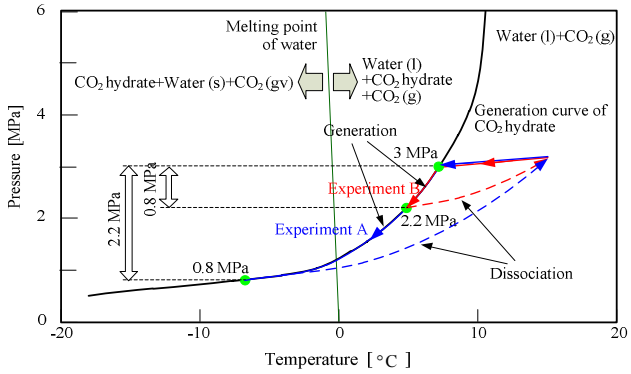
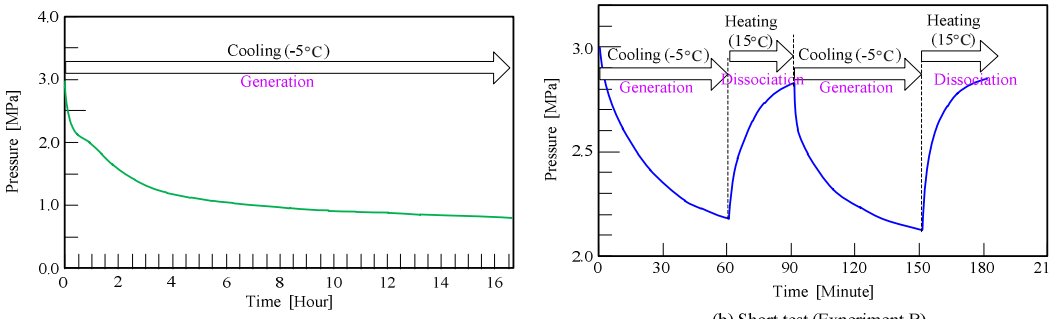


Fig. 4 Generation process of CO_2 hydrate



(a) Long test (Experiment A) (b) Short test (Experiment B)

Fig. 5 Experimental results of the pressure of CO_2 dissolution test

5. Results and Discussion

5.1 Generation Process of CO_2 Hydrate

Figure 4 shows the expected change of state in the long generation experiment of CO_2 hydrate (Experiment A) and the experiment with the repeated generation and dissociation steps (Experiment B). The examination space is fulfilled with CO_2 and pure water (respectively about 15 °C). Next, a cold medium was supplied to the inner pipe, and the fluid in the examination space was cooled. As a result and as shown in Fig. 4, it was expected that the temperature and the pressure would decline along the generation curve for CO_2 hydrate.

5.2 Generation Rate of CO_2 Hydrate

Figures 5 (a) and (b) are the experimental results of Experiment A and B, respectively. The heat-exchanger fluid temperature at the time of the hydrate generation in each experiment was -5 °C. Moreover, the heat-exchanger fluid temperature in the dissociation step in Experiment B was 15 °C. The generation of CO_2 hydrate was continued in Experiment A for 16 hours or more. In contrast, the generation of CO_2 hydrate for 1 hour and the dissociation for 30 minutes were repeated in Experiment B. As shown in Fig. 5(a), we found that if the test time exceeded 4 hours, the generation speed of CO_2 hydrate would decrease. Moreover, the generation rate for the first 30 minutes was the lowest compared with the other time zones. The generation time of CO_2 hydrate was 1 hour in Experiment B. Compared with the generation time of CO_2 hydrate, the speed of the gas dissociation was low. The gas dissociation of Experiment B was approximately 30 minutes. In the equation for the state of an ideal gas, the pressure drops by contraction upon gaseous cooling. Therefore, to clarify the difference between the decreased pressure accompanying the generation of CO_2 hydrate and the decreased pressure caused by contraction of CO_2, N_2 was used instead of CO_2. This result is shown in Fig. 6, where heat was automatically radiated after cooling for 1 hour. When N_2 was cooled, a decrease in pressure of approximately 0.2 MPa was seen at the maximum in Fig. 6. Therefore, the decreased pressure from the cooling of CO_2 was contained in the generation of CO_2 hydrate shown in Fig. 5.

Based on the experimental results of Experiment A and B, the amount of CO_2 consumption accompanying the generation of the CO_2 hydrate is plotted in Fig. 2. The results of this experiment were lower than each result of reference[7]. This is because each result of reference[7] was a value at an icy melting point because the generation rate of the hydrate was obtained very early in the process. Furthermore, the generation speed of a hydrate easily changes as the result of factors such as the structure and the churning state of the test equipment and the heat transmission in the examination space.

5.3 Generation Characteristics of CO_2 Hydrate

(1) Energy storage time

Although CO_2 hydrate can be used an operational fluid in a power generation system, CO_2 hydrate also has an energy storage function. That is, the energy from the pressure increase at the time of gas dissociation can be stored during the generation of CO_2 hydrate. Therefore, in this paper, the amount of energy stored and the storage time for CO_2 hydrate were investigated. Figure 7 shows the experimental results of the differences in pressure (difference between the highest pressure at the time of gas dissociation and the minimum

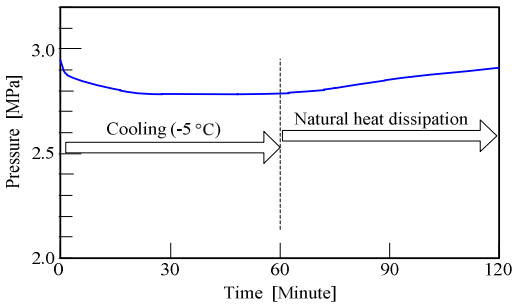


Fig. 6 Results of the reference test using N_2

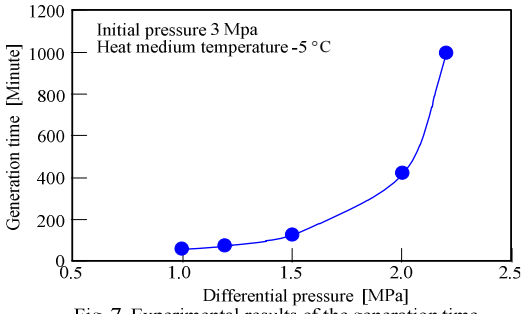


Fig. 7 Experimental results of the generation time for obtaining a pressure differential

pressure at the time of hydrate generation) and the CO_2 hydrate generation time obtained at the initial pressure of 3 MPa and a heat-exchanger fluid temperature of -5 °C. This result changes significantly with the setting of the heat-exchanger fluid temperature. In the result shown in Fig. 7, if the pressure difference is greater than 1.5 MPa, the generation time of the hydrate will rapidly become greater.

(2) The relationship between the temperature and the pressure difference of CO_2 hydrate

Figure 8 shows the difference in the highest pressure at the time of gas dissociation of CO_2 hydrate and the minimum pressure at the time of CO_2 hydrate generation (in this case, 15 °C and 6 MPa). For example, if CO_2 hydrate can be cooled to -10 °C, the differential pressure will be approximately 5 MPa. If the generation temperature of CO_2 hydrate is low, a large pressure difference can be obtained, as seen in Fig. 8, but at approximately 0 °C or less, the change in the pressure difference is small. It is thought that CO_2 hydrate continues to be generated at 0 °C or lower, although there is almost no increase in the pressure difference. Below 0 °C, it is surmised that the concentration ratio of CO_2 hydrate to water increases.

5.4 Energy Storage Amount

(1) Generation rate of CO_2 hydrate

Figure 9 shows the results of the consumption of CO_2 during generation of hydrates. The experimental results, with an initial pressure of 3 MPa (red curve) and the analytical result with an initial pressure of 6 MPa calculated using Eq. (4) are shown in the figure. The difference in the experimental results and the analytical results with an initial pressure of 3 MPa after 120 minutes is large. Furthermore, the characteristic of the experimental result after 20 minute differs greatly even from the beginning of the experiment. The difference between the experimental result after 120 minutes and the analytical result allows us to conclude that the dissolution of CO_2 in water was not high enough and that the heat exchange experienced an unsmooth phase change in the double-tube heat exchanger. Ice and CO_2 hydrate are formed on the outside of the inner tube early in the experiment, and the heat conduction with a quick rate of heat transfer is dominant in the growth of the hydrate. However, the resistance to heat transfer may increase because the thickness of the hydrate layer increases with time. It is necessary to further examine the cause of the difference between the experimental value after 120 minutes and the analytic value.

(2) Energy storage time

Figure 10 shows the experimental result and the analytical results of the generating time and the energy storage velocity when CO_2 hydrate is generated in 1 m^3 of water. The initial

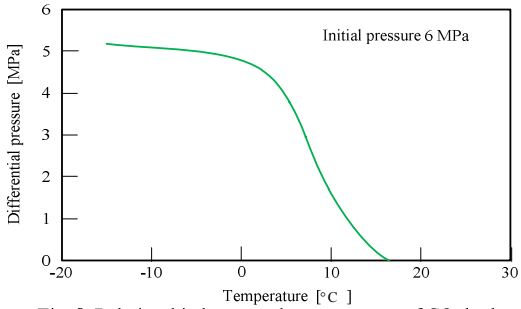


Fig. 8 Relationship between the temperature of CO_2 hydrate and the differential pressure

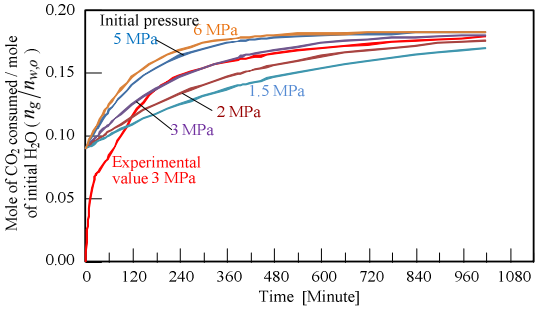


Fig. 9 Generation characteristics of CO_2 hydrate

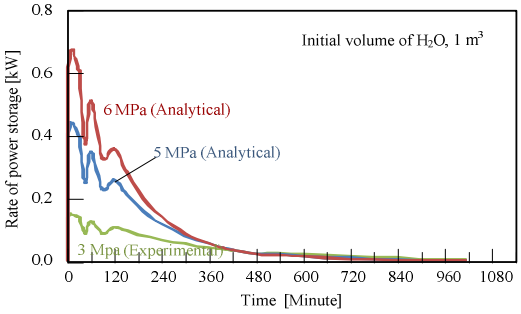


Fig. 10 Analytical results of the rate of power storage

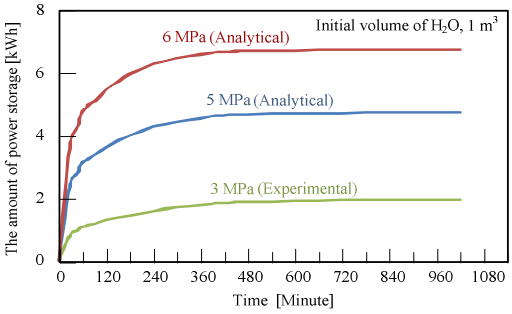


Fig. 11 Analytical results of the amount of power storage

pressure of 3 MPa in the figure is an experimental result, and the results with an initial pressure of 5 and 6 MPa were obtained from the numerical analysis. The analytical result was obtained by calculating the generated amount of CO_2 hydrate from $n_g/n_{w,o}$, as shown in Fig. 9, and then calculating Eq. (9) from Eq. (7) to obtain the storage pressure assumed from the above value. Finally, Eq. (10) was calculated, where K' in Eq. (4) is set equal to the value obtained from the experimental results for every sampling time and an initial pressure 3 MPa. For this reason, the fluctuation after 120 minutes that was observed in the experiment with an initial pressure of 3 MPa also appeared in the analytical results for initial pressures of 5 and 6 MPa. The energy storage velocity from the generation of CO_2 hydrate is the same regardless of the initial pressure after more than 360 minutes.

Figure 11 shows the ratio of the energy storage amount of CO_2 hydrate to 1 m^3 of water. An initial pressure of 3 MPa is an experimental result, and the pressures of 5 and 6 MPa in Fig. 11 are analytic results. Most increases in the energy storage amount are not seen after approximately 480 minutes, as shown in Fig. 11. The daily power consumption from an individual house, excluding the cooling and the heating load, is approximately 10 kWh. The energy storage capacity of a CH engine generator with an initial pressure of 6 MPa is approximately 45% of this value (4.5 kWh of generating end outputs). This result was used to calculate η_a and η_e from Eq. (11) as 0.8 and 0.85, respectively.

6. Conclusions

An actuator is operated by observing the differential pressure obtained from a given difference in temperature and CO_2 hydrate. This study aimed to develop a high-pressure gas engine generator for distributed power supplies. Therefore, in this paper, the generation characteristics of CO_2 hydrate, the generation rate, and the quantity of dissociation expansion energy which is available to be stored were investigated. The following conclusions were reached:

(1) The differential pressure between the generation and the gas dissociation of CO_2 hydrate increases so that the temperature of the hydrate is low. However, when the temperature of a hydrate is less than 0 °C, the increase in differential pressure will become very small. However, it is thought that the concentration ratio of CO_2 hydrate to water increases.

(2) The energy storage velocity accompanying the generation of CO_2 hydrate will become almost the same as the initial pressure when the generating time exceeds 360 minutes.

(3) When 1 m^3 of water is made to generate a hydrate for 480 minutes, the electric power corresponding to approximately 45% of the daily power consumption (4.5 kWh of generating end outputs) of an individual house, minus the cooling and heating load, can be stored.

The difference between the experimental result and the analytic result after 120 minutes of CO_2 hydrate generation is large and needs to be clarified.

Nomenclature

A : gas-liquid contact area [m^2/mol]

f_{eq} : fugacity of the gas in a three-phase equilibrium condition [MPa]

f_{ex} : fugacity of the gas for the experimental condition [MPa]

G : mass [kg]

H : heat [W]

h : specific heat [kJ/(kg·K)]

h_{ch} : latent heat of CO_2 hydrate [kJ/kg]

hn : the hydration number concerning generation of CO_2 hydrate

$H_{ch,l}$: the amount of latent heat of CO_2 hydrate [kJ]

$H_{CO_2,s}$: the amount of sensible heat of CO_2 [kJ]

H_d : the amount of heat of dissociation of CO_2 hydrate [kJ]

H_n : theoretical hydration number

H_r : the amount of heat of formation of CO_2 hydrate [kJ]

$H_{w,s}$: the amount of sensible heat of CO_2 [kJ]

K : velocity constant [/(MPa·min·m^2)]

K' : total velocity constant [/(MPa·min)] ($K' = K \cdot A$)

L : external work [J]

L_{chd} : work by the pressure increase of gas and water [J]

n_g : CO_2 gas volume incorporated into the hydrate [mol]

n_w : amount of water [mol]

$n_{w,o}$: the number of moles of the initial~~first~~ water [mol]

P : pressure [Pa]

q_1 : the number of moles of CO_2 included in 1 mol of water after hydrate completion [mol]

q_2 : the number of moles of CO_2 included in 1 mol of water of hydrate generation [mol]

R_{CO_2} : gas constant of CO_2 [kJ/(kg·K)]

T : temperature [K]

t : sampling time [s]

ΔT_{d-ost} : the difference in temperature between the dissociation temperature and the

outside air temperature [K]

ΔT_{ost-r} : the difference in temperature between the outside air temperature and the generation temperature [K]

V : volume [m^3]

W : power output of generating end [W]

Roman character

κ : ratio of specific heat

Subscript

a : entrance of the actuator

b : exit of the actuator

ch : CO_2 hydrate

w : water

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