Effects of physical and chemical properties of working fluids on thermodynamic performances of medium-low temperature organic Rankine cycles (ORCs)

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ABSTRACT

The diversity of organic fluids and performance criteria has posed a great challenge for engineers to select and evaluate working fluids for organic Rankine cycles (ORCs). To overcome this challenge, this paper reports on second-law-based analytical expressions for thermal efficiency and specific turbine volume (STV), which reveal key dimensionless parameters relating to operating temperatures and thermodynamic properties of organic fluids. A systematic screen was performed to examine more than 70 working fluids involving a wide range of physical and chemical properties. The working-fluid screen confirmed that STV generally increases with critical temperature, reduced ideal gas heat capacity, and the atom number of working fluids. Different-family fluids may lead to ten-fold relative differences in STV even though they have the same atom numbers (e.g., about $200\,m^3/MJ$ and $20\,m^3/MJ$ for benzenes and Alkanes, respectively). The thermal efficiency appears to be independent of critical temperature, or at most, a weak function of critical temperature for low boiling-point wet fluids and other halocarbons, partly due to Jacob number that is independent of or depends weakly on the critical temperature of organic fluids such as alkanes, alkenes, and benzenes.

1. Introduction

The urgent need to exploit low-grade heat sources has renewed a surge of interest in the thermodynamic analysis of organic Rankine cycles (ORCs) [1,2]. Low-grade heat sources, e.g., waste heat, solar and geothermal energy, differ from conventional heat sources in energy density and temperature levels, a difference that makes steam unsuitable for the conversion of low-grade thermal energy [3–5]. While organic working fluids make the Rankine cycles efficient at converting medium-low temperature heat into power, the selection and evaluation of working fluids for Rankine Cycles is still a great challenge because of the diversity of organic fluids and thermodynamic criteria [6–8].

There is a large and growing body of literature investigating the effects of working fluids on the performance of ORCs, including net power output [9,10], thermal efficiency [11–13], exergetic efficiency [14–16], minimum superheat degree [17–19], turbine expansion ratio [20,21], and component sizes [22,23]. Among these criteria, thermal efficiency has been the center of attention, and relationships between thermal efficiency and critical temperature [24,25], normal boiling point [26,27], molecular complexity [22,28–30], Jacob number [12,26,31], figure of merit [26], molar mass [32,33], acentric factor

[34], and reduced ideal gas heat capacity [35] have been examined. Most researchers agree that fluids of high molecular complexity are preferable [29], especially in regenerative cycles [30]. It is also commonly accepted that thermal efficiency of ORCs decreases with Jacob number [12,31], figure of merit [26], and acentric factor [33], but increases with molecular mass [32,33].

The most significant discussion in the ORC filed is how the critical temperature influence the thermal efficiency of ORCs. Some researchers have argued that thermal efficiency generally increases with the critical temperature of the used fluid [36–38]. On the other hand, several lines of evidence appear to suggest that thermal efficiency may be independent of critical temperature. For example, Liu et al. illustrated that thermal efficiency is a weak function of critical temperature [24]. Based on the second law of thermodynamics, Li and Zhao developed theoretical expressions for thermal efficiency, which are entirely independent of critical temperature [39]. Thus, it remains a subject of debate as to the effect of critical temperature on the thermal efficiency, and further investigations are needed.

Furthermore, there are two more limitations in the existing studies. First, the number of studies that discussed performance indexes relating to the turbine size [30,40,41] is small, pointing to the need for further

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investigation into the impact of working-fluid features on the design of turbine. Second, considerable research has devoted to explaining the effects of working-fluids only from the viewpoint of thermodynamics [12–14,16], rather less attention has been paid to exploring potential associations between performance indexes and chemical features of organic working fluids.

The primary aim of this paper is to fill the knowledge gaps identified above. For this purpose, this paper firstly develops a theoretical model for determining thermal efficiency of ORCs, an analytical expression that includes only the evaporating and the condensing temperatures, as well as several key working-fluid properties. To the best of our knowledge, the analytical expression is the first explicit formula for calculating thermal efficiency of ORCs without recourse to equations of state. Secondly, seventy-four fluids were screened to critically analyze the influences of thermodynamic and chemical characteristics on the thermodynamic performance of ORCs, including thermal efficiency, minimum superheat (MS), and turbine volume per unit work (i.e, specific turbine volume, STV). Great attention has been directed towards the understanding of impacts of critical temperature on STV and thermal efficiency, as well as relations between STV and chemical features of fluids. The findings of this study can provide new insight into these relationships and may be a new contributing step towards the synthesis of new organic fluids for medium-low temperature ORCs.

2. Theoretical analysis

2.1. Analytical equation for thermal efficiency

As illustrated in Fig. 1, Rankine cycles consists of the following four processes: isentropic compression in a pump (1–2), constant pressure heat addition in an evaporator (2–5), isentropic expansion in a turbine (5–6s), and constant pressure heat rejection in a condenser (6s–1). The irreversibilities in actual pumps and turbines can be characterized by isentropic efficiencies. Conventionally, the thermal efficiency of an ORC is calculated by

$$\eta = \eta_t \frac{h_5 - h_{6s}}{h_5 - h_1} \tag{1}$$

where h_i denotes the enthalpy of the ith state point, and η_t is the isentropic efficiency of the turbine:

$$\eta_t = \frac{h_5 - h_6}{h_5 - h_{6s}} \tag{2}$$

The determination of the enthalpies in Eq. (1) needs high-accuracy equations of state or property diagrams. To overcome this problem, Li and Zhao developed a set of theoretical expressions for the thermal efficiency of medium-low temperature ORCs [39]:

$$\eta = \eta_t \eta_C \left[1 - \frac{1 - \eta_C}{2} \frac{\frac{cT_3}{r} + \frac{c_{p,1}T_1}{r}\left(\frac{T_{6s} - T_1}{T_3 - T_1}\right)^2 \left(\frac{T_3}{T_1}\right)^3 - \frac{c_p T_3}{r}\left(\frac{T_5 - T_3}{T_3 - T_1}\right)^2}{\frac{1}{\eta_C} + \frac{cT_3}{r} + \frac{c_p T_3}{r}\frac{T_5 - T_3}{T_3 - T_1}} \right] \tag{3}$$

where r is the heat of evaporation of the working fluid at the evaporating temperature T_3, c denotes the average heat capacity of the saturated liquid during the preheating process 2–3, c_p is the average heat capacity of the vapor during the superheating process 4–5, $c_{p,1}$ is the average specific heat of the vapor during the desuperheating process 6–7, and η_C denotes the Carnot efficiency, $\eta_C = (T_3 - T_1)/T_3$.

Eq. (3) is applicable to ORCs including superheating and desuperheating processes. For dry fluids, superheating 4–5 may be unnecessary or insignificant [18,19]. In this case, Eq. (3) reduces to

$$\eta \approx \eta_t \eta_C \left[1 - \frac{1 - \eta_C}{2} \frac{\frac{cT_3}{r} + \frac{c_{p,1}T_1}{r}\left(\frac{T_{6s} - T_1}{T_3 - T_1}\right)^2 \left(\frac{T_3}{T_1}\right)^3}{\frac{1}{\eta_C} + \frac{cT_3}{r}} \right] \tag{4}$$
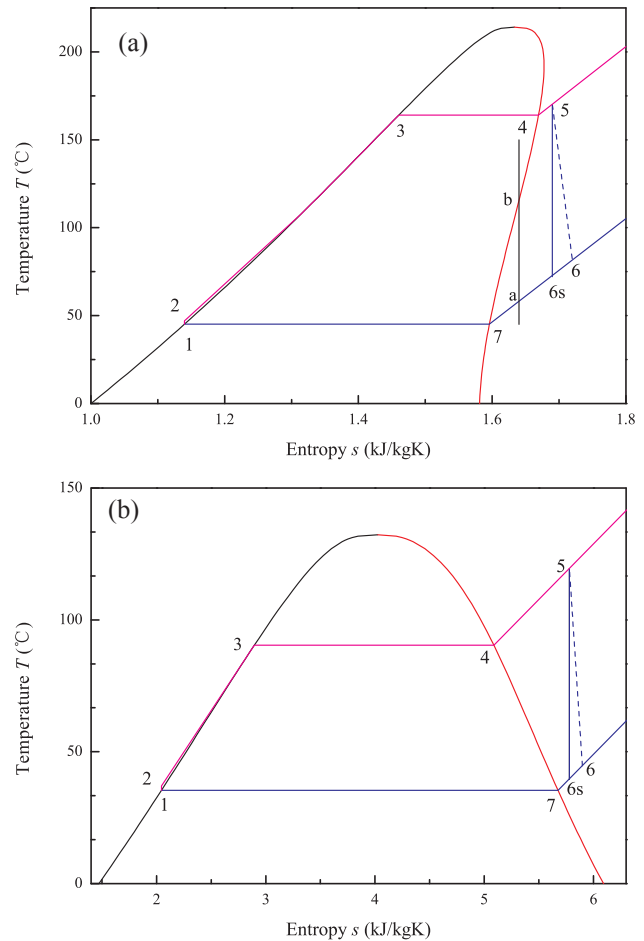

Fig. 1. Rankine cycles represented in temperature-entropy (*T–s*) diagrams. (a) A Rankine cycle using a dry fluid ($ds/dT > 0$). (b) A Rankine cycle using a wet fluid ($ds/dT < 0$).

For wet fluids, superheat 4–5 is necessary to avoid vapor condensation in the turbine, but desuperheating 6s–7 is generally insignificant; Eq. (3) can be simplified as

$$\eta \approx \eta_t \eta_C \left[1 - \frac{1 - \eta_C}{2} \frac{\frac{cT_3}{r} - \frac{c_p T_3}{r}\left(\frac{T_5 - T_3}{T_3 - T_1}\right)^2}{\frac{1}{\eta_C} + \frac{cT_3}{r} + \frac{c_p T_3}{r}\frac{T_5 - T_3}{T_3 - T_1}} \right] \tag{5}$$

For isentropic fluids, the entropy generation of desuperheating 6s–7 is generally offset by that of process 4–5 [39]; Eq. (3) reduces to the following extremely simple form:

$$\eta \approx \eta_t \eta_C \left[1 - \frac{1 - \eta_C}{2} \frac{cT_3}{r}\left(\frac{1}{\eta_C} + \frac{cT_3}{r}\right)^{-1} \right] \tag{6}$$

There is a problem with Eqs. (3) and (4), i.e., the determination of T_{6s} still depends on equations of state. It is desirable to develop an analytical equation for η that is only a function of the evaporating and condensing temperatures, as well as several key thermal properties. To eliminate T_{6s}, we need to calculate the temperature difference between T_{6s} and T_7:

$$T_{6s} - T_7 = \int_7^{6s} dT_a \tag{7}$$

where subscript a denotes a state between states 6s and 7 (Fig. 1a); since at constant pressure $Tds = c_p dT$, Eq. (7) becomes