

# PERFORMANCE OF OCEAN HYDRATE-BASED ENGINE FOR OCEAN THERMAL ENERGY CONVERSION SYSTEM

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## ABSTRACT

The performance of a theoretical thermodynamic cycle using clathrate hydrate as the working fluid (later we call it the hydrate cycle) is analyzed with emphasis on the application to “Ocean Thermal Energy Conversion (OTEC)” after organizing the processes in this cycle thermodynamically. OTEC is an electric power generation system utilizing a temperature difference of about 15 K to 25 K between the top and the bottom layers in the ocean. The organic Rankine cycle with fluorocarbons, ammonia or propane is considered to be one of the most effective methods for OTEC. There is, however, a growing tendency to avoid fluorocarbons in industries since they are powerful greenhouse gases. Ammonia is also improper because of not only its corrosion to metals but being a source of acid rain. This research proposes that the hydrate cycle may be an alternative to the above cycles for OTEC. In this cycle hydrate is formed at low temperature and dissociated at high temperature. Energy is generated through the alternate repetition of hydrate formation and dissociation. Various guest substances, neither corrosive nor influential in the environment like noble gases can form hydrates. When the hydrate cycle is operated with the high and low reservoirs at 280 K and 295 K, assuming the use in a temperate climate, the thermal efficiency of the hydrate cycle is 2.15 % for Kr hydrate and 2.58 % for Xe hydrate, which are comparable to that of the organic Rankine cycle: 2.24 % for  $\text{CH}_2\text{F}_2$ , 3.31 % for  $\text{C}_2\text{H}_3\text{F}_3$ , 3.34 % for  $\text{C}_3\text{H}_8$ . These results indicate the prospects of the hydrate cycle for OTEC as more environment-friendly than the organic Rankine cycle.

## INTRODUCTION

Growing number of countries follow the trend to avoid nuclear power generation after the Fukushima Daiichi nuclear disaster in Japan. For example, Germany and Switzerland have decided to phase out the use of nuclear power by 2022 for the former and by 2034 for the latter. This avoidance of utilizing nuclear power, however, brings out another problem of how to make up for the decrease in amount of generated power. So far in Japan, this problem has been dealt with by increasing dependence on fossil fuels: coal, petroleum and natural gas. This policy, unfortunately, has escalated the detrimental effect of greenhouse gas on the environment and dependence on economic, politic, or other conditions of import sources. For

these reasons, it is the interest of many societies that domestically feasible power generation systems which use renewable sources are commercially developed. It is envisioned that the negative environmental effects of greenhouse gases can also be reduced by the development of such technologies.

Ocean thermal energy is also one of the renewable energies. This thermal energy is caused by the temperature difference between top and bottom layers of the sea which is produced by radiant heat from the sun. For example, seawater temperature near the Ishigaki Island, Okinawa prefecture in Japan, at 700 meters deep and at the sea surface is below 280 K and 295 K to 302 K, respectively [1]. The present study concerns a power generation system utilizing this temperature difference of 15 to 22 K. There have been some previous studies converting aforementioned thermal energy into mechanical work. This technology is called “Ocean Thermal Energy Conversion (OTEC)” ever since d’Arsonval had proposed it for the first time in 1881 [2]. This energy generating system is considered to be most effective when we use it in the Rankine cycle with ammonia, fluorocarbons or propane as the working fluid [3], as these fluids are easy to make phase transitions between liquid and vapor within the temperature range of seawater. However, there is a growing tendency to avoid fluorocarbons from the industries because of their greenhouse effect [4]. Ammonia has corrosive properties towards metals as well as contributes to acid rain [5]. Using above substances as the working fluid in the Rankine cycle is therefore not recommended for OTEC. Instead, the present study proposes another method for OTEC by using clathrate hydrates (abbreviated “hydrate” hereafter) as the working medium instead of the Rankine cycle.

Hydrate is a crystalline solid consisting of cage structures of hydrogen-bonded water molecules outside and molecules of other substance inside. In contrast to calling the water molecules the “host”, we call the latter “guest” molecules. Thereby Methane hydrate means hydrate which contains methane as a guest.

In recent years, we can find progress in the studies to apply hydrates for industrial technologies. Storage media for natural gas utilizing high-holdability of gas [6], separation of carbon dioxide [7], and cool energy storage media [8] are the examples utilizing commercially beneficial properties of hydrates. Utilization of hydrate for a heat engine was proposed by Nishimura for the first time [9]. Obara made an analysis of  $\text{CO}_2$  hydrate engine concretely [10]. The present study will

theoretically formulate the thermal efficiency of the heat engine using hydrate. Then the theoretical thermal efficiency was numerically evaluated by the thermodynamic properties of the working medium which were specified corresponding to the temperature condition for OTEC. These results enables us to identify the most effective guest substances for the industrial use as well as compare the performance of the power cycle with that of the Rankine cycle.

## NOMENCLATURE

$\dot{\eta}_h$	[-]	Theoretical thermal efficiency of the hydrate cycle
$\dot{\eta}_R$	[-]	Theoretical thermal efficiency of the Rankine cycle
$\dot{W}_{ij}$	[kJ/s]	Mechanical work done in the states $i$ to $j$
$\dot{W}_{guest}$	[kJ/s]	Mechanical work done in adiabatic expansion by guest substance
$\dot{W}_j$	[kJ/s]	Mechanical work done in adiabatic expansion by water
$\dot{Q}_{ij}$	[kJ/s]	Required heat in the states $i$ to $j$
$\dot{m}_h$	[mol]	Formation rate of hydrate
$h_i$	[kJ/mol]	Molar enthalpy of the working fluid in the states $i$ in the hydrate cycle
$h_i$	[kJ/mol]	Molar enthalpy of the working fluid in the states $i$ in the Rankine cycle
$P$	[MPa]	Pressure
$V$	[m <sup>3</sup> ]	Molar volume
$T$	[K]	Temperature
$c_{p,h}$	[kJ/mol·K]	Specific heat capacity of hydrate
$L_h$	[kJ/mol]	Latent heat of hydrate
$\Sigma \nu$	[-]	The total amount of the Degree of freedom

## THEORY OF THE HYDRATE HEAT ENGINE

The hydrate cycle is a theoretical cycle, which generates mechanical work with alternate reactions of hydrate formation and dissociation. Since the temperature-pressure gradient of hydrate phase equilibrium curve is generally steeper than that in adiabatic process of the guest gas, a series of the following process: hydrate formation, dissociation and adiabatic expansion of the guest gas, makes the temperature of the guest substance lower than the initial temperature. Figure 2 conceptually illustrates the hydrate cycle on a  $p$ - $T$  diagram. Each of the process in the hydrate cycle is thermodynamically described below.

States 1 to 1': Hydrate is formed slowly. There must be some degree of temperature difference between the equilibrium temperature and the heat source temperature. This is because this hydrate formation, which is an exothermic reaction, completes only when working fluid releases its own latent heat outside.

States 1' to 2: Hydrate is pumped to raise the pressure by a compressor without heat exchange with outside. On this occasion we can assume the volume and temperature of hydrate to be fixed since hydrate is solid.

States 2 to 3: Hydrate is heated isobarically beyond the equilibrium temperature by heat from the high temperature reservoir.

States 3 to 3': Heat from the high temperature reservoir decomposes hydrate into guest gas and liquid water. Each fluid is sent to separate cylinders.

States 3' to 4: Guest gas and water separately enter the respective turbines and isentropically expand there.

States 4 to 1: Guest gas and liquid water that completed expansion severally join to be a thermodynamic equilibrium, then exchange heat with the low grade heat source to be the initial temperature.

Theoretical thermal efficiency is one of the most important indexes to evaluate the performance of heat engines. This index  $\eta$  can be calculated by dividing the total amount of supplied heats per unit time  $\dot{Q}$  into work done created in the system per unit time  $\dot{W}$ . In the hydrate cycle, the values required for calculating  $\eta$  are the total amount of heat supplied from the high temperature reservoir in the states 2 to 3  $\dot{Q}_{23}$  and 3 to 3'  $\dot{Q}_{33'}$ , work required to compress hydrate in a pump in the states 1 to 2  $\dot{W}_{in}$  and work done by the guest gas in the adiabatic process  $\dot{W}_{guest}$  and  $\dot{W}_{water}$ . The calculations of the values are described in detail below.

States 1 to 2: Since volume change of solid in an isentropic process is very small, we can use the approximation of  $V_1 \cong V_2$ . We can get a simple equation by using this approximation as

$$\dot{W}_{in} \cong \dot{m}_h V_1 (p_2 - p_1) \quad (1)$$

States 2 to 3: This process is an isobaric heating and thus the amount of the heat per unit time  $\dot{Q}_{23}$  is expressed as

$$\dot{Q}_{23} = \dot{m}_h \int_{T_1}^{T_3} c_{p,h} dT \quad (2)$$

States 3 to 3': The amount of heat per unit time required to decompose hydrate  $\dot{Q}_{33'}$  is

$$\dot{Q}_{33'} = \dot{m}_h L_h \quad (3)$$

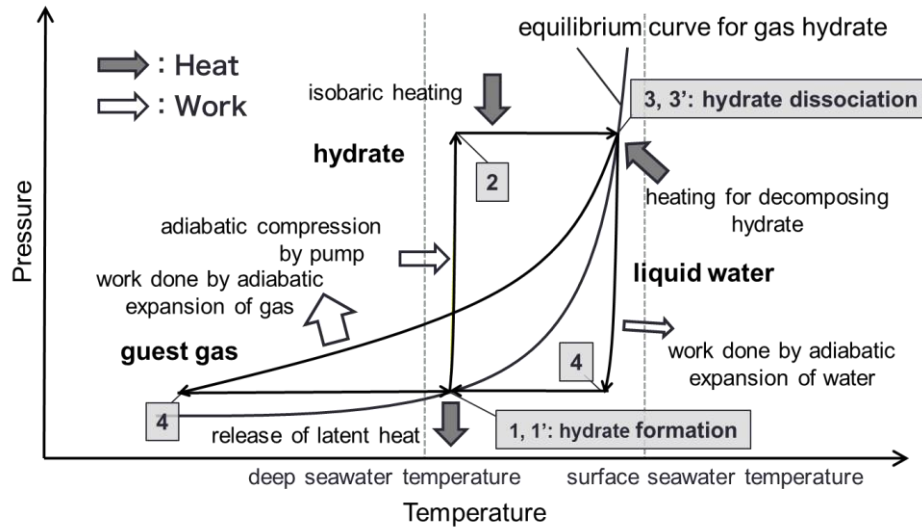
States 3' to 4: Guest gas and water separately expand in adiabatic processes. Work done in each turbine is calculated as follows.

$$\dot{W}_{guest} = \dot{m}_h (h_{3'}^g - h_4^g) \quad (4)$$

$$\dot{W}_{water} = \dot{m}_h (h_{3'}^w - h_4^w) \quad (5)$$

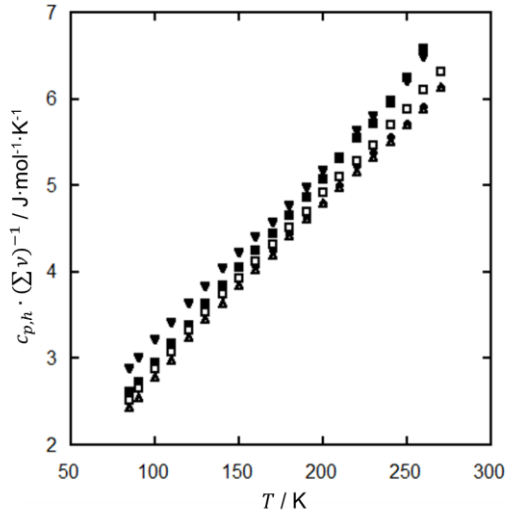
The behavior of liquid or solid in adiabatic process gives us another condition of  $T_1 \cong T_2$ . The theoretical thermal efficiency of this cycle  $\eta_h$  is described with this approximation and  $T_2 \cong T_3$  as

$$\eta_h = \frac{(h_{3'}^g - h_4^g) + n(h_{3'}^w - h_4^w) - V_1(p_2 - p_1)}{\int_{T_2}^{T_3} c_{p,h} dT + L_h} \quad (6)$$



**Figure 1** Conceptual diagram of hydrate cycle. Each of the numbers enclosed by a square is the state number.

## ILLUSTRICAL CALCULATION



**Figure 2**  $c_{p,h}$  divided by  $\sum v$  of hydrates; ●, CH<sub>4</sub> hydrate; ▼, C<sub>2</sub>H<sub>6</sub> hydrate; ■, C<sub>3</sub>H<sub>8</sub> hydrate; □, Kr hydrate; △, Xe hydrate.

Hydrate formation and dissociation need some degree of driving force, which is the temperature range between the equilibrium temperature and the reaction temperature of the system. Considering that the heat capacity of seawater is very large, we may assume the reaction temperature to be equivalent to the heat reservoir temperature. Thus, we can safely assume that the driving force directly depends on the heat source temperature and the equilibrium temperature. The equilibrium temperature varies depending on the system's pressure and guest substance, and therefore it will be an important factor for  $\eta_h$ . In the present analysis, the formation temperature  $T_1$  is set to be 282 K and the dissociation temperature  $T_3$  is set to be 293 K to secure a few degrees of temperature for the driving force.

Although  $c_{g,h}$  is vital to calculate  $\eta_h$ , we cannot necessarily get a favorable data of  $c_{g,h}$  each time since there are few data about the specific heat of hydrates at constant pressure  $c_{g,h}$  in

previous works. This paper tries to presume  $c_{g,h}$  for any hydrate from  $c_{g,h}$  data of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, Kr and Xe hydrates, all of which were reported by Handa [11, 12].  $c_{g,h}$  divided by the total amount of the degree of freedom of hydrate  $\sum v$  from 85 K to 260 K for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> hydrates and 85 K to 270 K for CH<sub>4</sub>, Kr and Xe hydrates are plotted in Figure 2. All of those hydrates estimate almost the same line in Figure 2, which can be explained by the equipartition theorem. We will define that  $c_{g,h}$  divided by  $\sum v$  is a linear function exclusively dependent on temperature regardless of the guest substance. Applying a least square method to the data in Figure 2, we will obtain the inclination and the intercept of the linear function as below:

$$c_{p,h} / \sum v = 1.99 \cdot 10^{-2} T + 9.70 \cdot 10^{-1} \quad (7)$$

From this equation  $c_{g,h}$  will be a function of  $T$  and  $\sum v$ .

$$c_{p,h} = (1.99 \cdot 10^{-2} T + 9.70 \cdot 10^{-1}) \sum v \quad (8)$$

When integrating a linear function  $f(x, y)$  with respect to  $x$  from  $\alpha$  to  $\beta$ , we can get the solution by just multiplying  $\alpha - \beta$  and  $f((\alpha + \beta)/2)$  if  $x$  and  $y$  are independent of each other.

By applying this property to calculating  $Q_{23}$ , it becomes

$$\dot{Q}_{23} = 9.95 \cdot 10^{-3} \dot{m}_h (T_1 + T_3 + 97.49) (T_3 - T_1) \sum v \quad (9)$$

$V_1$  depends on the hydration number and the crystal structure. Table 1 summarizes geometrical data of structure I, structure II and structure H. We will calculate  $V_1$  as

$$V_1 = 2.26 \cdot 10^{-5} n \quad (10)$$

for structure I,

$$V_1 = 2.29 \cdot 10^{-5} n \quad (11)$$

for structure II and

$$V_1 = 2.34 \cdot 10^{-5} n \quad (12)$$

for structure H.

Using equations (9) to (12), we will rewrite the equation (6) without integral signs.  $\eta_h$  equals to

$$\left\{ \begin{array}{l} \frac{(h_3^g - h_4^g) + n(h_3^w - h_4^w) - 2.26 \cdot 10^{-5} n(p_3 - p_1)}{9.95 \cdot 10^{-3} (T_1 + T_3 + 97.49)(T_3 - T_1) \Sigma \nu + L_h} (sI) \\ \frac{(h_3^g - h_4^g) + n(h_3^w - h_4^w) - 2.29 \cdot 10^{-5} n(p_3 - p_1)}{9.95 \cdot 10^{-3} (T_1 + T_3 + 97.49)(T_3 - T_1) \Sigma \nu + L_h} (sII) \\ \frac{(h_3^g - h_4^g) + n(h_3^w - h_4^w) - 2.34 \cdot 10^{-5} n(p_3 - p_1)}{9.95 \cdot 10^{-3} (T_1 + T_3 + 97.49)(T_3 - T_1) \Sigma \nu + L_h} (sH) \end{array} \right. \quad (13)$$

## PROCESSING OF RESULTS

Table 2 shows state functions,  $n$ ,  $\Sigma \nu$ ,  $L_n$  and  $\eta_h$  for five guest substances: Kr, Xe, CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>4</sub>. State functions are based on the data given by NIST [21].  $n$  are estimated on assumption that the guest molecules completely fulfill cavities they can theoretically occupy.  $L_n$  are cited from previous works if reported, otherwise calculated by applying a least square method to phase equilibrium data. The first two substances, noble gases, are monoatomic molecules and hence have lower specific heat. This leads to their low mechanical work per unit temperature change in an isentropic expansion. Low latent heat of noble gases is an advantage as the working fluid. This lowness mainly contributes to raising  $\eta_h$  beyond 2 % with Kr and Xe hydrates. Xe hydrate engine has much higher  $\eta_h$  than that of Kr hydrate engine. This would be caused by the difference of the pressure range between both systems; 3.43 MPa to 10.19 MPa for Kr hydrate and 0.42 MPa to 1.11 MPa for Xe hydrate, which makes an impact on the compressor work in the states 1' to 2 as indicated in the equation (1). Although polyatomic molecules such as fluorocarbons have higher specific heat than noble gases, the enthalpy change of the guest substance in the isentropic expansion  $h_3^g - h_4^g$  with CH<sub>3</sub>F or CH<sub>2</sub>F<sub>2</sub> hydrate is only the same level as that with noble gases.

Condensation of the vapor in the states 3' to 4 causes the inhibition of  $h_3^g - h_4^g$ . CH<sub>3</sub>F condenses at 240.51 K and CH<sub>2</sub>F<sub>2</sub> does at 256.52 K on condition of shown in Table 2. Substances with very low vapor pressure are thereby not recommended for the working fluid. Methane has the critical point at 4.60 MPa and 190.56 K [22] and is supercritical fluid beyond that pressure and temperature. This means that methane will never condense as long as above 190.56 K. In the methane hydrate cycle, however, pressure range is very high: 8.67 MPa to 20.11 MPa. This high pressure range increases the compressor work  $W_{12}$  to decrease  $\eta_h$ . The need of high pressure furthermore impacts cost in industrial use.

We will calculate thermal efficiency of Rankine cycle  $\eta_R$  with NH<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>F<sub>3</sub> and C<sub>3</sub>H<sub>8</sub> as the working fluid to compare them with the performances of the hydrate cycle. Heat reservoir temperatures of Rankine cycle is set to be same as those of the hydrate cycle: 280 K for the low temperature reservoir and 295 K for the high temperature reservoir. The calculation of  $\eta_R$  is made by the following formula [23].

$$\eta_R = (h'_3 - h'_4) / (h'_3 - h'_2) \quad (14)$$

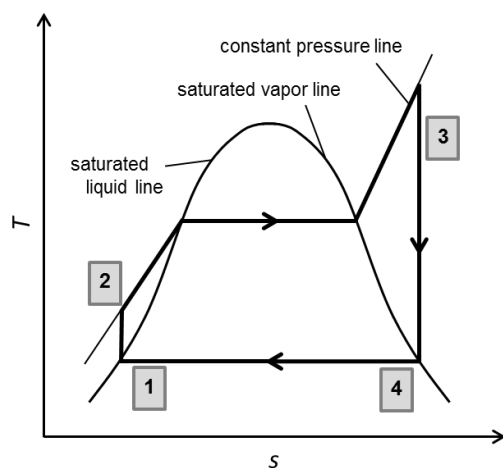
**Table 1** Geometrical data of hydrate on structure I, structure II and structure H [13]

Crystal structures	Structure I	Structure II	Structure H
Geometry of unit cell	Cubic	Cubic	Hexagonal
Lattice constant / Å	12	17.3	a = 12.26 c = 10.17
Number of water molecules per unit cell	46	136	34

**Table 2** Properties and estimated theoretical thermal efficiencies of some kind of hydrate cycles. Heat source temperature is 280 K for low grade and 293 K for high grade.

The guest	Structure	$n$	$\Sigma \nu$	$p_1$ / MPa $T_1$ / K	$p_3$ / MPa $T_3$ / K	$V_1$ / m <sup>3</sup> ·mol <sup>-1</sup>	$h_3^g - h_4^g$ / kJ·mol <sup>-1</sup>	$h_3^w - h_4^w$ / kJ·mol <sup>-1</sup>	$L_h$ / kJ	$\eta_h$
Kr	II	5.67	37.02	3.43 [14] 282.21 [14]	10.19 [14] 292.46 [14]	$6.25 \cdot 10^{-4}$	1.592 <sup>a</sup>	0.122 <sup>a</sup>	62.77 [15]	2.15 %
Xe	I	5.75	37.50	0.42 [16] 283.15 [16]	1.11 [17] 292.47 [17]	$5.46 \cdot 10^{-3}$	1.837 <sup>a</sup>	0.013 <sup>a</sup>	68.30 [15]	2.58 %
CH <sub>3</sub> F	I	7.67	52.02	0.75 [18] 283.20 [18]	2.05 [18] 292.20 [18]	$2.91 \cdot 10^{-3}$	1.762 <sup>a</sup>	0.023 <sup>a</sup>	76.05 <sup>a</sup>	2.17 %
CH <sub>2</sub> F <sub>2</sub>	I	7.67	52.02	0.46 [19] 283.15 [19]	1.08 [19] 290.95 [19]	$4.75 \cdot 10^{-3}$	1.508 <sup>a</sup>	0.011 <sup>a</sup>	73.50 <sup>a</sup>	2.04 %
CH <sub>4</sub>	I	5.75	40.50	8.67 [20] 284.70 [20]	20.11 [20] 291.70 [16]20	$2.28 \cdot 10^{-4}$	1.340 <sup>a</sup>	0.205 <sup>a</sup>	62.85 [15]	1.59 %

<sup>a</sup> calculated based on [21].



**Figure 3** Conceptual diagram of the Rankine cycle. Each of the numbers enclosed by a square is the state number

**Table 3** Enthalpies and estimated theoretical thermal efficiencies of Rankine cycle with  $\text{NH}_3$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{C}_2\text{H}_3\text{F}_3$  and  $\text{C}_3\text{H}_8$  as working fluid.

Guest	$h'_2/\text{J}^a$	$h'_3/\text{J}^a$	$h'_4/\text{J}^a$	$\eta'$
$\text{NH}_3$	6.548	27.859	27.491	1.73 %
$\text{CH}_2\text{F}_2$	11.231	27.231	26.873	2.24 %
$\text{C}_2\text{H}_3\text{F}_3$	21.631	41.856	41.188	3.30 %
$\text{C}_3\text{H}_8$	9.828	26.337	25.785	3.34 %

<sup>a</sup> calculated based on [21].

Table 3 shows  $h'_2$ ,  $h'_3$ ,  $h'_4$  and calculated  $\eta_R$  for each working fluid. In terms of theoretical thermal efficiency, the performance of the hydrate cycle with Kr, Xe,  $\text{CH}_3\text{F}$  or  $\text{CH}_2\text{F}_2$  is comparable to that of the Rankine cycle with  $\text{CH}_2\text{F}_2$  and is less than that with  $\text{C}_2\text{H}_3\text{F}_3$  and  $\text{C}_3\text{H}_8$ . This paper considers that a primary factor of this poorness is that the hydrate dissociation heat is much larger than evaporation heat of the guest gas, which must be caused by a large number of hydrogen bonds in a hydrate.

In OTEC, only substances which make a phase transition between vapor and another phase within the temperature range of  $T_1$  to  $T_3$  can be candidates for the working fluid of heat engine. While such substances for the Rankine cycle are restricted to fluorocarbons, ammonia and propane, the hydrate cycle allows a more diverse selection of guest substances including noble gases or hydrocarbons. Kr or Xe hydrate engine, having environmental-friendliness as well as the thermal efficiency comparable to the  $\text{CH}_2\text{F}_2$  Rankine cycle, may especially be a useful method for OTEC.

When another substance which is called "large molecule guest substance (LMGS)" is added to a gas and water system, this system will form structure H hydrate. Structure H hydrates can generally be formed under milder conditions than pure

hydrates. This would contribute to not only further variation of the working fluid for the hydrate cycle but also improve  $\eta_h$  with reducing the compressor work  $W_{12}$ .

## CONCLUSION

We analyzed a heat engine system using clathrate hydrate as its working fluid and calculate the performance of this system operated with a high temperature reservoir of 280 K and a low temperature reservoir of 295 K. These conditions are relevant to the application to "Ocean Thermal Energy Conversion (OTEC)". The Rankine cycle with fluorocarbons or ammonia is considered to be most effective method for OTEC. The recent industrial trend is avoiding usage of fluorocarbons, which are strong greenhouse gases. Ammonia is corrosive to metals as well as a source of acid rain. Propane is highly flammable. Clathrate hydrate, which captures many kinds of substances not restricted to such destructive ones, has the potential as the working fluid in OTEC. The thermal efficiency  $\eta_h$  for Kr and Xe hydrates were evaluated in the present study. The analysis showed that the dominant properties were dependent on enthalpy difference of the working fluid in the adiabatic expansion of the states 3' to 4, pressure range in the whole process and the dissociation heat of hydrate.  $\eta_h$  is 2.15 % for Kr hydrate and 2.58 % for Xe hydrate, which are comparable to the organic Rankine cycle with fluorocarbons: 2.24 % for  $\text{CH}_2\text{F}_2$ , 3.30 % for  $\text{C}_2\text{H}_3\text{F}_3$  and 3.34 % for  $\text{C}_3\text{H}_8$ . These results indicate the prospects of the hydrate heat engine for OTEC as an environment-friendly method.

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