International Conference on Renewable Energies and Power Quality (ICREPQ'19)
Tenerife (Spain), 10th to 12th April, 2019
Renewable Energy and Power Quality Journal (RE&PQJ)
ISSN 2172-038 X, No.17 July 2019

Theoretical performance analysis of hydrate-based refrigeration system

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Abstract.

This paper reports theoretical performance analysis of the hydrate-based refrigeration system. The hydrate-based refrigerator transfers thermal energy through the cycle of following processes: adiabatic compression of guest compounds and water, hydrate formation, adiabatic expansion of hydrates, hydrate dissociation. The theoretical analyses and COP calculations were performed in the each of the following hydrate-forming systems: HFC-32+cyclopentane(CP) +water, Kr+CP+water, and HFC-41+CP+water system. Practical utility of hydrate-based refrigerator is discussed based on the comparison with the Carnot cycle.

Key words

Clathrate hydrates, Refrigeration system, Heat pump, Renewable energy,

1. Introduction

The global electric power demand has increased considerably by the popularization of air-conditioning equipment and information communication equipment. Since the nuclear power plant accident in Japan in 2011, there has been a trend to avoid nuclear power generation in a large number of developed countries. For example, Germany and Switzerland decided to stop the use of nuclear power by 2022. To supplement the electric power, the thermal power generation which uses fossil fuels and emits carbon dioxide has grown. This causes development of the global warming and it has been necessary to reduce power use.

The rapid increase of air conditioners is considered as one of the main causes of increasing electric power use. According to the report of International Energy Agency, the global stock of air conditioners in buildings will grow to 5.6 billion by 2050, up from 1.6 billion in 2018[1]. To reduce power use, the higher efficiency air-conditioning system has been developed with the progress of technology. However, the coefficient of performance (COP) of the vapor compression type refrigerator for home and business use is less than 7. At present, hydrofluorocarbon (HFC) is commonly used for the working media of the conventional vapor compression type refrigerator and as a substitute, clathrate hydrates have been proposed for higher COP [2].

Clathrate hydrates are crystalline compounds that are constructed of hydrogen bonded water molecules forming cages and guest molecules stored in the cages. Hydrates have a large heat of formation/dissociation. The dissociation heat of the hydrate formed with HFC is 4 to 8 times larger than the latent heat of evaporation of HFC [3], [4]. Hydrates storing guest compounds that is appropriate for the intended use can be formed at suitable conditions of temperature and pressure.

Ohfuka and Ohmura [5] established a theoretical analysis method for engines of ocean thermal energy conversion that utilize hydrates formed with Kr, difluoromethane (HFC-32), and fluoromethane (HFC-41) as the working media and calculated the thermal efficiency. The thermal efficiency differs depending on the guest compounds of hydrates and when selecting the guest compounds, it is important for selection of guest compounds to formulate thermal efficiency theoretically and clarify the thermodynamic parameters affecting the thermal efficiency. The inverse cycle of the hydrate engine is close to the refrigeration cycle of conventional vapor compression type heat pumps.

Ogawa et al. [6] designed a hydrate-based refrigerator utilizing hydrates formed with HFC-32 and cyclopentane (CP) and calculated the COP for the practical selection of the devices and the settings of the thermodynamic parameters. They reported that the COP of the hydrate-based refrigeration system was calculated about 8. This COP calculated in the experimental study was higher than that of the conventional refrigeration system. However, the theoretical analysis of the cycle based on thermodynamic properties of hydrates has not been reported.

Therefore, the objective of this study is to establish the theoretical analysis method for the hydrate-based refrigerator. We investigate appropriate guest compounds for the working media and calculate the COP. Then we evaluate it by thermodynamic properties of hydrates.

2. Method

A. *Modelling of the hydrate refrigeration cycle*

The cycle model of hydrate-based refrigerator is shown in Fig 1. The detailed explanation of each state is shown as follows.

・States 1 to 2 : Adiabatic compression

The temperature of guest compound and water is set to be the initial temperature T_1 287 K. Guest compounds and water are adiabatically compressed and the temperature of each compound increases. The temperature at which each compound is turned to the thermal equilibrium state is defined as T_2.

・States 2 to 3 : Isobaric cooling

Hydrates are formed by decreasing temperature to the hydrate-formed condition while releasing the heat outside. The hydrate formation temperature T_3 is set to be 295 K so that it is close to river water temperature in summer.

・States 3 to 4 : Adiabatic expansion

After hydrate formation, hydrates are adiabatically expanded to the initial pressure. The temperature of the working media decreases to the hydrate equilibrium temperature T_4 at the initial pressure with partial hydrate dissociation.

・States 4 to 1 : Isobaric heating

The dissociation heat of hydrates is produced by increasing temperature. When the temperature of the working media increases to initial temperature, guest compounds and water are adiabatically compressed again.

The above processes are defined as one cycle of the hydrate-based refrigerator.

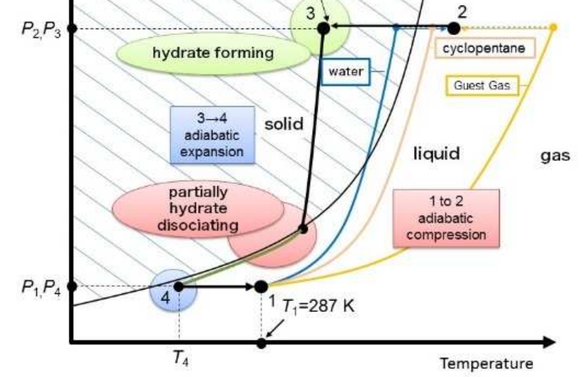

Fig. 1. The cycle model of hydrate-based refrigerator.

B. *Formulation of COP on hydrate-based refrigerator*

COP is generally defined as the following equation

$$\varepsilon_{\mathrm{R}} = \frac{Q_{\mathrm{L}}}{W} \tag{1}$$

where W is the input work and Q_L is the heat received from the low temperature heat source. W was calculated based on the amount of enthalpy change in the adiabatic compression process in the states 1 to 2. The heat received from the cooling space Q_L is expressed as the dissociation heat of hydrate in the states 3 to 4 and 4 to 1.

In the states 1 to 2, the input work W is defined as follows

$$W = 2\Delta h_{\mathrm{gg}} + \Delta h_{\mathrm{gl}} + 17\Delta h_{\mathrm{w}} \tag{2}$$

where Δh_{gg}, Δh_{gl}, and Δh_{w} are the amounts of enthalpy change in the process of adiabatic compression of the guest gas, the second guest (CP in the present study), and the water, respectively. The coefficients are calculated based on the stoichiometric ratio of the hydrates.

In the states 3 to 4, a part of the dissociation heat of hydrates that was used for decreasing the temperature of the working media is defined as follows

$$Q_{34} = \int_{T_3}^{T_4} c_{\mathrm{p,gg}} dT + \int_{T_3}^{T_4} c_{\mathrm{p,gl}} dT + \int_{T_3}^{T_4} c_{\mathrm{p,w}} dT \tag{3}$$

where $c_{\mathrm{p,gg}}$, $c_{\mathrm{p,gl}}$ and $c_{\mathrm{p,w}}$ are specific heats at constant pressure of the guest gas, CP, and the water, respectively.

In the states 4 to 1, the dissociation heat of hydrate is calculated from the following Clausius-Clapeyron equation

$$\frac{d\ ln\ p}{d\,(1/T)} = -\frac{\Delta H_{\mathrm{h}}}{zR} \tag{4}$$

where p is the pressure of the system and T is the temperature of the system. ΔH_{h} was calculated under the condition that the compression factor z is defined as 1.0 and the gas constant R is defined as 8.31 J/mol K.

By using the above mentioned definitions, COP of the hydrate-based refrigerator is formulated as follows

$$\varepsilon_{\mathrm{R}} = \frac{\Delta H_{\mathrm{h}} - Q_{34}}{2\Delta h_{\mathrm{gg}} + \Delta h_{\mathrm{gl}} + 17\Delta h_{\mathrm{w}}} = \frac{\Delta H'_{\mathrm{h}}}{\Delta H_{\mathrm{glw}}} \tag{5}$$

where ΔH_{glw} is the total of enthalpy change of the guest gas, CP, and water, respectively. ΔH_{h} is defined as the heat of hydrate dissociation and $\Delta H'_{\mathrm{h}}$ is the heat of hydrate dissociation after the one used to decrease the temperature is excluded. Enthalpy in specific temperatures and pressures is obtained from REFPROP in NIST [4] and the dissociation heat was calculated with the phase equilibrium data [3],[7],[8].

C. *Selection of guest compounds*

As analysis targets in this study, we chose the three systems: HFC-32+CP+water, Kr+CP+water, and HFC-

41+CP+water because the phase equilibrium conditions in these systems are relatively high in temperature and low in pressure. Structure II hydrates are formed in the above three systems [3], [7], [8]. The amounts of gas, CP, and water in the cycle are 2 mol, 1 mol, and 17 mol, respectively and these values are calculated from the stoichiometric ratio.

3. Results and Discussion

A. *Calculation of COP on various hydrates and conditions*

The calculated results of COP of the three systems, HFC-32+CP+water, Kr+CP+water, and HFC-41+CP+water, are shown in Table I. T_2 was calculated from the temperature after adiabatic compression and the specific heat at constant pressure of each compound. In the condition (i), the initial pressure P_1 was 0.1013 MPa and P_2 was 1.0 MPa. In the condition (ii), P_1 was 0.1013 MPa and P_2 was 1.5 MPa.

As the indicator to compare with the COP calculated in this study, we used $\varepsilon_{\rm R,\,Carnot}$ of the inversed Carnot cycle.

$$\varepsilon_{\rm R,Carnot} = \frac{T_{\rm L}}{T_{\rm H} - T_{\rm L}} \qquad (6)$$

where $T_{\rm H}$ and $T_{\rm L}$ are the temperatures of high- and low-temperature heat sources, respectively. In this analysis, $T_{\rm H}$ was set to 295 K supposing the temperature of river water and $T_{\rm L}$ was set to 286 K as the cooling temperature.

In the condition (i), the COP in the system of HFC-32+CP+water was the highest because the heat of dissociation is the largest and the input work $\Delta H_{\rm glw}$ is the lowest. Although $\Delta H'_{\rm h}$ in the system of HFC-41+CP+water was lower than that in the system of Kr+CP+water, the COP in the system of HFC-41+CP+water was higher than that in the system of Kr+CP+water because of the higher $\Delta H_{\rm glw}$ in the system of Kr+CP+water.

When P_2 increased as shown in the condition (ii), the COP decreased on the all systems. This is because more input work is needed when the compression ratio increases. To obtain higher COP, it is necessary to raise the initial pressure P_1 and lower P_2. Therefore, P_1 was raised to the phase equilibrium pressure of the hydrates and the COP in that condition was calculated. The phase equilibrium pressures in the systems of HFC-32+CP+water, Kr+CP+water, and HFC-41+CP+water at 287 K are 0.162 MPa, 0.237 MPa, and 0.119 MPa, respectively. The initial pressure in the system of HFC-41+CP+water could not be raised because the phase equilibrium pressure of HFC-41 at 287 K is close to the atmospheric pressure 0.1013 MPa. The results of the calculated COP are shown in the Table II. The calculated COP was higher than those of the conditions (i) and (ii) on all the systems because $\Delta H'_{\rm h}$ increased and $\Delta H_{\rm glw}$ decreased by lowering the compression ratio.

On the other hand, it is necessary to obtain enough driving force for hydrate formation if we consider the practical use of the hydrate refrigeration system. Driving force for hydrate formation increases when the difference between the hydrate phase equilibrium and the temperature after adiabatic compression becomes larger. In the previous study [9], it was shown that temperature that is higher than 2 K is needed as the difference between the hydrate phase equilibrium temperature and

Table I. the temperature and pressure conditions and calculated COP in each system of the hydrate-based refrigirator

Guest compound	condition	P_1 / MPa	P_2 / MPa	Compression ratio	T_2 / K	$\Delta H_{\rm glw}$ / kJ	$\Delta H'_{\rm h}$/ kJ	$\varepsilon_{\rm R,\,Carnot}$ *	COP	COP/$\varepsilon_{\rm R,\,Carnot}$ /%
HFC-32+CP	(i)	0.1013	1.0	9.9	313	13.7	228	31	16.7	52
	(ii)	0.1013	1.5	15	319	16.8			13.6	43
Kr+CP	(i)	0.1013	1.0	9.9	313	18.2	220		12.1	38
	(ii)	0.1013	1.5	15	318	23.7			9.29	29
HFC-41+CP	(i)	0.1013	1.0	9.9	313	14.2	202		14.2	45
	(ii)	0.1013	1.5	15	319	17.5			11.6	36

Table II. the calculated COP in each system of the hydrate-based refrigerator under the condition that P_1 increased

Guest compound	P_1 / MPa	P_2 / MPa	Compression ratio	T_2 / K	$\Delta H_{\rm glw}$ / kJ	$\Delta H'_{\rm h}$ / kJ	$\varepsilon_{\rm R,\,Carnot}$ *	COP	COP/$\varepsilon_{\rm R,\,Carnot}$ /%
HFC-32+CP	0.13	1.0	7.7	310	11.9	230	31	19.4	61
	0.15	1.0	6.7	309	10.9	231		21.2	67
Kr+CP	0.2	1.0	5.0	305	11.1	224		20.3	64

Table III. the calculated COP in each system considering driving force for hydrates

Guest compound	P_1 / MPa	P_2 / MPa	Compression ratio	T_2 / K	$\Delta H_{\rm glw}$ / kJ	$\Delta H'_{\rm h}$ / kJ	$\varepsilon_{\rm R,\,Carnot}$ *	COP	COP/$\varepsilon_{\rm R,\,Carnot}$ /%
HFC-32+CP	0.15	1.0	6.7	309	10.9	231	31	21.2	67
Kr+CP	0.2	1.3	6.5	316	13.7	224		16.4	52
HFC-41+CP	0.1013	0.8	5.9	310	12.5	202		16.2	51

the hydrate formation temperature to obtain enough driving force for hydrate formation. The equilibrium pressure at 297 K in the three system of HFC-32+CP+water, Kr+CP+water, and HFC-41+CP+water are 0.893MPa, 1.294MPa, and 0.557MPa, respectively. These values become the lower limits of P_2 of each system. Therefore, P_1 and P_2 are now set as the upper and lower limits and the COP in this condition is calculated. The results are shown in the Table III. The highest COP of 21.2 was calculated in the system of HFC-32+CP+water considering the driving force for hydrate formation. Because the COP of the conventional vapor compression type refrigerator is 7, it is said that the hydrate-based refrigerator has the higher efficiency cycle than that of the conventional refrigerator.

B. Evaluation of COP based on thermodynamic properties of hydrates

In this section, we evaluate the calculated COP by thermodynamic properties of hydrates. From the above analyses, we found that the hydrate that has large dissociation heat should be selected as the working media for the hydrate refrigeration system. The magnitude of hydrate dissociation heat depends on the interaction between the guest compounds and the cage formed by water molecules [10]. Generally, the dissociation heat of hydrates increases when the molecular size of guest compounds and the size of cages are in an appropriate relationship. Moreover, the hydrate containing a guest gas whose temperature increase before and after adiabatic compression is small should be used for the hydrate refrigeration system because the input work increases when the temperature of guest gas raises after adiabatic compression. The input work of guest gas is defined as follows.

$$\Delta h_{\mathrm{gg}} = \int_{T_1}^{T_2} c_{\mathrm{p,gg}} dT = c_{\mathrm{p,gg}} \Delta T \qquad (7)$$

Although c_{p} is a function of temperature, it is considered constant in this study because c_p varies in the range of only 0.01 %. Therefore, the input work is influenced by the specific heat at constant pressure of the guest gas and the temperature difference of the guest gas before and after adiabatic compression.

Specific heat at constant pressure is defined as the following equation

$$c_{\mathrm{p}} = \left(\frac{v}{2} + 1\right) R \qquad (8)$$

where v is the degree of freedom of the molecule. The degree of freedom of a polyatomic molecule such as HFC-41 and HFC-32 is 6. The degree of freedom of a monoatomic molecule like Kr is 3. c_{p} of polyatomic molecules is 1.6 times as large as that of monoatomic molecules.

On the other hand, the temperature difference of guest gas before and after adiabatic compression is defined as follows

$$\Delta T = T_2 - T_1 = T_1 \left(\left(\frac{p_2}{p_1}\right)^{\left(1 - \frac{1}{\kappa}\right)} - 1 \right) \qquad (9)$$

where κ is the specific heat ratio. Specific heat ratios of polyatomic molecules and monoatomic molecules are 1.3 and 1.7, respectively. If the compression ratio is set to be 10, ΔT of monoatomic molecules is 2.0 times higher than that of polyatomic molecules. Therefore, the effect of ΔT on the input work is larger than that of c_{p}. For this reason, polyatomic molecules should be selected as a guest gas for the hydrate refrigeration system.

4. Conclusion

We evaluated COP of the hydrate-based refrigeration system by the formulation using the heat of hydrate dissociation and the enthalpy change of fluids. The illustrative calculation indicates that the COP of 21.2 in the system of HFC-32+CP+water is the highest when P_1 is 0.15 MPa and P_2 is 1.0 MPa of all conditions in this study. It is considered that the hydrate that has a large dissociation heat and contains a polyatomic molecule as a guest gas is useful for the hydrate-refrigeration system. The usefulness of the hydrate-based refrigerator was shown by comparison with COP of the conventional refrigerator and $\varepsilon_{\mathrm{R,\ Carnot}}$.

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