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A NOVEL COMBINED POWER AND REFRIGERATION CYCLE BASED ON ZEOTROPIC MIXTURES HYDRATE

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ABSTRACT

Clathrate hydrate has various applications, for example, cold storage, gas transportation, CO_2 capture and storage, sea water desalination, etc. Hydrate could even be applied to separate zeotropic mixtures, and the separation processes are accompanied with heat absorbing and releasing. Thus, the hydrate separation method is proposed be used in the component adjustable Organic Rankine cycle, replacing the conventional separator. In this paper, we presented a novel combined power and refrigeration cycle based on zeotropic mixtures hydrate. For the separation work could be utilized in the form of heat and there are better matching of working fluids and thermal processes, the novel cycle could meet the combined cooling and power supply, and the cycle efficiency is improved.

Keywords: combined power and refrigeration cycles, Organic Rankine cycle, compositions adjustable, cycle efficiency, zeotropic mixtures, clathrate hydrate

NONMENCLATURE

Abbreviations	
Q_c	Refrigeration capacity
ORC	Organic Rankine cycle
T	Temperature
M	Molar mass
W	Power consumption or work
ΔH_{diss}	Hydrate dissociation enthalpy
Symbols	
h	Convection coefficient
s	Entropy
n	The number of certain molecules in a hydrate cell
$\dot{m}$	Mass flow rate
η	Cycle efficiency

1. INTRODUCTION

With the rapid development of world economy and the sharp growth of energy demand, energy storage and environment pollution are becoming increasingly serious. Efficient and rational energy utilization has become a top priority. Energy conversion is the sticking point of energy utilization, which is achieved mainly through thermodynamic cycles. Affected by the physical properties of the working medium, the cycle efficiency of the actual thermodynamic cycle is far lower than that of the Carnot cycle [1]. Compared with the organic Rankine cycle with non-adjustable components, the thermal efficiency of the organic Rankine cycle with adjustable components was improved by 2.52% and 2.39%, respectively, and the thermodynamic perfection was improved by 9.01% and 8.55%, respectively [2].

In thermodynamic cycles driven by mechanical energy, for example, positive and negative cycles originating from Carnot cycle, mechanical energy is first converted to the thermal energy, and then, the thermal energy would be readily used or further converted to mechanical energy. While in thermodynamic cycles driven by thermal energy, for example, absorption refrigeration cycle and adsorption refrigeration cycle, thermal energy is first converted to the chemical energy, whereafter, the chemical energy is converted to thermal energy or mechanical energy.

Dreos et al. [3] promoted a hybrid solar energy system, which involves a molecular solar thermal energy storage system and a solar water heating system. In the molecular solar thermal energy storage system, solar thermal energy is converted to chemical energy, being stored in covalent bonds of molecular

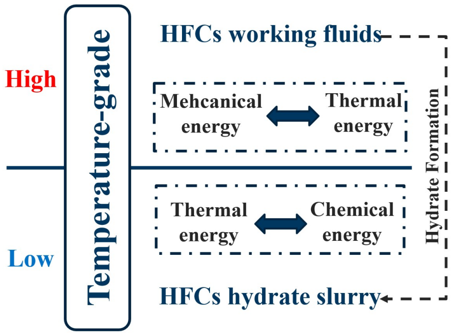

Fig. 1 Energy stepped utilization of power and refrigeration cogeneration system based on Zeotropic mixtures hydrate

structure.

In this work, a novel power and refrigeration cogeneration system based on zeotropic mixtures hydrate was presented. As shown in Fig. 1, HFCs is used as working medium for positive cycle in high temperature-grade, HFCs hydrate slurry is applied for negative cycle in low temperature-grade. By changing the structure of working fluid, the physical properties of working fluid could be changed, achieving a better match with the environment. On the one hand, the novel power and refrigeration system could realize energy stepped utilization; on the other hand, the negative cycle subsystem could regulate the working fluid component in positive cycle subsystem, improving the cycle efficiency of positive cycle subsystem.

2. CONSTRUCTION METHOD

Figure 2 is the schematic diagram of hydrate-based refrigeration cycle. As different gas hydrates have different equilibrium curves. Under a certain low temperature and high pressure condition, A and B working fluid mixtures enter the hydrate formation tank to form A hydrate, then B flows out of the formation tank; after that, formation tank is heated or depressurized, A hydrate dissociates, then A and B mixtures flows out; the formation and dissociation processes are linked through other parts. In this way,

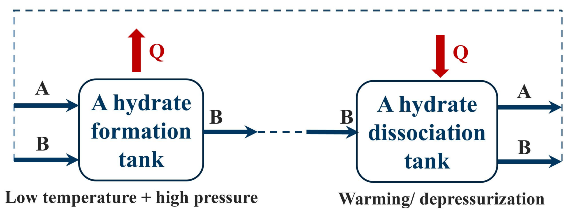

Fig 2 schematic diagram of hydrate-based refrigeration cycle

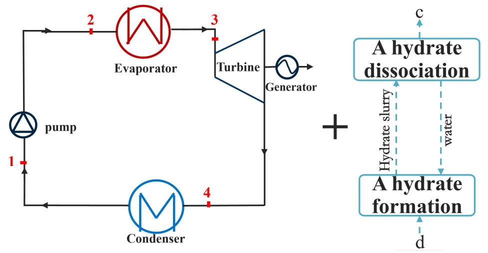

Fig 3 Construction method's schematic diagram

the negative cycle subsystem could play a role as component regulator.

The novel power and refrigeration cogeneration system includes a positive cycle subsystem (Organic Rankine cycle system) and a negative cycle subsystem (the hydrate-based refrigeration cycle system). The positive cycle subsystem is divided into four thermodynamic processes, and there are inserted four interfaces between the thermodynamic processes. The number of the four interfaces is '1', '2', '3', and '4'; The negative cycle subsystem has two interfaces, numbered 'c' and 'd', just as shown in Fig. 3.

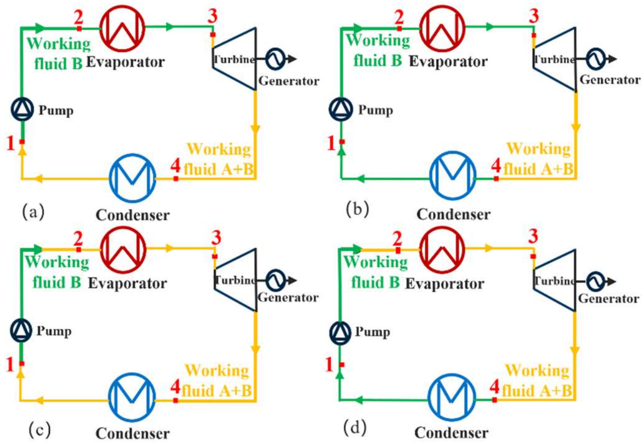

Fig 4 Four combinations

Since there are two compositions in negative cycle subsystem, only two thermodynamic processes could be coupled with suitable composition. We name the working fluids as 'working fluid A+B' and 'working fluid B'. Pump and turbine are selected as the optimization parts, because they are the main power consuming part and power generation part respectively. As the mass rate of 'working fluid A+B' is larger than that of working fluid B. In order to obtain low power consumption of pump and high turbine work, 'working fluid B' should flow through pump, and 'working fluid A+B' should flow through turbine. Thus, interface 'c' could connect to interface '1' or '4', while interface 'd' could connect to interface '2' or '3'. All combinations are shown in Fig. 4.

3. OPTIMAL SELECTION PRINCIPLE

We introduced the third dimension, component (θ),

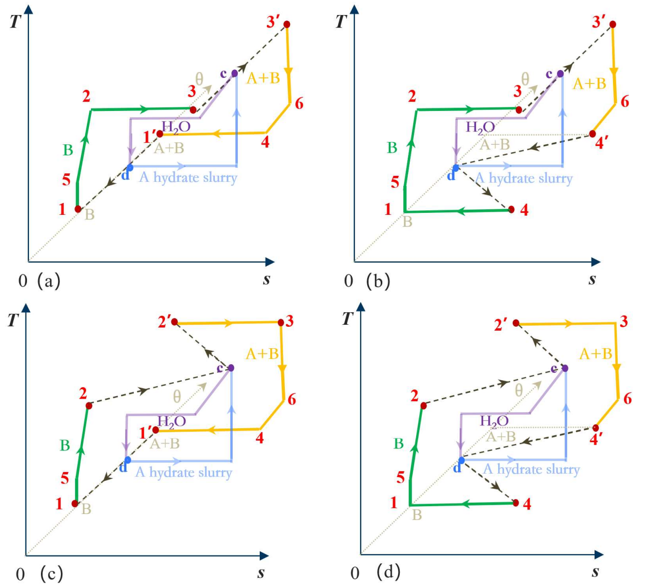

Fig 5 Optimal selection principle

to the conventional *T*-*s* diagram [2]. The *T*-*s*-θ diagrams of the four combinations are as shown in Fig. 5 (a) - (d). Different matching condition responds to different changing path. As there is no reversible process in real conditions, the longer the path, the higher the input work is. Among the four combinations, Fig. 5 (a) is the best match, because the paths '3-c-3'' and '1-d-1'' are the shortest. And its schematic diagram of the power and refrigeration cogeneration system based on zeotropic mixtures hydrate is as shown in Fig. 6.

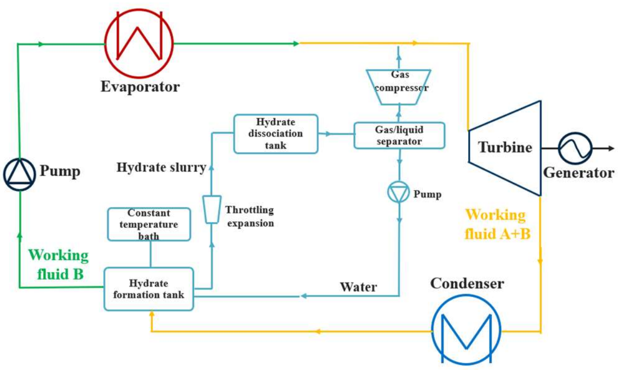

Fig 6 Schematic diagram of the novel power and refrigeration cogeneration system based on Zeotropic mixtures hydrate

4. CYCLE EFFICIENCY

The refrigeration capacity (Q_c) of negative cycle subsystem is calculated by Eq. (1):

$$Q_c = h \cdot (T_0 - T_{in}) \cdot A \qquad (1)$$

Where *h* is the convection coefficient of heat-side and cold-side liquid, T_0 is the temperature of environment, T_{in} is the temperature of cold-side liquid, *A* is the heat transfer areas.

The mass flow of A hydrate in negative cycle subsystem is confirmed by Eq. (2):

$$\dot{m}_{\mathrm{hydrate}} = \frac{Q_c}{\Delta H_{\mathrm{diss}}} \qquad (2)$$

Where $\dot{m}_{\mathrm{hydrate}}$ is the mass flow rate of 'A hydrate', ΔH_{diss} could be calculated through the Clapeyron equation [4].

The mass flow of 'working fluid A' in negative cycle subsystem is confirmed by Eq. (3):

$$\dot{m}_{\mathrm{A}} = \frac{\dot{m}_{\mathrm{hydrate}} M_{\mathrm{A}} \mathrm{n}_{\mathrm{A}}}{M_{\mathrm{hydrate}}} \qquad (3)$$

Where $\dot{m}_{\mathrm{A}}$ is the mass flow rate of 'working fluid A', M_A is the molar mass of 'working fluid A', n_A is the number of 'A molecule' in a hydrate cell, $M_{hydrate}$ is the ideal molar mass of 'A hydrate'.

The mass flow of H_2O in negative cycle subsystem is confirmed by Eq. (4):

$$\dot{m}_{\mathrm{H_2O}} = \frac{\dot{m}_{\mathrm{hydrate}} M_{\mathrm{H_2O}} \mathrm{n}_{\mathrm{H_2O}}}{M_{\mathrm{hydrate}}} \qquad (4)$$

The turbine work is calculated by Eq. (5):

$$W_{\mathrm{turbine}} = \dot{m}_{\mathrm{A+B}} \cdot (h_3 - h_6) \cdot \eta_{\mathrm{turbine}} \qquad (5)$$

Where $\dot{m}_{\mathrm{A+B}}$ is the mass flow rate of 'working fluid A+B', $\eta_{turbine}$ is the efficiency of turbine.

The power consumption of pump is calculated by Eq. (6):

$$W_{\mathrm{pump}} = \dot{m}_{\mathrm{B}}(h_5 - h_1) \cdot \eta_{\mathrm{pump}} \qquad (6)$$

Where η_{pump} is the efficiency of pump.

The efficiency of the power and refrigeration cogeneration system based on zeotropic mixtures hydrate could be calculated by Eq. (7).

$$\eta_{\mathrm{system}} = \frac{W_{\mathrm{turbine}} - W_{\mathrm{pump}} + (\Delta H_{\mathrm{diss}} - W_{\mathrm{slurry\ pump}})}{Q_{\mathrm{evap}}} \qquad (7)$$

Where η_{system} is $W_{\mathrm{slurry\ pump}}$ is the power consumption of slurry pump in negative cycle subsystem, Q_{evap} is the heat absorption of evaporator in positive cycle subsystem.

Generally, the Coefficient of Performance (COP) of conventional compression refrigeration cycle ranges from 2.8-3.4. Set the COP value to 3.0, then divide ΔH_{diss} by 3.0 (the COP of conventional compression refrigerant cycle). In this way, ΔH_{diss} is converted into power consumption of pump. Zhang et al. [4] simulated the refrigeration cycle based on methyl fluoride and monofluoro cyclopentane hydrate. They investigated that the COP was 7.58-8.97, which is 2-4 times of that of conventional compression refrigeration cycle. Kim et al. [5] conducted the CO_2+THF hydrate refrigeration system, and they estimated the COP as 11.55. Therefore, $(\Delta H_{diss} - W_{slurry\ pump}) > 0$. Moreover, according to the component regulation of hydrate-based refrigeration subsystem, the power consumption of pump and turbine work of ORC subsystem are lower or higher than before respectively. Thus, Eq. (7) could be presented in Eq. (8).

$$\eta_{\mathrm{system}} = \frac{W_{\mathrm{turbine}} \uparrow - W_{\mathrm{pump}} \downarrow + \left(\Delta H_{\mathrm{diss}} - W_{\mathrm{slurry\ pump}}\right) > 0}{Q_{\mathrm{evap}}} \quad (8)$$

As we can see from Eq. (8), the efficiency of the power and refrigeration cogeneration system based on zeotropic mixtures hydrate has been improved significantly.

5. CONCLUSIONS

In order to use energy more effectively, we promote a novel power and refrigeration cogeneration system based on zeotropic mixtures hydrate.

(1) The construction method is from the perspective of component regulation and energy stepped utilization.

(2) The optimal scheme of four combinations is screened by three-dimensional construction analysis. And the optimal scheme is determined by selecting the match, which has the shortest path in three-dimensional T-s-θ diagram.

(3) The mass flow rates are calculated by energy conservation formula, and the cycle efficiency is also determined. The result shows that the cycle efficiency has been improved significantly.

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