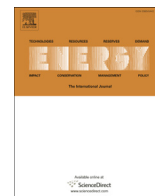




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## Thermodynamic analysis of hydrate-based refrigeration cycle

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### ABSTRACT

Clathrate hydrates (hydrates) have a larger dissociation heat than an evaporation heat of the working fluid of conventional refrigeration systems. This property can be applied to a novel refrigeration system. In this study, theoretical performance analysis of the refrigeration system utilizing hydrates as its working medium was conducted. We modeled the thermodynamic cycle of the hydrate-based refrigeration system composed of following processes: adiabatic compression, hydrate formation at high temperature, adiabatic expansion, and hydrate dissociation at low temperature. Based on the thermodynamic cycle, the coefficient of performance (COP) of the hydrate cycle was theoretically formulated with thermodynamic state functions of the working medium. Using the formula, COP was calculated on the three hydrate forming systems including HFC-32 + cyclopentane (CP) + water, Kr + CP + water, and HFC-41 + CP + water. The analysis based on the calculated results revealed that the dissociation heat of hydrates and the enthalpy change of guest gas were dominant factors to COP and polyatomic molecules would be appropriate for guest gas of hydrates. The maximum COP values on the hydrate cycle were comparable to those of the reversed Rankine cycle. The hydrate-based refrigeration system outperformed conventional refrigeration systems in terms of safety and environmental-friendliness.

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### 1. Introduction

The global electric power demand has expanded considerably in step with the economic growth and increasing population. The thermal power generation which utilizes fossil fuels such as coal, petroleum, and natural gas accounts for the greatest part of power generation. However, the utilization of fossil fuels should be reduced because decreasing the amount of CO<sub>2</sub> emission has been obligated by international treaties such as Paris Agreement. To achieve the CO<sub>2</sub> reduction target of Paris Agreement, development of environmental technology toward energy saving and enhancement of the energy efficiency is required.

One of the main causes of the rise in electric power supply is the rapid spread of air conditioners. International Energy Agency reported that the global stock of air conditioners in buildings will grow to 5.6 billion by 2050, up from 1.6 billion in 2018 [1]. Increasing air conditioning load not only pushes up the overall power needs, but also the need for generation and distribution

capacity to meet the demand at peak times. Developing a higher efficiency air-conditioning equipment plays a significant role for solving the problems of increasing energy demand.

In the most of air-conditioning equipment, a vapor-compression refrigeration system is utilized. The refrigerant of the vapor-compression refrigeration system absorbs heat from a cool environment and releases it to a warm environment through vapor-liquid phase transition. The conventional vapor-compression refrigeration systems use ammonia [2,3], CO<sub>2</sub> [4,5], and a hydro-fluorocarbon [6–8] as the working medium. However, in these systems, coefficient of performance (COP) has hit a peak recently [9]. A novel refrigeration cycle using a new working medium is required to obtain a higher COP. Clathrate hydrates are suggested as the new working media in this work.

Clathrate hydrates (called hydrates from this point onwards) are crystalline solids consisting of water molecules which form cages by hydrogen-bonding and enclosing other molecules (guests) in each cage. By the use of unique hydrate properties, hydrate technology may be applied to various industrial technologies including transport and storage of hydrogen or natural gas [10–12], carbon capture [13], gas separation [14,15], and thermal energy storage [16,17]. One of the notable hydrate properties is a large formation

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**Nomenclature***Abbreviations*

HFC-32	difluoromethane
HFC-41	fluoromethane
CP	cyclopentane
COP	coefficient of performance

*Parameters and variables*

$\varepsilon_R$	reversed Carnot cycle efficiency
$L_h$	hydrate dissociation heat, $\text{kJ mol}^{-1}$
$L_h'$	net hydrate dissociation heat used for cooled space, $\text{kJ mol}^{-1}$
$h$	enthalpy, $\text{kJ mol}^{-1}$
$Q_H$	amount of exothermic heat, $\text{kJ mol}^{-1}$
$Q_L$	amount of endothermic heat, $\text{kJ mol}^{-1}$
$W$	work, $\text{kJ mol}^{-1}$
$P$	pressure, MPa
$T$	temperature, K
$v$	molar volume, $\text{m}^3 \text{mol}^{-1}$
$z$	compressibility factor

$R$	gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
$c_p$	specific heat capacity at constant pressure, $\text{kJ mol}^{-1} \text{K}^{-1}$
$\kappa$	specific heat ratio
$\gamma$	compression ratio
$\nu$	degree of freedom of molecule
$\alpha$	ratio of decomposed hydrates

*Subscripts*

1	state 1 in refrigeration cycle
2	state 2 in refrigeration cycle
3	state 3 in refrigeration cycle
4	state 4 in refrigeration cycle
H	high-temperature thermal reservoir
L	low-temperature thermal reservoir
g	guest gas
CP	cyclopentane
w	water
h	hydrate
in	input
out	output

and dissociation heat. Generally, the heat of formation and dissociation of fluorocarbon hydrates is several times as large as an evaporative latent heat of fluorocarbon refrigerants per mole. For instance, the heat of formation and dissociation of difluoromethane (HFC-32) hydrate was estimated to be  $70 \text{ kJ mol}^{-1}$  [18], whereas the evaporative latent heat of HFC-32 is  $16 \text{ kJ mol}^{-1}$  [19]. This property can lead to the development of a more efficient air conditioning system. Hydrate refrigeration system may be superior to the conventional refrigeration systems in terms of safety. Because the formation pressures of some hydrates are lower than the vapor pressures of hydrofluorocarbon and  $\text{CO}_2$  in the range of the operating temperature of refrigeration systems, hydrate refrigeration system can be operated under lower pressures than the conventional refrigeration. Moreover, hydrates containing noble gases such as krypton (Kr) which is safer than ammonia for human health can be utilized as working media of the refrigeration system.

There are a few previous studies on the hydrate-based refrigeration system [20–22]. However, these studies are still premature as briefly reviewed below. Ogawa et al. [20] presented the conceptual but very practical design of a refrigeration system including the specified selection of the equipment such as compressor, pump, and motor with a working media of HFC-32 and cyclopentane (CP) hydrate. They performed a construction and an actual operation of the hydrate-based refrigeration system in a laboratory-scale and showed the practical utility of the above system. Fan et al. [21] analyzed the performance of the hydrate refrigeration system using a process simulator software, Aspen Plus. Xie et al. [22] proposed the design of  $\text{CO}_2$  hydrate-based refrigeration system and calculated COP by using Aspen plus.

One of the significant drawbacks of the above previous studies is a lack of thermodynamic theory which shows the formulations of COP on the basis of the state functions of the hydrate forming system. It is difficult to reveal a dominant factor to an efficiency index from the calculation by the simulation tool such as Aspen Plus since the process simulators simply provide the final numerical outputs. Establishment of an explicit formula with thermodynamic state functions is an effective method to clarify the dominant factor. This paper represents the first derivation of the set of theoretical formulae containing the thermodynamic state

functions. Because thermophysical properties of hydrates such as phase equilibrium conditions and dissociation heats depend on guest compounds, the proper hydrate as the working media is different depending on the operational conditions of refrigeration systems. It is essential for selecting appropriate guest compounds to formulate COP by the state functions of the hydrate forming system and reveal predominant factors for COP by the calculation. Hence, establishment of the thermodynamic theory based on the state function of the hydrate forming system is crucial for future experiments and implementations of the hydrate-based refrigeration system under various operational conditions.

Ohfuka and Ohmura [23] established a method of theoretical analysis to evaluate the performance of hydrate-based heat engine system. The analysis was performed for the hydrates in a cycle similar to the Rankine cycle. The inversed cycle of the hydrate engine is close to that of the refrigeration system. Using the inversed cycle, we can develop the concept of the hydrate refrigeration system taking into account the thermodynamic properties of hydrates.

In this study, we thermodynamically modeled the cycle of the hydrate-based refrigeration and specifically formulated the efficiency index. Using the efficiency index, the COP was evaluated in the three hydrate forming systems: HFC-32 + CP + water, Kr + CP + water, and fluoromethane (HFC-41) + CP + water. The influence of thermodynamic factors on the refrigeration efficiency of the three systems was analyzed.

**2. Theory***2.1. Conceptual theory of the hydrate-based refrigeration system*

A hydrate-based refrigeration system is similar to a vapor compression refrigeration system and its working medium is a hydrate. Fig. 1 shows the conceptual thermodynamic cycle of the hydrate refrigeration system together with the hydrate equilibrium curve. The working medium undergoes a cyclic process including compression, hydrate formation, expansion, and hydrate dissociation. A space is cooled by absorbing the dissociation heat of the hydrate in the process. The theoretical analysis of the hydrate cycle

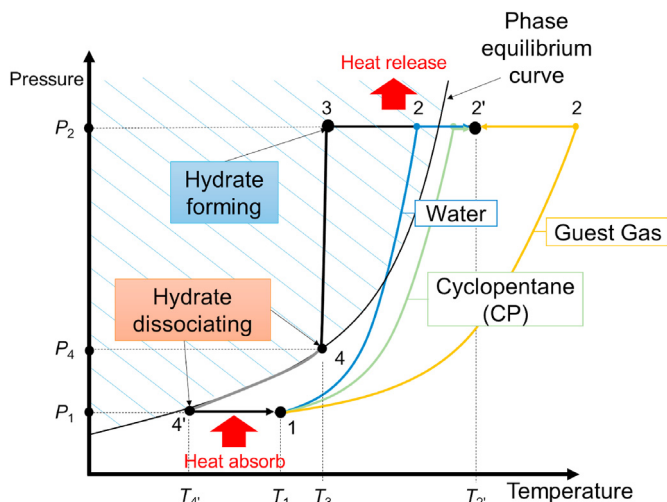


Fig. 1. Conceptual thermodynamic cycle of the hydrate-based refrigeration system.

was conducted under the assumption of an ideal thermodynamic condition, which is the same as that of other thermodynamic cycles such as the reversed Rankine cycle.

In this cycle, guest compounds and water are mixed at a stoichiometric ratio of the hydrate, which means a ratio of water and guest molecules assuming that an occupancy of guest gas in hydrate cages is 100% [24]. Each thermodynamic process on the hydrate-based refrigeration system is explained as follows.

States 1 to 2: The guest gas, CP, and water are separately and adiabatically compressed to a prescribed pressure value.

States 2 to 2': The guest gas, CP, and water are mixed and reach the thermal equilibrium condition without heat release to outside. State 2' is the state that all compounds have the same temperature.

States 2' to 3: To form a hydrate, the temperature of the working medium is decreased with releasing its heat to a surrounding environment under a condition of constant pressure. Because the guest gas, CP and water are mixed at a stoichiometric ratio of the hydrate, all molecules in the system are converted into the hydrate in state 3.

States 3 to 4: The hydrate is adiabatically expanded to decrease the pressure. In this process, we assume that the temperature of the working medium is not changed because the hydrate is solid. A part of the hydrate decomposes in state 4 which is the phase equilibrium point.

States 4 to 4': The working medium is adiabatically decompressed to the initial pressure. Using the endothermic heat of hydrate dissociation, the temperature of working medium is decreased along the phase equilibrium curve. State 4' is under the same pressure as state 1 and at the phase equilibrium temperature.

States 4' to 1: After adiabatically expanding the working medium to the initial pressure, the target space is cooled by the dissociation heat of hydrate. In this process, the temperature of working medium increases to the initial temperature.

## 2.2. Selection of working medium

We selected a hydrate-forming system with relatively low pressure and high temperature phase equilibrium. Materials less harmful to the human body are desirable because the refrigeration system is used in household environments and close to human residences. Taking account of the above mentioned requirements, the three systems; HFC-32 + cyclopentane (CP) + water, Kr + CP + water, and HFC-41 + CP + water were used in the present

study. Phase equilibrium data of these systems were reported in the previous studies [25–27]. The phase equilibrium curves are shown in Fig. 2. In these systems, structure II hydrates are formed. The molar ratio of guest molecule, CP and water in the system is 2:1:17, from the basis of stoichiometric ratio of structure II hydrate.

## 2.3. Conditions

The temperatures of the high and low temperature reservoirs,  $T_3$  and  $T_1$  were set to be 297 K and 287 K as the typical water temperature of a river in temperate regions in summer and the suitable temperature for air-conditioning use, respectively. The initial pressure  $P_1$  was set to be 0.1013 MPa or greater, which was determined based on the condition that the hydrate is not formed under the state 1.

In the case that the pressure  $P_2$  is larger than the vapor pressure of guest gas, the temperature could not be dramatically changed by the compression because the guest gas turns liquid. The pressure after the compression  $P_2$  is set to be a lower pressure than a vapor pressure of guest molecule. The temperature in state 4',  $T_{4'}$  is the temperature at atmospheric pressure or greater on phase equilibrium curve to guarantee hydrate dissociation.

## 3. Formulation of the efficiency index

### 3.1. Theoretical efficiency index

The efficiency index of cooling system is generally represented by a coefficient of performance (COP). The COP is defined as follows

$$\text{COP} = \frac{Q_L}{W_{in}} \quad (1)$$

where  $Q_L$  is the amount of endothermic heat and  $W_{in}$  is the input work. In hydrate-based refrigeration systems, the input work is equivalent to the work to adiabatically compress the guest compounds and water at the states 1 to 2. In this study, the work of adiabatic compression was calculated from the enthalpy difference before and after the adiabatic compression process at the states 1 to 2.  $Q_L$  in one cycle of the hydrate-based refrigeration system is a total of the amount of dissociation heat of the hydrate excluding a part of

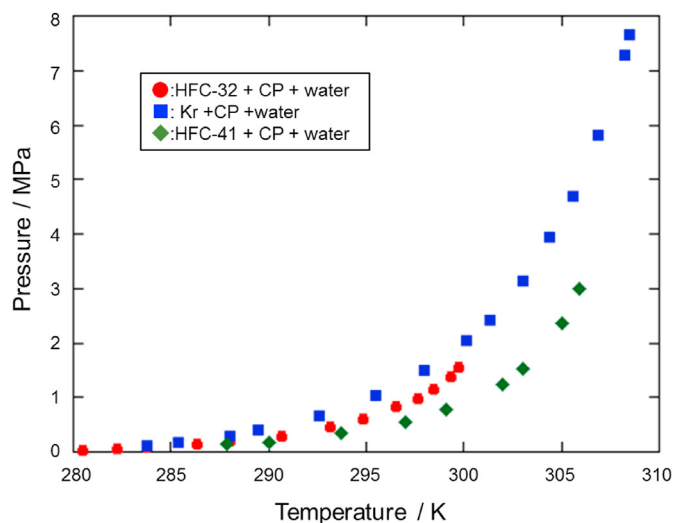


Fig. 2. Phase equilibrium data of HFC-32 + CP + water, Kr + CP + water, and HFC-41 + CP + water. ●: HFC-32 + CP + water system [25]. ■: Kr + CP + water system [26]. ◆: HFC-41 + CP + water system [27].

dissociation heat lost in the process from the states 4 to 4' and a sensible heat of the working medium absorbed in the process from the states 4 to 1. Therefore, the COP in the hydrate-based refrigeration system is given by

$$\text{COP} = \frac{L_h'}{\Delta H} \quad (2)$$

where  $L_h'$  is the net hydrate dissociation heat used for cooling a space and  $\Delta H$  is the molar enthalpy difference of the working media in adiabatic compression process. The cooling power which is expressed with a unit of "W" corresponds to the dissociation heat of hydrates and varies depending on the operating condition such as a flow rate and a volume of a utilized space. For example, Ogawa et al. [20] designed a hydrate refrigerator with the cooling power of 65.1 kW. The refrigerator is operated with the 557 kg/h of water and 100 kg/h of HFC-32. The detailed calculation methods of these values are described in the next sections.

### 3.2. Estimation of input work

The input work in the hydrate-based refrigeration system is equivalent to the work in the adiabatic compression process at the states 1 to 2. It has been reported that the input work except the enthalpy change of working media, such as work by a circulation pump of water and hydrate slurry, was calculated to be less than 10% of a total input work on the thermodynamic simulation of the hydrate refrigeration system by Ogawa et al. [20] The input work of guest gas and CP in the adiabatic compression is calculated with the molar enthalpy difference between states 1 and 2. The enthalpy is determined using REFPROP version 10.0 [28]. The enthalpy in state 1 is evaluated using the temperature  $T_1$  and the pressure  $P_1$ . The adiabatic compression at the states 1 to 2 is an isentropic process. Therefore, the enthalpy in state 2 can be calculated with the entropy in state 1 and the pressure  $P_2$ . The input work for adiabatic compression of water is calculated with Bernoulli's equation. The total enthalpy difference is calculated with the following equation:

$$\Delta H = \Delta h_g + n_{CP} \Delta h_{CP} + n_w \Delta h_w \quad (3)$$

$$\Delta h_w = \int_1^2 v_w dP \cong v_w (P_2 - P_1) \quad (4)$$

where  $\Delta h_g$ ,  $\Delta h_{CP}$ , and  $\Delta h_w$  are the enthalpy difference of guest gas, cyclopentane and water in adiabatic compression process at the states 1 to 2, respectively.  $v_w$  is the molar volume of water, which was calculated to be  $1.80 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  on the pressure and temperature condition in this study by REFPROP [28]. Each coefficient  $n_i$  is determined based on the stoichiometric molar ratio of hydrate. The value of  $n_i$  depends on the structure of hydrates. In the

$$\text{COP} = \frac{L_h'}{\Delta H} = \frac{L_h - (n_h c_{p,h} (T_4 - T_{4'}) + \sum_{i=1}^3 n_i \Delta h_i) + \sum_{i=1}^3 n_i c_{p,i} (T_1 - T_{4'})}{\Delta h_g + 0.5 \Delta h_{CP} + 8.5 \Delta h_w} \quad (9)$$

present study,  $n_{CP}$  and  $n_w$  were calculated 0.5 and 8.5, respectively, because the stoichiometric molar ratio of guest gas, CP, and water is 2:1:17 for the structure II hydrate.

### 3.3. Estimation of hydrate dissociation heat

The dissociation heat of hydrate is given by the Clausius-Clapeyron equation as follows

$$\frac{d(\ln P)}{d\left(\frac{1}{T}\right)} = -\frac{L_h}{zR} \quad (5)$$

where  $P$  and  $T$  denote the equilibrium pressure and temperature, respectively. The molar dissociation heat of hydrate  $L_h$  was estimated based on Equation (5) applied to the  $P$ - $T$  phase equilibrium data under the condition that the compressibility factor  $z$  is 1.0 and the gas constant  $R$  is  $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ . Considering that a part of the hydrate is dissociated at the states 4 to 4' and a sensible heat of the working medium is absorbed from the cooled space at the states 4' to 1, the net heat used for cooling a space is described as following equation:

$$L_h' = L_h - (n_h c_{p,h} (T_4 - T_{4'}) + \sum_{i=1}^3 n_i \Delta h_i) + \sum_{i=1}^3 n_i c_{p,i} (T_1 - T_{4'}) \quad (6)$$

where  $c_p$  is the specific heat capacity at constant pressure.  $n_i$  is the coefficient based on the stoichiometric ratio of the hydrate.  $\Delta h_i$  is the enthalpy change of each compound at the states 4 to 4'. Guest gas, CP, water, and a hydrate are numbered by 1, 2, ...,  $i$ , ..., 4. The terms which contains the symbol of sigma in Equation (6) can be rewritten as following forms.

$$\sum_{i=1}^3 n_i \Delta h_i = n_g \Delta h_g + n_{CP} \Delta h_{CP} + n_w \Delta h_w \quad (7)$$

$$\sum_{i=1}^3 n_i c_{p,i} (T_1 - T_{4'}) = (n_g c_{p,g} + n_{CP} c_{p,CP} + n_w c_{p,w}) (T_1 - T_{4'}) \quad (8)$$

Each specific heat of guest gas, CP, and water was calculated from REFPROP [28]. Since the specific heat capacity of HFC-32, Kr, and HFC-41 + cyclopentane hydrates selected in the present study has not been reported, it was estimated by extrapolating the specific heat capacity of tetrahydrofuran structure II hydrate [29]. The ratio of a absorbed heat by the hydrate  $n_h c_{p,h} (T_4 - T_{4'})$  to the dissociation heat of hydrates  $L_h$  were calculated to be 3–4%. The calculated COP changes by only 0.3–0.6% even if the value of  $c_{p,h}$  changes by 10%. The second term on the right side of Equation (6) represents a lost heat by the dissociation of a part of the hydrate at the states 4 to 4'. The third term on the right side represents the sensible heat absorbed from the cooled space at the states 4' to 1.

From the above calculations, the theoretical COP in this hydrate-based refrigeration system is formulated as following equation.

The first law of thermodynamics for the other processes, which are thermal equilibration of the working medium (2 to 2'), hydrate



formation (2' to 3), and adiabatic expansion (3 to 4), and partially hydrate decomposition (4 to 4'), are expressed as following equations, respectively.

$$n_g c_{p,g}(T_2 - T_{2'}) = (n_{CP} c_{p,CP} + n_w c_{p,w})(T_{2'} - T_2) \quad (10)$$

$$Q_H = L_h + (n_g c_{p,g} + n_{CP} c_{p,CP} + n_w c_{p,w})(T_{2'} - T_3) \quad (11)$$

$$W_{out} = n_h v_h (P_2 - P_4) \quad (12)$$

$$\alpha L_h = n_h c_{p,h}(T_4 - T_{4'}) + n_g \Delta h_g + n_{CP} \Delta h_{CP} + n_w \Delta h_w \quad (13)$$

where  $Q_H$  and  $W_{out}$  denote the amount of exothermic heat and the output work, respectively.  $v_h$  is the molar volume of hydrates.  $\alpha$  shows the ratio of decomposed hydrates. Energy conversion on the above processes does not influence the theoretical COP as shown in Equation (9).

## 4. Results and discussion

### 4.1. Calculation of COP on various hydrates and conditions

Table 1 shows the calculated COP and other properties used for the calculation in the three systems; HFC-32 + CP + water, Kr + CP + water, and HFC-41 + CP + water under various pressure conditions. In the condition (a), the initial pressure  $P_1$  and the pressure after adiabatic compression  $P_2$  were set to be 0.1013 MPa and 1.0 MPa, respectively. In the condition (b),  $P_1$  was 0.1013 MPa and  $P_2$  was 1.5 MPa  $\gamma$  is the compression ratio, which is expressed as  $P_2/P_1$  in the present study. To ascertain the reliability of the formula used to calculate the COP in a hydrate-based refrigeration system, the reversed Carnot efficiency was computed in the conditions of the present study. The reversed Carnot efficiency shows the theoretical maximum efficiency. We confirmed that the COP in the present study did not exceed the reversed Carnot efficiency. The reversed Carnot efficiency is defined as the following equation:

$$\epsilon_R = \frac{T_L}{T_H - T_L} \quad (14)$$

where  $T_H$  and  $T_L$  are the highest and lowest temperatures in the cycle, respectively. In the present study,  $T_L$  and  $T_H$  are regarded as  $T_1$  and  $T_3$ , which are 287 K and 297 K, respectively. The reversed Carnot efficiency was calculated 28.7 using Equation (14). The ratio of COP to the reversed Carnot efficiency  $COP/\epsilon_R$  was evaluated in the all systems.

In the condition (a), the highest COP was calculated 17.95 in HFC-32 + CP + water system. In HFC-32 + CP + water system, the net hydrate dissociation heat  $L_h'$  was the largest and the input work

$\Delta H$  was the smallest among the three systems. This could lead to the highest COP in HFC-32 + CP + water system as indicated in Table 1. Similarly, the COP in Kr + CP + water system was the lowest because  $L_h'$  was the smallest and  $\Delta H$  was the largest of the three systems.

When  $P_2$  increased to 1.5 MPa as shown in the condition (b), the COP dropped by 19-23% on the all systems. Although the value of  $L_h'$  did not vary depending on the pressure condition, the value of  $\Delta H$  rose by 23-30% on the all systems. Because over 95% of the input work  $\Delta H$  was occupied by the enthalpy change of guest gas  $\Delta h_g$  shown in Table 1, the variation of  $\Delta H$  would be significantly influenced by that of  $\Delta h_g$ . The increase in  $\Delta h_g$  would be ascribed to the rise of the compression ratio. Each of the enthalpy change  $\Delta h_i$  at the states 1 to 2 is described as follows

$$\Delta h_i = \int_1^2 c_{p,i} dT \quad (15)$$

Assuming that the specific heat is constant,  $\Delta h_g$  is described by using the compression ratio as follows

$$\Delta h_g = c_{p,g} \Delta T = c_{p,g}(T_2 - T_1) = c_{p,g} T_1 \left[ \gamma^{\left(\frac{\kappa-1}{\kappa}\right)} - 1 \right] \quad (16)$$

where  $\kappa$  is a specific heat ratio and  $\gamma$  is the compression ratio. This equation applies to an ideal gas, but clearly shows the factors affecting the input work. From Equation (16), a high compression ratio increases  $\Delta h_g$ . Therefore, lowering the compression ratio would improve the COP in hydrate-based refrigeration systems.

To estimate the maximum COP on each system,  $P_1$  and  $P_2$  were set to be the upper and lower limits respectively and the COP was calculated under this pressure condition. The results of the COP and other properties are shown in Table 2. The upper limit of  $P_1$  in this study was regarded as the phase equilibrium pressure of the hydrates at the initial temperature 287 K to guarantee the hydrate dissociation. To obtain enough driving force for hydrate crystal growth and guarantee the hydrate formation at the state 3, the lower limit of  $P_2$  was set to be the phase equilibrium pressure at 299 K, which is 2 K higher than the temperature of the high-temperature thermal reservoir  $T_3$ .  $P_1$  and  $P_2$  were calculated by interpolating of the phase equilibrium data of the hydrate formation system. The COP increased on the all systems compared to the COP results shown in Table 1. The highest COP of the three systems was calculated as 18.66 in HFC-41 + CP + water system. Although  $L_h'$  in HFC-32 + CP + water system was larger than that in HFC-41 + CP + water system, the lowest compression ratio and  $\Delta H$  would lead to the highest COP in HFC-41 + CP + water system.

**Table 1**

Calculated COP and properties of the three hydrate formation systems for various pressure conditions.  $P_1$  and  $P_2$  in the condition (a) were set to be 0.1013 MPa and 1.0 MPa, respectively.  $P_1$  and  $P_2$  in the condition (b) were set to be 0.1013 MPa and 1.5 MPa, respectively.  $\gamma$  is the compression ratio. The reversed Carnot efficiency  $\epsilon_R$  was calculated 28.7 from the temperature condition in the previous study.

Guest compounds	Condition	$\gamma$	$T_4$ /K	$\Delta h_g^a$ /kJ mol <sup>-1</sup>	$\Delta h_{CP}^a$ /kJ mol <sup>-1</sup>	$\Delta h_w^a$ /kJ mol <sup>-1</sup>	$\Delta H$ /kJ mol <sup>-1</sup>	$L_h^b$ /kJ mol <sup>-1</sup>	$L_h'/$ kJ mol <sup>-1</sup>	COP	COP/ $\epsilon_R$ /%
HFC-32 + CP	(a)	9.87	284.7	6.65	0.08	0.02	6.83	134.69	122.62	17.95	62.5
	(b)	14.80	8.11	0.13	0.03	8.38				14.63	51.0
Kr + CP	(a)	9.87	283.3	8.94	0.08	0.02	9.12	118.75	105.35	11.55	40.3
	(b)	14.80	11.57	0.13	0.03	11.85				8.89	31.0
HFC-41 + CP	(a)	9.87	286.7	6.91	0.08	0.02	7.09	121.70	110.76	15.62	54.4
	(b)	14.80	8.47	0.13	0.03	8.75				12.66	44.1

<sup>a</sup> The enthalpy data obtained from REFPROP version 10.0 [28].

<sup>b</sup> The dissociation heat calculated using the Clausius-Clapeyro equation with the least square method of phase equilibrium data [25-27].

**Table 2**

Maximum COP and other properties of the three hydrate formation systems.  $P_1$  and  $P_2$  were calculated by interpolating of the phase equilibrium data.  $L_h$  and  $\epsilon_R$  are the same as those described in Table 1.

Guest compounds	$P_1^a$ /MPa	$P_2^a$ /MPa	$\gamma$	$\Delta h_g^b$ /kJ mol <sup>-1</sup>	$\Delta h_{CP}^b$ /kJ mol <sup>-1</sup>	$\Delta h_w^b$ /kJ mol <sup>-1</sup>	$\Delta H$ /kJ mol <sup>-1</sup>	$L_h$ /kJ mol <sup>-1</sup>	COP	COP/ $\epsilon_R$ /%
FC-32 +CP	0.139	1.344	9.67	6.53	0.11	0.02	6.77	123.36	18.22	63.5
Kr + CP	0.234	1.733	7.41	7.31	0.14	0.03	7.61	106.79	14.03	48.9
HFC-41 +CP	0.108	0.787	7.23	5.81	0.06	0.01	5.94	110.89	18.66	65.0

<sup>a</sup> The phase equilibrium pressure interpolated from the previous experimental data using the Clausius-Clapeyron equation [25–27].

<sup>b</sup> The enthalpy data obtained from REFPROP version 10.0 [28].

#### 4.2. Effect of thermodynamic factors on the COP

From the formulas and the calculated results, the COP of the hydrate-based refrigeration system depends in a large part on the hydrate dissociation heat and the enthalpy change of the working medium in the adiabatic compression. The larger hydrate dissociation heat and the smaller enthalpy change increase the COP as indicated in Equation (2) and calculated results. The hydrate dissociation heat is determined by the number of hydrogen bonds in hydrates and the magnitude of an interaction between guest and water molecules which form the cage of the hydrate [30]. The hydrate with a larger number of hydrogen bonds and a stronger interaction between guest and water molecules has a greater dissociation heat. The interaction between guest and water molecules becomes stronger when the molecular size of the guest encapsulated in the cage is closer to the size of the cage. On the other hand, the hydrate which has a large dissociation heat shows a high temperature dependency of the phase equilibrium pressure. The high temperature dependency of the phase equilibrium pressure causes the rise of the pressure ratio in the compression and leads to the increase in the input work. Therefore, obtaining a large dissociation heat of hydrates is not compatible with lowering the input work. It should be considered that the balance between the magnitude of the dissociation heat and the input work to search for suitable hydrates for the hydrate-based refrigeration system.

On the hydrate forming systems selected in this study, the enthalpy change of guest gas  $\Delta h_g$  occupied more than 95% of the total enthalpy change  $\Delta H$  shown in Tables 1 and 2. Therefore, the input work depends heavily on  $\Delta h_g$  and the guest gas with smaller  $\Delta h_g$  contributes significantly to the increase in COP.  $\Delta h_g$  is represented as Equation (16). The specific heat  $c_p$  and specific heat ratio  $\kappa$  included in Equation (16) are described as following equations:

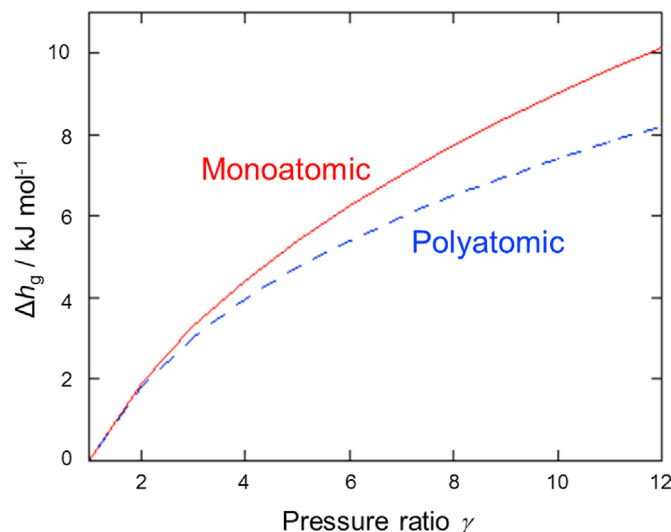
$$c_p = \left(\frac{\nu}{2} + 1\right)R \quad (17)$$

$$\kappa = \frac{\nu + 2}{\nu} \quad (18)$$

where  $\nu$  is the degree of freedom of the guest molecule.  $\nu$  of a monoatomic molecule such as Kr or a polyatomic molecule such as HFC-32 is 3 or 6, respectively. By using Equations (17) and (18),  $\Delta h_g$  can be rewritten as follows:

$$\Delta h_g = \left(\frac{\nu}{2} + 1\right)RT_1 \left[ \gamma^{\left(\frac{2}{\nu+2}\right)} - 1 \right] \quad (19)$$

By using Equation (19), the relationships between  $\gamma$  and  $\Delta h_g$  of monoatomic and polyatomic molecules were organized in Fig. 3. The gas constant  $R$  and the initial temperature  $T_1$  were set to be 8.31 J mol<sup>-1</sup> K<sup>-1</sup> and 287 K, respectively.  $\Delta h_g$  of the polyatomic



**Fig. 3.** Relationships between  $\gamma$  and  $\Delta h_g$  of monoatomic and polyatomic molecules calculated by using Equation (19). The solid line shows  $\Delta h_g$  of monoatomic molecules. The broken line shows  $\Delta h_g$  of polyatomic molecules.

molecule was smaller than that of the monoatomic molecule except in the case when  $\gamma$  is 1. The difference of  $\Delta h_g$  between the polyatomic and monoatomic molecules increased with the rise of  $\gamma$ . These trends can be observed in the calculated results shown in Table 1. Because smaller  $\Delta h_g$  increases COP, polyatomic molecules would be more appropriate for the guest gas of the hydrate utilized as the working medium of the hydrate-based refrigeration system than monoatomic molecules under the same pressure ratio.

#### 4.3. Comparison of the hydrate cycle with the reversed rankine cycle

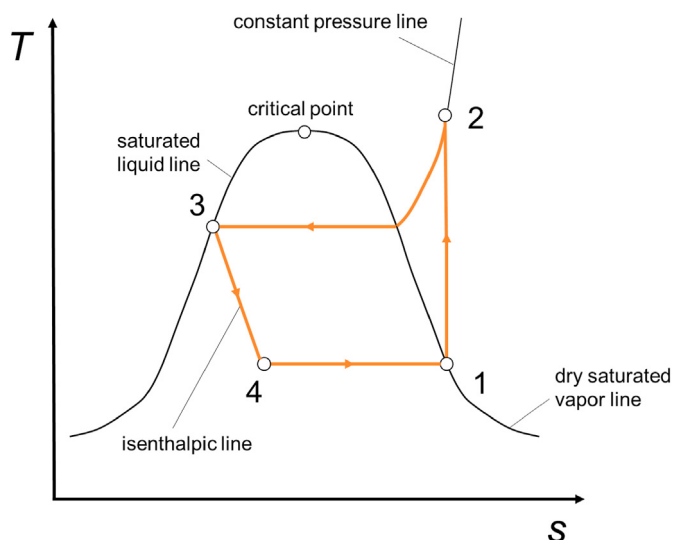
To compare the performance of the hydrate-based refrigeration cycle with that of the vapor compression refrigeration system, the COP of the reversed Rankine cycle utilizing HFC-32, HFC-41, and CO<sub>2</sub> as the working medium was estimated. Table 3 shows the calculated COP, pressure conditions and enthalpies for each working medium. The conceptual diagram of the reversed Rankine cycle is shown in Fig. 4. The COP of the reversed Rankine cycle is defined as the following formula:

$$\text{COP} = \frac{h_1 - h_4}{h_2 - h_1} \quad (20)$$

where  $h$  is the molar enthalpy of the working medium. Each subscript number of  $h$  is the state number shown in Fig. 4. The temperatures of high and low temperature reservoirs and were set

**Table 3**COP and other properties on the reversed Rankine cycle using HFC-32, HFC-41, and CO<sub>2</sub> as the working media.  $\epsilon_R$  is the same as that described in Table 1.

Compounds	$P_1/\text{MPa}$	$P_2/\text{MPa}$	$\gamma$	$h_1/\text{kJ mol}^{-1}$	$h_2/\text{kJ mol}^{-1}$	$h_4/\text{kJ mol}^{-1}$	COP	COP/ $\epsilon_R$ %
HFC-32	1.239	1.728	1.39	26.89	27.54	12.66	21.99	76.6
HFC-41	2.930	3.911	1.33	17.76	18.20	9.34	18.77	65.4
CO <sub>2</sub>	4.948	6.561	1.33	18.41	18.82	11.76	16.14	56.2

**Fig. 4.** Conceptual diagram of the reversed Rankine cycle.

to be the same as those of the hydrate cycle, which are 297 K and 287 K, respectively. To compare the performance of the reversed Rankine cycle with the maximum COP of the hydrate cycle shown in Table 2,  $P_1$  and  $P_2$  were set to be the saturated vapor pressures of the working medium at 287 K and 299 K, respectively. Pressure values and enthalpies were determined using the NIST Chemistry Webbook.

The maximum COP values on HFC-32 + CP + water and HFC-41 + CP + water systems of the hydrate cycle were higher than that of the reversed Rankine cycle with CO<sub>2</sub> and comparable to that of the reversed Rankine cycle with HFC-41. The net dissociation heat of the hydrate  $L_h'$  was 13.2–14.7 times as large as the evaporation heat of the HFC-41, which is represented as  $h_1 - h_4$  in the reversed Rankine cycle. In contrast, the input work of the hydrate cycle was 11.0–12.5 times as large as that of the reversed Rankine cycle with HFC-41 defined as  $h_2 - h_1$  owing to high compression ratio of the hydrate cycle. Since the effect of the input work on COP is approximately the same as that of the latent heat of the working medium, the same level of COP would be calculated on the reversed Rankine cycle compared with the hydrate cycle. On the other hand, the values of  $P_1$  and  $P_2$  on HFC-32 + CP + water and HFC-41 + CP + water systems of the hydrate cycle were much lower than those of the reversed Rankine cycle with HFC-32 and HFC-41. Moderating of operating pressures could lead to enhancement of the safety [31,32]. Because HFC-32 + CP and HFC-41 + CP hydrate systems have equivalent COP and a higher level of safety compared with the conventional refrigeration system utilizing HFC-41, they would be useful as the working media of refrigeration systems.

Although the maximum COP on the Kr + CP + water system was lower than those of HFC-41 and HFC-32, Kr is a noble gas and more environment-friendly than hydrofluorocarbons such as HFC-41 and HFC-32. Kr + CP + water system showed comparable COP and lower pressure values than the reversed Rankine cycle with CO<sub>2</sub> which is a non-Freon gas as well as Kr. Therefore, Kr + CP hydrate

refrigeration system has the advantages of environmental friendliness and safety while it shows the same level of COP as the conventional refrigeration system using CO<sub>2</sub> as the working medium. The established theory and illustrative results in this work would be fundamental knowledge to perform experiments and implementation of the hydrate-based refrigeration system as future works.

## 5. Conclusion

We established the thermodynamic cycle of the hydrate-based refrigeration system and formulated COP by the thermodynamic state functions including the dissociation heat of hydrates, enthalpy changes of guest compounds and water, and specific heats of guest compounds and water. The COP was calculated for HFC-32 + CP + water, Kr + CP + water and HFC-41 + CP + water systems. The each maximum COP on the three systems was 18.22 for HFC-32 + CP + water system, 14.03 for Kr + CP + water system, and 18.66 for HFC-41 + CP + water system when the temperatures of high and low temperature reservoirs were set to be 297 K and 287 K, respectively. The calculated results and the established formula of the hydrate refrigeration cycle indicated that the large dissociation heat of hydrates and the small input work improve the COP and the input work is dominated by the enthalpy change of the guest gas. The analysis focusing on the degree of freedom of the guest molecule revealed that hydrates containing polyatomic molecules as guest compounds would be suitable for the working media of the hydrate-based refrigeration system under the same pressure condition. HFC-32 + CP and HFC-41 + CP hydrate refrigeration systems showed superior safety to the conventional refrigeration system while maintaining the same level of COP as the reversed Rankine cycle. Kr + CP hydrate refrigeration system has a lower environmental burden than the refrigeration systems utilizing hydrofluorocarbons and a higher level of safety than the reversed Rankine cycle with CO<sub>2</sub>.

## Credit author statement

**Riku Matsuura:** Conceptualization, Methodology, Formal analysis, Writing-Original Draft, Visualization; **Kosuke Watanabe:** Conceptualization, Methodology; **Yuji Yamauchi:** Conceptualization, Methodology; **Haruka Sato:** Conceptualization, Methodology; **Li-Jen Chen:** Writing-Reviewing and Editing; **Ryo Ohmura:** Writing-Original Draft, Writing-Reviewing and Editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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