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Analysis of zeotropic mixtures used in high-temperature Organic Rankine cycle

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ABSTRACT

The paper investigates the performance of high-temperature Organic Rankine cycle (ORC) with zeotropic mixtures as working fluid. A numerical model, which has been validated by comparing with the published data, is developed to predict the first law thermal efficiency of the cycle. The effects of mixture concentration, temperature gradient of the heat transfer fluid, pinch temperature difference, pressure ratio, and condensation pressure on the first law efficiency are presented firstly using a purposely designed program, and then the suitable conditions for the described ORC are suggested based on the results of the simulation. It is demonstrated that the use of zeotropic mixtures leads to an efficiency increase compared to pure fluids.

1. Introduction

The accelerated fossil fuel consumption poses a serious threat to energy safety and environment protection. Low grade heat from renewable thermal energy or waste heat is potential to meet the energy demand and alleviate environmental problem. As conventional steam cycle cannot efficiently recover these low grade heat sources [1], various thermodynamic power cycles for low grade heat source have been studied widely during these years. Organic Rankine cycle (ORC) is proposed as a promising cycle for the recovery of low temperature heat sources due to its high efficiency and reliability, small size, and low emission [2].

ORC is similar with the principle of the steam Rankine cycle while using organic substance as working fluid. The selection of a proper working fluid is vital for an ORC system. Many organic working fluids used in ORC have been studied, such as refrigerants R113 [2–5], R123 [2,6–9], R245fa [7,10–14], and R134a [7,11,14–18], hydrocarbons butane [11,19,20], pentane [7,11,21–23], and hexane [20,23], siloxanes hexamethyldisiloxane (MM) [20,24,25] and octamethyltrisiloxane (MDM) [20,25].

Previous research about working fluids of ORC mostly focused on the pure organic fluids. However, the limitation of a pure fluid used in ORC is due to the isothermal characteristics during the evaporation and condensation processes. The temperature profiles between heat transfer medium and working fluid cannot match mutually, causing a large entropy generation in the phase transition steps. This problem was partially solved by zeotropic mixture because that temperature of zeotropic mixtures is variable during the corresponding processes (hereinafter referred to as "temperature glide"). Only few authors have investigated using zeotropic mixtures as ORC working fluids. Venkatarathnam et al. [26] considered that there were certain limits for the temperature glide of the heat transfer fluid in the evaporator and condenser to avoid pinch point, which could be used to evaluate the suitability of zeotropic mixtures for glide matching. Angelino and Colonna di Paliano [27] and Wang and Zhao [28] respectively evaluated the merits of organic-fluid mixtures as working fluid for Rankine power cycles. However, no increase was found in the efficiencies of multi-component conversion cycles comparing to those obtained with pure fluids under their given conditions. Wang et al. [29] compared the performance of low temperature ORC using pure fluid (R245fa) and mixtures (R245fa/R152a) based on the experimental research. The result showed that the collector and thermal efficiency of zeotropic mixtures were comparatively higher than pure fluid. Chen et al. [30] proposed a supercritical Rankine cycle using zeotropic mixtures for the low grade heat. The result showed that thermal efficiencies of the cycles using mixtures (0.7R134a/0.3R32) were 10–30% higher than the cycle with pure R134a. Li et al. [31] analyzed the effects of recuperator on both pure fluid ORC and mixtures ORC. It was found that the increase in thermal and exergy efficiency by adding a recuperator were higher for the mixtures R141b/RC318 than for R141b. Chys et al. [32] considered several commonly used pure fluids as potential components of mixtures used in ORC. For heat sources at two different grades, a potential increase was about 6% and 16% in cycle efficiency. Heberle et al.

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[33] presented the simulations of the second law efficiency of the ORC with isobutene/isopentane and R227ea/R245fa as working fluids. For heat source temperatures below 120 °C, the raise of the efficiency was up to 15% over that of pure fluids.

Studies of ORC with zeotropic mixtures were usually conducted according to certain predefined conditions. The claims for best mixture composition with highest efficiencies are correct only for special conditions. Besides, some authors [10,25,34] propose that ORC is a good option when maximum temperature falling below 370 °C. However, there was no detailed research into the performance of mixtures in high-temperature (greater than 200 °C) ORC.

In this paper, zeotropic mixtures of siloxanes are investigated as working fluids for high-temperature ORC. The effects of mixture concentration, temperature gradient of the heat transfer fluid, pinch temperature difference, pressure ratio, and condensation pressure on the first law efficiency are presented using a purposely designed program. At last, the paper provides the proposal for the suitable operating conditions for the similar ORC.

2. System description

A schematic representation of ORC system considered in this paper is shown in Fig. 1. This figure shows five main components of the cycle: the pump, recuperator (internal heat exchanger), evaporator, expander, and condenser. The working fluid is pressured by the pump firstly, and then is heated in the recuperator and evaporator successively. The working fluid coming from the evaporator enters into the expander at the saturated vapor state. After an expansion process, the steam exhaust passes through the recuperator. Finally, the working fluid condenses against the heat sink fluid and re-enters into the pump. Here, the recuperator is a commonly used equipment to improve the performance of ORC [31].

Fig. 2 presents the corresponding temperature–entropy curve of the cycle using 0.4/0.6 MM/MDM as working fluid. As mentioned before, the advantage of using mixture in ORC is the non-isothermal behavior during the evaporation and condensation processes. It is apparent that the temperature during the corresponding processes (6′–1 and 3′–4) is variable.

Table 1 summarizes the initial conditions for the ORC system. Due to the high temperature heat source, Therminol 62 [35], a high temperature synthetic oil, is chosen as the heating fluid. Note that under the given conditions, the cycle may not work with highest efficiency. Later, several operating parameters will be justified to investigate the optimal operating conditions.

3. Working fluid selection

The selection criterion of pure fluids used in ORC is adopted to select the potential components, which has been extensively

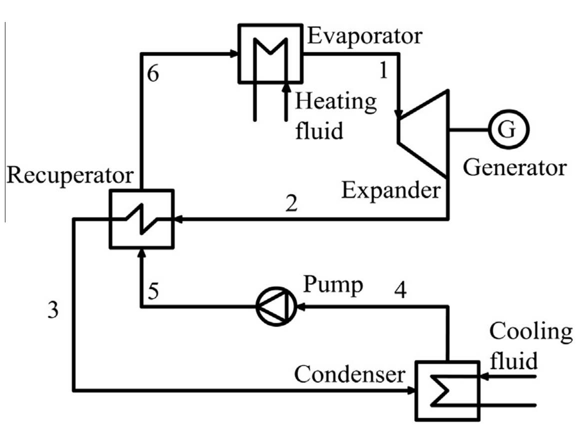

Fig. 1. Schematic of the ORC system.

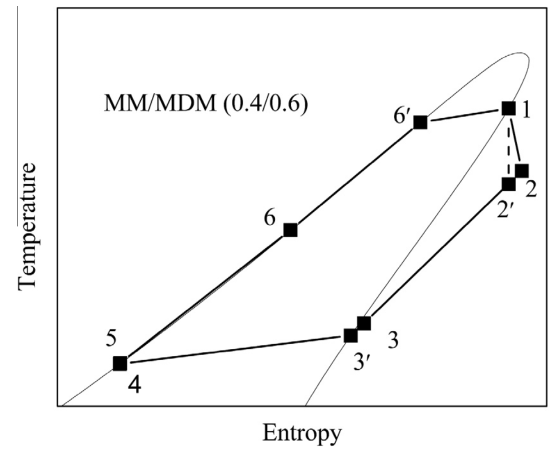

Fig. 2. Saturated *T*–*s* curve of the ORC.

Table 1
Conditions for the heat source, heat sink and ORC process parameters.

Heating fluid	Therminol 62
Inlet temperature of the heat source	280 °C
Outlet temperature of the heat source	240 °C
Heat release of the heat source	80 kW
Cooling fluid	Water
Inlet temperature of the heat sink	40 °C
Outlet temperature of the heat sink	60 °C
Pressure of the cooling fluid	5 bar
Pinch temperature difference in the evaporator	35 °C
Pinch temperature difference in the condenser	35 °C
Pinch temperature difference in the recuperator	25 °C
Isentropic efficiency of the pump	0.8
Isentropic efficiency of the expander	0.75

Pinch temperature difference is defined as the minimum temperature difference in the heat exchanger.

discussed in previous work [7,14,16,19,36,37]. A proper working fluid should meet the demand of suitable thermal property and chemically stability. For the heat source with high temperature, siloxanes present the desired technological characteristics as ORC working fluids: low toxicity and flammability, low foul formation over heat transfer surfaces, good material compatibility, and good thermal stability [25]. In order to avoid extremely low condensation pressure, MM and MDM with lower boiling temperature in the family of siloxanes are selected as components. The properties of fluid are given in Table 2 Fernández et al. [25] and Colonna et al. [38,39].

Fig. 3 shows the saturation curves for MM, MDM, and MM/MDM (0.4/0.6), represented in the *T*–*s* diagram. According to the positive slopes of the saturated vapor lines in the diagram, the proposed fluids should be classified into dry fluids [25]. Hence, superheating is not required to avoid the two-phase flow at the expander outlet, which can also avoid the decrease in efficiency [40].

4. Assumption and model equation

For the described cycle, the simulation is performed by an original program with MATLAB. It provides an interface to implement the fluid property database REFPROP Version 9.0 [41], which is developed by the National Institute of Standards and Technology.

Several assumptions are defined before modelling:

1. The components in the cycle operate at steady state.
2. The heat exchangers in the cycle are counter-flow.