



Theoretical performance analysis of hydrate-based heat engine system suitable for low-temperature driven power generation



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ABSTRACT

We analyzed a heat engine using clathrate hydrate as its working media and evaluate the performance of this system operated with high and low temperature reservoirs of 295 K and 280 K “OTEC (Ocean Thermal Energy Conversion)” may be a prospective example of the technologies utilizing the small-temperature difference for power generation. This heat engine generates mechanical power through the cycle of following processes: hydrate formation at low temperature, pumping of hydrate, isobaric heating of hydrate, hydrate dissociation and adiabatic expansions of dissociated gas and water. The thermal efficiency for Kr, Xe, CH₃F, CH₂F₂ and CH₄ hydrates were evaluated. The analysis showed the dominant properties were the enthalpy difference of the working media in the adiabatic expansions, the pressure range in the whole process and the dissociation heat. The thermal efficiency is 2.20% for Kr hydrate and 2.89% for Xe hydrate. While these are slightly inferior to those of Rankine cycle: 3.30% for C₂H₃F₃ and 3.34% for C₃H₈, Kr and Xe hydrates are greatly favorable in terms of environmental friendliness. These results indicate the prospects of the hydrate heat engine for the power generation utilizing a small temperature difference as an environment-friendly technology.

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1. 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 power generation. 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 great interest of many societies to commercially develop the domestically feasible power generation systems using renewable sources. 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 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 m deep and at the sea surface is below 280 K and 295 K–302 K, respectively [1]. The present study concerns a power generation system utilizing this temperature difference of 15–22 K. There have been some previous studies converting aforementioned thermal energy into mechanical work. This technology is called “OTEC (Ocean Thermal Energy Conversion)” ever since d’Arsonval had proposed it for the first time in 1881 [2]. Previous studies reported that ammonia, refrigerants or propane would be best as the working fluid [3–5] on the Rankine cycle under very low-grade energy sources, 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 [6], much less chlorofluorocarbons for ozone depletiveness [7]. Ammonia has corrosive properties towards metals as well as contributes to acid rain [8]. Propane is a highly flammable gas. 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.

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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 the guest.

In recent years, we can find progress in the studies to apply hydrates for industrial technologies as well as utilization of natural gas hydrate bearing in sediments [9]. Storage media for natural gas utilizing high storage capacity of gas [10], capturing carbon dioxide [11], which is toward the application IGCC (integrated gasification combined cycle) [12], and cool energy storage media [13] are the examples utilizing commercially beneficial properties of hydrates. The concept of hydrate-based heat engine was first proposed by Nishimura [14]. Later Obara et al. proposed utilization of hydrate engine combined with a proton exchange membrane fuel cell [15], which was followed by a detailed analysis of CO₂ hydrate engine [16]. Hydrate based refrigeration system, which is practically reversed system of the hydrate heat engine, was studied by Ogawa et al. [17]. This found that refrigeration system with CH₂F₂ hydrate will makes higher COP than conventional ones. The performance of the hydrate-based heat engine should be greatly dependent on the guest compounds. Nevertheless, the selection of guest suitable for the hydrate-based engine was not studied. 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.

2. Theory

2.1. Conceptual theory of hydrate heat engine

The performance of the hydrate cycle is theoretically analyzed by formulating the mechanical work with alternate actions 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, the temperature of the guest substance becomes lower than the initial temperature after a series of the following processes: hydrate formation, dissociation and adiabatic expansion of the guest gas. Fig. 1 conceptually illustrates the hydrate cycle on a p - T diagram together with the hydrate phase equilibrium curve. Each of the process in the hydrate cycle is thermodynamically described below. Although the states 1 and 1' have the same coordinate point in the diagram, they are differ in phase. While the state 1 is mixture of water and guest substance, the working media is form of hydrate in the state 1'. Hydrate formation is undergone between the two states. Similarly, states 3 and 3' are form of hydrate and mixture of water and the guest, respectively.

2.2. Thermodynamic processes of hydrate heat engine

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 unchanged since the hydrate is a 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 then sent to respective 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 respectively join to be a thermodynamic equilibrium, and then release heat to the low temperature reservoir to be the initial temperature.

2.3. Theoretical thermal efficiency

Theoretical thermal efficiency is one of the most important indexes to evaluate the performance of heat engines. This index η 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} .

$$\eta = \frac{\dot{W}}{\dot{Q}} \quad (1)$$

In the hydrate cycle, the values required for calculating η are the total amount of heat supplied from the high temperature reservoir in the states 2 to 3 \dot{Q}_{23} and $3 \rightarrow 3'$ $\dot{Q}_{33'}$, 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 these 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

$$\dot{W}_{in} = \dot{n}_h(p_2V_2 - p_1V_1) \cong \dot{n}_hV_1(p_2 - p_1) \quad (2)$$

where \dot{n}_h is the formation rate of hydrate in the states 1 to 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

$$\dot{Q}_{23} = \dot{n}_h \int_{T_2}^{T_3} c_{p,h} dT \quad (3)$$

where $c_{p,h}$ is the molar heat capacity of hydrate at constant pressure.

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

$$\dot{Q}_{33'} = \dot{n}_h L_h \quad (4)$$

where L_h is the molar latent heat of hydrate.

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

$$\dot{W}_{guest} = \dot{n}_h (h_{3'}^g - h_4^g) \quad (5)$$

$$\dot{W}_{water} = n \dot{n}_h (h_{3'}^w - h_4^w) \quad (6)$$

where h_i^g and h_i^w are the molar enthalpy in state i of the guest and the water, respectively. n is the hydration number of the hydrate.

The behavior of liquid or solid in adiabatic process gives us another condition of $T_2 \cong T_1$. The theoretical thermal efficiency of this cycle η_h will be described with this approximation and $T_3 \cong T_{3'}$ as

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