ANALYSIS OF PURE FLUID AND ZEOTROPIC MIXTURES USED IN LOW-TEMPERATURE REHEATING ORGANIC RANKINE CYCLES FOR POWER GENERATION
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ABSTRACT
The shortage of fossil energy sources boosts the development and utilization of renewable energy. Among various novel techniques, recovering energy from low-grade heat sources including industrial waste heat, geothermal energy and solar energy through power generation via organic Rankine cycle (ORC) has been one of the focuses. ORC is one of the effective methods to recover low-grade heat, which makes use of environment-friendly organics as working fluids, and low temperature thermal energy as the driving energy. Investigations have indicated that reheating ORC can improve the thermal performance of the system. In this paper, the cycle performance is measured by the system net power output. By using pure fluid R245fa, R123 and zeotropic mixtures R245fa/R21, R123/R21, R245fa/R123 as the cycle working fluids, the influences of working fluid, mixtures component ratio and reheat pressure ratio on low-temperature reheating ORC system are investigated. The optimal reheat pressure ratios of reheating ORC system using different working fluids are obtained. In addition, zeotropic mixtures R245fa/R21(0.65/0.35) is superior in the improvement of the system net power output. In practical application, the optimal reheat pressure ratio and component ratio should be determined based on the mixture and evaporation temperature to ensure the net power output of reheating ORC system maximum.

1. INTRODUCTION
As the world's energy situation becomes aggravate, the recovery of low-temperature heat sources has become one of the research focuses. Due to the fact that conventional steam Rankine cycle does not allow efficient energy conversion at low temperatures, organic Rankine cycle (ORC) has been extensively studied for the conversion of low-grade heat into power for its simplicity and relatively high efficiency (Chen et al., 2011).
Recently, some researchers have studied the reheating ORC system. Li et al. (2012) investigated the net power output and thermal efficiency of pure R245fa in reheating ORC system aiming at low-temperature heat source below 120°C. Xu et al. (2009) proposed a determination method for optimal reheating pressure of ORC system using R123 as working fluid, which could ensure a highest system efficiency. Li et al. (2013) studied the low-temperature heat source utilization of reheating ORC systems using different working fluids, then gained the variation regularity of the net power output and thermal efficiency with evaporation temperature and reheate pressure ratio. Wang et al. (2013) chose R601 and R245ca as the working fluids and investigated the influence of the reheat pressure ratio on the net power output, thermal efficiency and exergy efficiency of the system, then obtained the optimal reheat pressure ratios.

In order to improve the efficiency of ORC system, using mixtures has become an important method (Zheng et al., 2008). The temperature glide of zeotropic mixture in phase transformation zone can provide a good temperature matching of cold and heat fluids for heat-exchanges, which could reduce the irreversible entropy production caused by the heat transfer temperature difference (Maiazza et al., 2001). Wang et al. (2010) compared low-temperature solar ORC systems using pure fluid and zeotropic mixture as the working fluid by experiments, and the results showed that using zeotropic mixture as working fluid could improve both output work and exergy efficiency of the system. Angelino et al. (1998) calculated performance of waste heat recovery ORC system and geothermal power generation ORC system using mixtures as working fluids which were composed of silicone oil and different hydrocarbon by the PRSV state equation and WS mixing rule. The results indicated that cycle performance was closely related to the component ratio of mixtures, so the component ratio must be optimized when mixture was used.

Above studies indicate that reheating process and zeotropic mixtures can both effectively improve the thermodynamic performance of ORC system. At present, very few studies on low temperature reheating ORC system for power generation using zeotropic mixtures are reported, and the optimal component ratio of zeotropic mixtures has not been fully studied. In this paper, influences of zeotropic mixtures' kind and component ratio, as well as the reheating pressure ratio on the net power output of reheating ORC system are investigated. The results show that zeotropic mixtures can effectively improve the net power output of reheating ORC system when the mixture's kind and component ratio are suitable.

2. ANALYSIS OF REHEATING ORC SYSTEM AND SELECTION OF WORKING FLUIDS

2.1 Reheating ORC System

Compared with the simple ORC system, Reheating ORC system includes a high pressure expander and a low pressure expander instead of a single expander. A reheating ORC system includes evaporator, high pressure turbine 1, reheater, low pressure turbine 2, condenser and pump, as shown in Figure 1. The circulation specifically include the following processes:

5-6: Adiabatic compression process. The saturated liquid working fluid is compressed adiabatically into high pressure unsaturated liquid in pump, then enters evaporator.

6-1: Isobaric heating process. High pressure unsaturated liquid is heated into high temperature and high pressure saturated vapor by absorbing heat of the low-temperature heat source in evaporator, then enters high pressure turbine 1.

1-2: Adiabatic expansion process. Saturated vapor expands in high pressure turbine 1 to do work and generate electricity, and the pressure and temperature of working fluid drop, then enters the reheate.

2-3: Isobaric heating process. Vapor is heated in reheater, and its temperature increases to the same value of that of state 1, then enters low pressure turbine 2.

3-4: Adiabatic expansion process. Vapor expands in low pressure turbine 2 to do work, then becomes low temperature and low pressure superheated vapor.

4-1: Isobaric condensation process. Vapor is condensed into saturated liquid by heat exchange with cooling water in condenser.
In this paper the system is in a stable flow state, and no heat exchange occurs between each thermal device and the environment. The pressure losses of evaporator, reheater, condenser and the connecting pipes are negligible. The working fluid at outlet of the condenser is saturated liquid while the working fluid at outlet of the evaporator is saturated vapor. The tephigram of reheating ORC system is shown in Figure 2.

2.2 The Choice of Working Fluids

Studies of simple ORC system show that choice of the working fluid has an important influence on the system thermal performance (Ni et al., 2013). The working fluid should have superior stability, good environmental protection and excellent thermal physical properties which match well with heat source (Maizza et al., 1996). Drying and wetting of working fluid is an important feature in low grade heat source ORC system, which is determined by the slope of saturated vapor line in the tephigram. The slope of dry working fluid is greater than zero while the slope of wet working fluid is lower than zero, and the slope of isentropic fluid is close to zero. High temperature and high pressure vapor of dry working fluid and isentropic working fluid becomes superheated vapor after expanding in turbine, thus there is no droplet appearing in the process (Gu et al., 2008).

Table 1: Thermophysics property parameters of working fluids.

<table>
<thead>
<tr>
<th>Working Fluid</th>
<th>Molecular Weight /kg mol⁻¹</th>
<th>Standard Boiling Point /K</th>
<th>Critical Temperature /K</th>
<th>Critical Pressure /Mpa</th>
<th>ODP</th>
<th>GWP (100 Years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R21</td>
<td>102.92</td>
<td>282.01</td>
<td>451.48</td>
<td>5.1812</td>
<td>0.04</td>
<td>151</td>
</tr>
<tr>
<td>R245fa</td>
<td>134.05</td>
<td>288.29</td>
<td>427.16</td>
<td>3.6510</td>
<td>0</td>
<td>1050</td>
</tr>
<tr>
<td>R123</td>
<td>152.93</td>
<td>300.97</td>
<td>550.0</td>
<td>3.6618</td>
<td>0.01</td>
<td>77</td>
</tr>
</tbody>
</table>

R21, R123 and R245fa are common working fluids used in ORC system, and the values of ODP (Ozone Depression Potential) and GWP (Global Warming Potential) of the three fluids are relatively small, which means they are eco-friendly (Gu et al., 2007). Thermophysics property parameters of three pure working fluids are shown in Table 1 (Calm et al., 2011). Using R245fa/R21 as working fluid could effectively improve the net power output of the ORC system (Li et al., 2012). Therefore, we select R21, R123, R245fa as pure fluids and R245fa/R21, R123/R21, R245fa/R123 as zeotropic mixtures in this paper. In this study, the working fluid is set as saturated vapor at the outlet of the evaporator, and dry working fluid or isentropic working fluid should be used to avoid the water hammer at the tail of turbine (Xu et al., 2011). R21 is a typical wet working fluid while R245fa and...
R123 are dry working fluids. To guarantee the zeotropic mixtures are dry working fluids or isentropic working fluids, the mass fraction of R21 must be no more than 0.35 in mixture R245fa/R21 and no more than 0.2 in mixture R123/R21 from REFPROP's calculations. Figure 3 is the tephigram of saturated R245fa/R21 (0.65/0.35), and Figure 4 is the tephigram of saturated R123/R21 (0.8/0.2). As shown in two figures, these two mixtures are isentropic working fluids under the corresponding proportion.

![Figure 3](image1.png)

**Figure 3:** Tephigram of saturated R245fa/R21 (0.65/0.35)

![Figure 4](image2.png)

**Figure 4:** Tephigram of saturated R123/R21 (0.8/0.2)

### 3. THE PERFORMANCE ANALYSIS OF REHEATING ORC SYSTEM

#### 3.1 System Parameters Setting and The Research Method

In this research, the condensing temperature is 300K which is constrained by environmental temperature. In the case of zeotropic mixtures, the temperature of working fluid at outlet of the condenser is regarded as the condensing temperature. The heat source temperature is 400K, and the maximal evaporation temperature is 380K which is constrained by heat source temperature. In the
case of zeotropic mixtures, the temperature of working fluid at outlet of the evaporator is regarded as the evaporation temperature. The adiabatic efficiency of the turbines is 85%, and the mechanical efficiency is 90%. The adiabatic efficiency of the pump is 80%, and the mass flow of working fluid is 1 kg·s⁻¹. In addition, the working fluid is set as saturated liquid at the outlet of the condenser and saturated vapor at the outlet of the evaporator. The Reheat pressure ratio is defined as the ratio of inlet pressure of Turbine 2 and that of Turbine 1. To ensure the inlet pressure of Turbine 2 is greater than its outlet pressure, which is condensation pressure, we set the minimal reheat pressure ratio as 0.3. The parameter values of each state point are calculated by REFPROP.

For low-temperature heat energy generating system, the important thing is to improve the total output work, not the thermal efficiency. Therefore the system performance is evaluated by net power output of the reheating ORC system in this article. Fundamental equations are as follows:

**Work of high pressure turbine 1:**

\[ W_1 = \dot{m}(h_1 - h_2) \eta_m \]  

(1)

**Work of low pressure turbine 2:**

\[ W_2 = \dot{m}(h_3 - h_4) \eta_m \]  

(2)

**Consumed work of pump:**

\[ W_p = \dot{m}(h_6 - h_5) \]  

(3)

**Net power output of the system:**

\[ W = W_1 + W_2 - W_p \]  

(4)

Where: \( \dot{m} \) is mass flow of the working fluid, which is 1 kg·s⁻¹ in this research; \( h_1 \) is specific enthalpy of the working fluid at inlet of high pressure turbine 1, kJ·kg⁻¹; \( h_2 \) is specific enthalpy of the working fluid at outlet of high pressure turbine 1, kJ·kg⁻¹; \( h_3 \) is specific enthalpy of the working fluid at inlet of low pressure turbine 2, kJ·kg⁻¹; \( h_4 \) is specific enthalpy of the working fluid at outlet of low pressure turbine 2, kJ·kg⁻¹; \( \eta_m \) is the mechanical efficiency of the turbines, which is 90% in this research; \( h_5 \) is specific enthalpy of the working fluid at inlet of pump, kJ·kg⁻¹; \( h_6 \) is specific enthalpy of the working fluid at outlet of pump, kJ·kg⁻¹.

### 3.2 The Performance Analysis of Reheating ORC System Using Pure Working Fluid

![Figure 5: The influences of reheat pressure ratio and evaporator temperature on net power output (working fluid is R245fa)](image-url)
Figure 6: The influences of reheat pressure ratio and evaporator temperature on net power output (working fluid is R123)

Net power outputs of the reheating ORC system using R245fa and R123 as working fluids are calculated at different temperatures (340K-380K) and different reheat pressure ratios (0.3-0.9), and the results are shown in Figure 5 and Figure 6. $T_1$ denotes evaporation temperature in the figures.

As shown in the two figures, the net power output increases gradually with the increasing evaporating temperature. net power output of the reheating ORC system using R245fa as working fluid is about 9% greater than that of the reheating ORC system using R123 at the same evaporating temperature and reheat pressure ratio, indicating that the performance of R245fa is better than that of R123.

Table 2: The optimal reheat pressure ratios

<table>
<thead>
<tr>
<th>Evaporating Temperature/K</th>
<th>Working Fluid</th>
<th>Optimal Reheat Pressure Ratios</th>
<th>Maximum Net Power Output /kJ·s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>R245fa</td>
<td>0.56</td>
<td>17.743</td>
</tr>
<tr>
<td></td>
<td>R123</td>
<td>0.55</td>
<td>16.141</td>
</tr>
<tr>
<td>350</td>
<td>R245fa</td>
<td>0.50</td>
<td>21.741</td>
</tr>
<tr>
<td></td>
<td>R123</td>
<td>0.49</td>
<td>19.829</td>
</tr>
<tr>
<td>360</td>
<td>R245fa</td>
<td>0.46</td>
<td>25.566</td>
</tr>
<tr>
<td></td>
<td>R123</td>
<td>0.44</td>
<td>23.387</td>
</tr>
<tr>
<td>370</td>
<td>R245fa</td>
<td>0.43</td>
<td>29.211</td>
</tr>
<tr>
<td></td>
<td>R123</td>
<td>0.40</td>
<td>26.895</td>
</tr>
<tr>
<td>380</td>
<td>R245fa</td>
<td>0.40</td>
<td>32.665</td>
</tr>
<tr>
<td></td>
<td>R123</td>
<td>0.37</td>
<td>30.112</td>
</tr>
</tbody>
</table>

In addition, with reheat pressure ratio increases, net power outputs of reheating ORC system using different working fluids all first increase then decrease. The reheat pressure ratio which makes the net power output maximum is regarded as the optimal one and the optimal reheat pressure ratio is related to working fluid type and evaporating temperature. The optimal reheat pressure ratios under different evaporating temperatures are gained through further calculations, and the results are shown in Table 2. From Table 2 we can see that, the optimum reheat pressure ratios of reheating ORC systems using this two kinds of working fluids gradually reduce with the evaporating temperature increasing; and the optimum reheat pressure ratio is smaller when R245fa is used as working fluid at the same evaporating temperature.
3.3 The Performance Analysis of Reheating ORC System Using Zeotropic Mixtures

We select 360K as characteristic evaporation temperature and respectively calculate the net power outputs of ORC system using R245fa/R21, R123/R21 and R245fa/R123 as working fluids under different reheating pressure ratios and component ratios. The results are shown in Figure 7-9.

**Figure 7:** The influences of reheating pressure ratio and component ratio on the net power output (working fluid is R245fa/R21)

**Figure 8:** The influences of reheating pressure ratio and component ratio on the net power output (working fluid is R123/R21)
Figure 9: The influences of reheat pressure ratio and component ratio on net power output
(working fluid is R245fa/R123)

Figure 7 shows that with an increase in the component ratio of R245fa, the net power output of reheating ORC system gradually decreases. As we can see from Figure 7, net power output of the reheating ORC system using R245fa/R21 as working fluid is greater than that of the reheating ORC system using pure R245fa when the component ratio of R245fa is less than 0.9. This is because that zeotropic mixtures present variable temperature profile during the phase change process, which could considerably reduce the mismatch between heating or cooling sources and the evaporating or condensing working fluid mixtures respectively, so the system irreversibilities could be minimized. Consequently, an appropriate choice of zeotropic mixtures could improve the enthalpy drop between the turbine import and export, thus raising the net power output of ORC system. Net power output of the reheating ORC system using R245fa/R21 (0.65/0.35) as working fluid is about 4% greater than that of the reheating ORC system using pure R245fa at the same reheat pressure ratio. With a further calculation, we acquire that when the evaporation temperature is 360K, the optimal reheat pressure ratio of the reheating ORC system using R245fa/R21 (0.65/0.35) as working fluid is 0.47, and the maximum net power output is 26.622kJ·s⁻¹, which is 4.13% greater than that of the reheating ORC system using pure R245fa.

Figure 8 shows that the net power output of reheating ORC system using R123/R21 (0.8/0.2) or pure R123 as working fluid is relatively large while the net power output of reheating ORC system using R123/R21 (0.9/0.1) is smallest. With a further calculation, we acquire that when the evaporation temperature is 360K, the optimal reheat pressure ratio of the reheating ORC system using R123/R21 (0.8/0.2) as working fluid is 0.47, and the maximum net power output is 23.399kJ·s⁻¹, which is 0.05% greater than that of the reheating ORC system using pure R123. We could obtain that using mixtures R123/R21 as working fluid could hardly improve the net power output of reheating ORC system.

Figure 9 shows that net power output of the reheating ORC system using R245fa/R123 as working fluid is smaller than that of the reheating ORC system using pure R245fa. It is interesting to find that when the component ratio of R123 is larger than 0.5, net power output of the reheating ORC system using R245fa/R123 as working fluid is even smaller than that of the reheating ORC system using pure R123. We could obtain that using mixtures R123/R21 as working fluid could not improve the net power output of reheating ORC system.
4. CONCLUSIONS

In this paper, the research object is reheating ORC system utilizing low temperature waste heat, and the evaluation standard is net power output of the ORC system. The reheating ORC systems using R245fa,R123, R245fa/R21,R123/R21 and R245fa/R123 as working fluids were investigated. The main conclusions can be extracted as follow:

- For reheating ORC systems using pure R245fa and R123 as working fluids, with an increase in evaporation temperature, the net power output gradually increases. Net power output of the reheating ORC system using pure R245fa as working fluid is about 9% greater than that of the reheating ORC system using pure R123 at the same temperature and reheat pressure ratio. There is an optimal reheat pressure ratio making the net power output of ORC system maximum. The optimal reheat pressure ratios of reheating ORC systems using pure R245fa and R123 as working fluids decrease with the evaporation temperature increasing. The optimal reheat pressure ratio of reheating ORC system using pure R245fa as working fluid is slightly smaller than that of reheating ORC system using pure R123 at the same evaporation temperature.

- When the evaporation temperature is 360K, the maximum net power output of reheating ORC system using mixtures R245fa/R21 as working fluid is 4.13% greater than that of reheating ORC system using pure R245fa while the maximum net power output of reheating ORC system using mixtures R123/R21 as working fluid is only 0.05% greater than that of reheating ORC system using pure R123. The optimal mixtures component ratios are R245fa/R21 (0.65/0.35) and R123/R21 (0.8/0.2). Using mixture R245fa/R123 as working fluid cannot increase the net power output of reheating ORC system.

- Zeotropic mixture can effectively improve the net power output of reheating ORC system when the mixture's category and component ratio are suitable. In practical application, the optimal reheat pressure ratio and component ratio should be determined based on the mixture and evaporation temperature to ensure the net power output of reheating ORC system maximum.

REFERENCES


