Characteristics of Organic Rankine Cycles with Zeotropic Mixture for Heat Recovery of Exhaust Gas of Boiler

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Abstract

In order to overcome the shortage of pure fluid with constant phase change temperature, zeotropic mixtures were employed to construct the organic Rankine cycle (ORC) system for waste heat recovery of exhaust gas of boiler in coal-fired power plant. The temperature glide of zeotropic mixture can reduce the mismatch of temperature in order to make it approach ideal Lorenz cycle. Different types of hydrocarbons (HCs) were selected as basic fluid according to their physical properties, which were of high energy efficiency, low cost and environmental friendliness for organic Rankine cycle. To promote the security level, high-effective fire retardants R1311/R245fa were added to form binary zeotropic mixtures. Thermodynamic models of ORC with and without internal heat exchanger (IHX) using zeotropic mixture as working fluid were established, by which the power generating capability per unit heat transfer area, exergy efficiency and net power output as functions of proportion of pure fluids were obtained to access the performance of ORC in recovering the waste heat of exhaust gas of boiler. In addition, the factors affecting performance of ORC, including volume flow rate, expansion ratio, and the presence of IHX in system, were investigated to optimize the system design.

Keywords: organic Rankine cycle; zeotropic mixtures; exhaust gas of boiler; waste heat recovery

1. Introduction

Boiler is one of the most important equipments in coal-fired power plant, of which the heat loss of flue gas accounts for about 4%-8% of overall thermal energy. Organic Rankine cycle (ORC) is a promising technology for medium or low grade heat recovery for its simple configuration, strong practicability and miniaturization. Typical heat source of ORC applications includes geothermal energy [1], solar energy [2], bioenergy [3] and ocean thermal energy [4-5] etc.. The potential application of ORC in recovering
exhaust heat of boiler in power plant may improve energy utilization efficiency and reduce environmental pollution. The properties of ORC working medium are the dominant factor influencing system performance. Numerous studies have been carried on selecting a working fluid matching well with heat source, which is one of the most important steps in building organic Rankine cycle [6-8]. Most researches concentrate in single component and few concerns binary or ternary. However, no single pure fluid has been identified as optimal working medium for ORC, which is mainly due to the strong interdependence among optimal working fluid, working conditions and cycle architectures [9-10]. Another important limitation of pure fluids is the constant evaporating temperature which is not suitable for the variable-temperature heat source. Recently, three kinds of pure fluid and one mixture R141b/RC318 were selected as working fluids and their parametric changes were calculated by Li et al. [11] without considering the relationship between heat source and working fluids in evaporator. The results showed that ORC with mixture working fluid has lower system efficiency than that with pure, nevertheless it can extend the selection of working fluids. Wang and Zhao made a theoretical analysis of zeotropic mixtures R245fa/R152a used in low-temperature solar Rankine cycles. The thermal efficiencies with internal heat exchanger were also discussed [12]. In further, they validated the superiority of R245fa/R152a by experimental method [13]. The simulation of ChemCAD [14] and Cycle Tempo [15] also display that zeotropic mixtures can achieve higher thermal efficiencies than pure. Kai et al. [16] investigated the cycle performance based on experimental results aiming at recovering exhaust energy for a diesel engine. Chys et al. [17] studied the effect of using mixtures as working fluids in ORC and found a potential increase of 16% and 6% in cycle increase for heat source temperature at 150°C and 250°C.

In the present study, novel HCs/fire-suppressants mixtures are investigated as working fluids for heat recovery from exhaust gas of boiler in coal-fired power plant. As a function of proportion of pure fluids, the power generating capability per unit heat transfer area, exergy efficiency and work output are obtained, which is beneficial for selecting optimal working fluid of ORC system. Different from traditional Rankine cycle, turbine outlet temperature of ORC is higher than inlet temperature of evaporator, thus internal heat exchanger (IHX) is considered in system, and its performance is investigated.

2. Thermodynamic model of ORC with zeotropic mixture

Considering the previous experimental data and environmental factors, Hydrocarbons (HCs) are the best choice as working fluid of organic Rankine cycle, with high energy efficiency, low cost and high environmental friendliness. The property of high molecular weight alkanes are always stable, hence R600, R600a, R601, R601a, benzene and cyclohexane can be selected as the basic components. Due to the flammable and explosive characteristics of HCs, fire retardant is added for obtaining a more environmental friendly and safety substitute. In this paper, R245fa and R1311 were used as suppressants. R1311 has been found to be non-ozone depleting, miscible with mineral oil and compatible with refrigeration system materials. It also has an extremely low GWP value and acute toxicity. Therefore, it is considered as a promising alternative, especially as a component in mixtures, for HFCs/HCFCs.

The properties of zeotropic mixtures largely depend on their composition and concentration. Lower exergy loss can be obtained when the working fluid temperature profile matches well with that of heat source. Therefore, saturated vapor pressure of two basic fluids should be bigger to get a more significant temperature glide. After primary screening, four mixtures, R245fa+R601a, R245fa+R601, R1311+R601a and R1311+R601, were selected for the subsequent analysis. Garg et al. [18] has put forward a method analyzing the flammability limit based on Zabetakis’ work [19]. According to their analysis, flammability
of R601a/R601 could be suppressed by a mole fraction of 0.18 of R245fa, or 0.1 of R1311. In this paper, a more extensive fraction range has been considered for overall analysis.

Physical model of ORC was established for waste heat recovery of exhaust gas of coal-fired boiler in power plant. Two types of cycle configurations are considered with the only difference in presence of internal heat exchanger (IHX). And two typical thermodynamic cycles with working fluids of R245fa and R1311+R601(0.9+0.1) and with the state points, respectively, were shown in Fig. 1.

Referring to the traditional refrigerating system, the cycle highest temperature of the zeotropic mixtures is set to be 403.15K with 10K pinch temperature for evaporator. 5K or no superheat is used for different working fluids, in order to avoid entering into two-phase region at the outlet of expander and leading to steam hydraulic hammer hazard. Then the temperature profile in evaporator can be obtained by the local thermal equilibrium between exhaust gas and working fluid under the given mass flow rates. In this study, the design heat sink temperature is assumed to be 293.15K on the basis of the environmental conditions and the local annual average temperature of power plants in north China. The pinch temperature in condenser is set to be 5K. For the major purpose of the present study is discussing the performance of different mixtures on ORC using recycled heat from exhaust gas. Thus it mainly focused on heat source side.

Assuming that the isentropic efficiency of turbine and pump is set to be 0.8, respectively, working fluid mass flow driven by exhaust gas can be acquired by,

\[ m_{\text{gas}}(h_{07}-h_{08})=m_{\text{fluid}}(h_{04}-h_{03}) \]  

\[ m_{\text{fluid}} = \frac{m_{\text{gas}} (h_{07} - h_{08})}{h_{04} - h_{03}} \]  

The power generating capability of exhaust gas, \( W_{\text{gas}} \),

\[ W_{\text{gas}} = w_{\text{net}} \times m_{\text{fluid}} \]
The exergy efficiency from gas to organic working fluid, $\eta_{g,f}$, can be then obtained by,

$$\eta_{g,f} = \frac{m_{\text{fluid}}[(h_{04} - h_{02}) - T_0(s_{04} - s_{02})]}{m_{\text{gas}}[(h_{07} - h_{09}) - T_0(s_{07} - s_{09})]} \quad (4)$$

The overall exergy efficiency, $\eta_{II}$, is,

$$\eta_{II} = \frac{W_{\text{gas}}}{m_{\text{gas}}[(h_{07} - h_{09}) - T_0(s_{07} - s_{09})]} \quad (5)$$

where the subscript 0 represents the environmental condition, i.e., 293.15K and 0.1013MPa for the present study.

An ORC system should not only consider cycle efficiency but also economy investment. According to Cayer's study [20], the overall heat transfer coefficient, $U$, of heat transfer equipment such as preheater, evaporator, and condenser multiplied heat transfer area, $A$, as a normal system economic indicator. The values of $UA$ can be calculated from the following model with assumed heat exchanger of counter-flow configuration.

Evaporation pressure, $p_{\text{fluid}}$, and saturation temperature, $T_{\text{fluid,04}}$, of working fluid are assumed. The change of temperature of working fluid in evaporator is obtained as,

$$T_{\text{fluid}} = f(UA) \quad (6)$$

The inlet temperature of heat source, $T_{s,05}$, is known. Giving the outlet temperature, $T_{s,06}$, the temperature of heat source in evaporator with $UA$ can be expressed as,

$$T_{s,UA} = T_{s,06} + \int_0^{Q_{ua}} \frac{dQ}{c_{p,s}m_s} = T_{s,06} + \int_0^{T_{\text{fluid}}_{s,UA}} \frac{c_{p,\text{fluid}}m_{\text{fluid}}dT_{\text{fluid}}}{c_{p,s}m_s} \quad (7)$$

of which, $T_{\text{fluid}}_{s,UA}$ is the temperature of working fluid with $UA$ in evaporator. When the calculated temperature, $T_{s,UA}$, equals to $T_{s,05}$, the integrating process come to the end, under which condition, the $UA$ of the evaporator can be acquired by,

$$UA = \int_0^{Q_{ua}} \frac{dQ}{t_s - T_{\text{fluid}}} \quad (8)$$

The ratio of net power output to the product of overall heat transfer coefficient by the area is expressed by $\mu$,

$$\mu = \frac{W_{\text{gas}}}{UA} \quad (9)$$
Thermodynamic model was built and solved by MATLAB 2010a and REFPROP Version 8.0, with which, physical properties of working fluids could be acquired. Mass flow rate of exhaust gas, \( m_{\text{gas}} \), is assumed 1 kg. The REFPROP data base used for the properties of the present fluids come from the empirical equations of state for mixtures based on experimental data. These data are used to determine the structures, coefficients, and parameters of the correlation equations and to evaluate the behavior of the equation of state in different fluid regions. The Kunz et al. [21] and Lemmon and Jacobsen [22] models are used for calculating the thermodynamic data in REFPROP.

The simulating results in the present study are compared to the calculations of Wang et al. [12] for thermal efficiency and work output. The accuracy ranges between 0.21% and 0.54% for thermal efficiency, and between 0.73% and 1.19% for work output, which is acceptable for the calculation in this paper.

3. Results with discussions

3.1. Power output of ORC without IHX

![Fig. 2. Net work output per unit working fluid mass of ORC without IHX](image1)

![Fig. 3. T-S diagram of R245fa+R601a cycle with different mass fractions](image2)

Fig. 2 shows the variation of work output with different concentration of zeotropic mixtures. It is obvious that HCs get a higher \( w_{\text{net}} \) than that of other fluids under the same mass fraction. It can be found that the work output almost increases linearly with HCs mass fraction. On the aspect of \( w_{\text{net}} \), zeotropic mixtures are superior to R245fa and R1311, while no advantage over hydrocarbons.

As shown in Fig. 3, from the ORC curve in T-S diagram, taking R245fa+R601a as example, it can be found that when the fraction of R601a increases, the saturated liquid line and saturated vapor line move left, and the saturated liquid line moves larger. At the same time, the evaporating temperature of mixture increases. All these lead to a larger area enclosed in T-S diagram and more work output, as showed in Fig. 2 and Fig. 3.

3.2. Economic analysis of ORC without IHX

Using zeotropic mixtures as working fluid can significantly improve the work output of ORC, nevertheless the total \( UA \) of evaporator, condenser and regenerator increases significantly. Fig. 4 shows
the total $UA$ of evaporator under different HCs mass fractions. The $UA$ values are affected by exhaust temperature and temperature difference between heat source and working fluid. As a result, curves have a maximum, which shows that $UA$ value rises with HCs mass fraction at the beginning and then decreases.

Achieving maximum benefit from the power output and system investment is critical to organic Rankine cycle system. The optimization of the system can be done by maximizing the composite economic performance index, $\mu$, which is summarized in Fig. 5. The results show that, in most cases, zeotropic mixtures prevail over the HCs. HCs have the properties of flammable and explosive and it's dangerous to be used solely. Fire-suppressants material can significantly increase the system security level with an increase of $\mu$ value at the same time. Based on comprehensive consideration of energy, economy, environmental kindness and safety, zeotropic mixtures are deemed to possess a broad application prospect.

3.3. The factors affecting the performance of ORC

Fig. 6 shows the specific volume value $V_4$ at the turbine inlet. It can be found that the curve has a maximum with the HCs mass fraction. For some mixtures, the value of $V_4$ is higher than that of pure fluid. On the other hand, another factor, volume ratio, $\epsilon$, has a minimum as given in Fig. 7. The using of mixtures is favorable because of the low values of $\epsilon$ for a majority of HCs/fire-suppressants mixtures compared with pure fluids.

Fig. 8 illustrates that the evaporating and condensing pressure decrease with increasing of HCs concentration. Zeotropic mixture can reduce the material requirements and overall equipment investment. What's more, the condensing pressure of high HCs concentration for mixtures with R1311 and mixtures with R245fa are near atmospheric pressure. The cooling water operates in the condenser at the atmospheric pressure. For the reason that a smaller pressure difference for two sides in condenser could reduce its cost, atmospheric pressure at the working fluid side can increase the performance of the condenser.

In order to take full advantage of waste heat, reduce heat exchange area in condenser, the internal heat exchanger (IHX) is usually added to the system. Taking HCs/fire-suppressants mixtures R1311+R601a as
example, working fluid at turbine outlet point 05t is cooled to dew point 05a (P_{5a}=P_{5t} and T_{5a}=T_{5t}), as shown in Fig. 1(b). Similarly, 02-02a is the preheat process before evaporator.

Fig. 6. Variation of specific volume at the inlet of turbine with HCs mass fraction.  

Fig. 7. Variation of outlet/inlet volume flow ratio with HCs mass fraction.

Fig. 8. Variations of evaporating and condensing pressure with HCs mass fraction.  

Fig. 9. System efficiencies of ORC with and without IHX.

Fig. 10. Exhaust gas temperature with and without IHX.

The use of IHX makes no difference to \( W_{gas} \). However, the available energy from heat source is reduced. This phenomenon results in an exergy efficiency increasing, shown in Fig. 9. IHX cycle also has
the benefit of increasing exhaust gas temperature for waste heat recovery system, which is illustrated in Fig. 10. As is known, low exhaust gas temperature will cause acid corrosion to the boiler. By adding IHX, some working fluids with high performance, while unfortunately with low exhaust temperature, can be used in engineering application, which greatly extends the selection of working fluid for ORC.

4. Conclusions

Zeotropic mixtures have the character of temperature glide during phase change, which can match the heat source well and reduce the overall system exergy loss. An investigation on ORC with and without IHX has been performed based on novel HCs/fire-suppressants mixtures with different proportions. The following conclusions could be made.

1. Using zeotropic mixtures as working fluid can significantly increase work output, \( W_{\text{gas}} \), but the total \( UA \) and system equipment investment also improve.

2. Different mixtures with fraction of pure fluids lead to different cycle performances, which can extend the range of selection according to requirements.

3. The variation trends of mixtures with R601 or R601a are approximately the same. While the performance parameters, \( \mu \), \( V_4 \), \( \iota \) and condensing pressure of mixtures with R601a are better than that of R601.

4. By adding IHX in the ORC system, the \( UA \) increases and the outlet temperature of heat source rises, which can avoid acid corrosion of exhaust gas to the boiler.

5. The work output per unit \( UA \) of zeotropic mixtures with low HCs mass fraction are higher than those of pure hydrocarbon fluids. And fire-suppressants material can significantly increased the security level of the entire system. The proportion of R245fa in mixture has a relatively smaller impact than that of R1311 on cycle performance.

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