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Carbon footprint analysis of organic Rankine cycle system using zeotropic mixtures considering leak of fluid

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Abstract

The energy demand and severe environmental pollution problems have drawn global attentions. Organic Rankine cycle (ORC) as a waste heat power generation technology has broad application prospects. Emissions of carbon dioxide equivalent ($CO_{2,eq}$) for measuring global warming potential and the emission reductions during life-time can directly reflect the environmental impact of ORC. A carbon footprint evaluation method for ORC using zeotropic mixture is developed in life cycle perspective. The security, thermodynamic and environmental criteria of binary mixture in ORC are also incorporated to evaluate the system environmental influence. Zeotropic mixtures, including R134a/R290, R134a/R600, R134a/R600a, R245fa/R600a, R245fa/R290, R227ea/R600a and R227ea/R290, are selected as the working fluids. Results showed that ORC with R245fa/R600a operated under environmental criterion produced the minimum $CO_{2,eq}$ emission of 26.30 g $CO_{2,eq}$/kWh and the system with R227ea/R600a operated under thermodynamic criterion possessed the highest emission reduction of 5595.76 tons $CO_{2,eq}$. Compared with the cases operated under security and environmental criteria, ORC operated under thermodynamic criterion generated a higher net power output at the expense of larger emissions. The primary source of $CO_{2,eq}$ emission from equipment is the heat exchangers while the counterpart from working fluid is during leak process. Meanwhile, the implementation of environmental criterion reduces the $CO_{2,eq}$ emissions of working fluid in ORC significantly, compared with cases under security and thermodynamic criteria. In consideration of the maximum emission reductions of $CO_{2,eq}$, the compositions of the mixtures, i.e. R245fa/R600a and R245fa/R290, are mainly determined according to the environmental criterion. In addition, it is found the emission reductions decrease linearly with the leak rates of working fluids in ORCs in this work.

Keywords: Waste heat recovery; Organic Rankine cycle; Carbon footprint; Emission reductions; Zeotropic mixture.

1. Introduction

The ever-increasing energy demand and severe environmental pollution have caused many social problems. In order to address these issues, harnessing renewable energies and enhancing energy efficiency have been recognized as potential solutions (Rahbar et al., 2017). Some significant efforts have been made to recover the low-grade waste heat for reducing the fuel consumption and thereby promoting the energy conversion efficiencies. Among the available technologies, i.e. osmotic heat engine (OHE), Trilateral Flash cycle, Kalina cycle, Goswami cycle and organic Rankin cycle (ORC), the ORC with easy maintenance and simple structure has been recognized as a more reliable technology. While most of the ORC studies focused on the investigation of the following aspects, the working fluid selection (Miao et al., 2019), parameters optimization (Yi et al., 2017), economic analysis (Heberle and Brüggemann, 2015), and the environmental evaluation (Liu et al., 2013), and they lack enough studies focusing on the carbon dioxide equivalent ($CO_{2,eq}$) emissions and emission reductions of ORC systems.

Since ORC system performance majorly depends on the thermo-physical properties of working fluid, the fluid selection has become fundamentally important. According to the 'Mobile air conditioning (MAC) Directive' and 'F-gases Regulation' adopted from European Union (Le et al., 2014), the zero ozone depletion potential (ODP) and low global warming potential (GWP) are required to meet by the organic fluids. Therefore, hydrofluoroolefins (HFOs) (Huo et al., 2017) and hydrocarbons (HCs) are gradually treated as the alternatives to hydrochlorofluorocarbons (HCFCs), chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs). Nowadays, the fluid selection depends on the several aspects, including economic, thermodynamic and sustainable criteria. Yang and Yeh, (2015) carried out thermo-economic optimization of ORC system with four different working fluids using the exhaust gas from large marine diesel engine. They concluded that the system using working fluid R245fa possessed the best economic performance followed by the system using R600 and R600a. Ashouri et al., (2015) developed a thermodynamic and economic evaluation of ORC and carried out a comparison of six working fluids. Results showed that the working fluid benzene possessed the best thermodynamic performance and the highest total cost. Zhu et al., (2018) conducted a thermos-economic analysis of ORC system for marine diesel engine waste heat recovery. Seven organic fluids were chosen as potential working fluids including R245fa, R123 and R600a. It is found that the system with R141b produced the maximum net power output under multi-objective evaluations, followed by R113 and cyclohexane. Wang et al., (2013) conducted a theoretical model based on an ideal ORC to analyze the thermal efficiency and power output of system and carried out a comparison of 25 pure organic fluids including dry, isentropic and wet fluids. The optimal fluid selection principle corresponding to the heat source temperature level was determined. For example of R600a and R600, the optimal heat source temperature ranges are from 420 to 445K and 445 to 465K, respectively. Moreover, Long et al., (2014) proposed an exergy analysis of ORC system containing fluid selection. The system with R600a exhibited the highest overall exergy efficiency while the system using R141b demonstrated the lowest. Abam et al., (2018) evaluated the performance of different system configurations, including ORC-basic, ORC-internal heat exchanger, ORC-turbine bleeding and so on, using thermo-sustainability indicators with three working fluids. The system using R245fa performed the maximum exergetic sustainability index of 1.5 while the environmental effect factor was 1.58 at the same evaporator pressure range.

On the other hand, the binary mixtures with excellent thermodynamic properties have also drawn widespread attentions. For instance, Tian et al., (2017) established the thermo-economic model of ORC system using siloxanes mixtures for engine waste heat recovery. Results revealed that the dual-loop ORC system using D4/R123 (0.3/0.7) had the best thermodynamic performance while the system using MD2M/R123 (0.35/0.65) could achieve the best economic benefit. Xi et al., (2017) conducted the thermo-economic model of ORC with zeotropic mixture using R245fa as flame retardant. They found that ORC with zeotropic mixture produced better economic benefits than the systems using pure fluids of R601, R600 and R601a. Furthermore, Heberle and Brüggemann, (2015) also conducted the thermo-economic evaluation of ORC with mixtures for geothermal power generation and found that the using of zeotropic mixtures could improve the economics of geothermal ORC systems. Collings et al., (2016) proposed the dynamic model of ORC system. The zeotropic mixtures were chosen as working fluids. Results revealed that dynamic system was suitable for low temperature heat source and significantly improved the efficiency of the plant. Except for the influence of zeotropic mixtures on system performance, the flammable limits directly reflect the security of zeotropic mixtures. The flame-inhibiting of some zeotropic mixtures comprising of flame-retarding fluid and environmental fluid has been discussed extensively. Yang et al., (2013) conducted theoretical and experimental investigations on flame-retarding of R245fa and the results showed that the flame-retarding performance of R245fa is worse than that of R134a and R227ea. In addition, experimental studies were also carried out to investigate the inert effect of R134a, R227ea and R125 on the explosion limits of flammable refrigerants, such as R1234yf, R32, HCs and HFCs. Thus, in this study the security criterion of zeotropic mixtures is taken into consideration based on the above references, and the mass fractions of binary mixtures are all obtained from the available experimental data.

The environmental impact assessment of ORC plays an important role in system design. Life cycle assessment (LCA) and carbon footprint assessment (CFA) are the two most commonly used methods, and they are also widely used for environmental pollution assessment of ORC systems. Liu et al., (2013) evaluated the environmental impact of ORC through LCA, and results found construction phase of system during life-cycle time contributed the most to GWP and eutrophication potential (EP). Hickenbottom et al., (2018) also established the LCA model of ORC and conducted the comparison with a novel OHE system. They found that environmental impacts of OHE during both construction and operation stage were higher than that of ORC. Moreover, the $CO_{2,eq}$ emissions had been selected as a crucial indicator on environmental criterion for multi-objective optimization. Aminyavari et al., (2014) established the exergetic, economic and environmental analysis for a refrigeration system and calculated the CO_2 emissions during its life-time. Zhang et al., (2019) built up the energetic, exergetic, economic and environmental analysis (4E) model to evaluate the trans-critical ORC. The CO_2 emissions during life-time were contained in the environmental model. Results found that trans-critical ORC with R290 produced the maximum emission reduction of 8019 tons $CO_{2,eq}$.

In addition, it could be faster and more convenient to obtain ORC working conditions by employing optimization algorithm. The frequently-used optimization algorithms include genetic algorithm (GA), differential evolution algorithm, particle swarm optimization (PSO), and ant colony optimization, etc. Among them, the PSO, which is inspired by the bird flocking's social behavior, as originally described by Eberhart and Kennedy, (1995) has been widely used. The advantages of PSO are simple structure of program, less adjustment parameters and suitable for the solve of complex constrains. Clarke and McLeskey Jr, (2015) evaluated the thermodynamic performance of binary geothermal power plants using the multi-objective PSO method, and the PSO algorithm performed better than GA for the constrained, simulation-based, non-linear optimization. Furthermore, Garg and Orosz, (2018) also conducted the economic optimization of ORC with mixtures and pure fluids through PSO method.

As reviewed, it can be concluded that the environmental impacts of ORC system, for both emissions of $CO_{2,eq}$ and emission reductions of $CO_{2,eq}$ have attracted more and more attentions. However, ORCs adopting different working fluids usually bring variable emission reductions. The previous works (Aminyavari et al., 2014; Zhang et al., 2019) focused on the environmental impact analysis of ORCs, including sub-critical and trans-critical ORCs, using pure organic fluid as working fluid and there is no thermodynamic variation when considering leak phenomenon in ORC. However, for zeotropic mixtures, working fluid leakage would alert the mass fraction of zeotropic mixture and further affect the thermodynamic performance of ORC (Wang et al., 2018). The environmental evaluation of ORC system using mixtures is more complex. Until now, there is no study focusing on the evaluation of $CO_{2,eq}$ emissions and the emission reductions of ORC system using zeotropic mixtures considering the leak of working fluid.

This work presented the CFA on ORC system using zeotropic mixture as working fluid. Meanwhile, the security, the thermodynamic and the environmental criteria of binary mixtures by altering mass fractions of fluids are also discussed. Firstly, the working conditions of ORC based on different criteria are calculated by employing PSO algorithm. Then, the net power output (W_{net}), the mass of each component and the $CO_{2,eq}$ emissions for each phase are analyzed and compared. Finally, the $CO_{2,eq}$ emissions and the emission reductions of ORC with different zeotropic mixtures are calculated, and the correlations between the $CO_{2,eq}$ emission reductions and the leak rates are also obtained.

2. System modeling and calculation conditions

2.1. System description

The ORC system consists of two basic parts, the organic fluid and the equipment. The equipment contains at least five components, such as an evaporator, an expander coupling with electric generator, a condenser, a liquid receiver and a pump. The working flow process of zeotropic mixture in ORC can be illustrated as follow: the saturated fluid is pressured into the evaporator by the pump (process 3-4). The pressured organic fluid absorbs energy from the waste flue gas (process 4-1). Generated high pressure saturated or superheated vapor expands in the expander to drive the generator generating electricity (process 1-2). Then the expanded fluid is cooled by cooling source to convert saturated liquid (process 2-4) and flows back to the liquid receiver. The schematic diagram and the *T*-*s* chart of ORC system are shown in Fig. 1a and 1b, respectively.

In the system modeling, the initial parameters of ORC system are given in Table 1. The discharged temperature constraint of flue gas is set as 355.15 K to prevent the corrosion caused by the low-temperature flue gas (Wang et al., 2019). Additionally, the introduced assumptions regarding the ORC operation are: (1) ORC system operates in steady state; (2) No pressure drops in pipes and heat exchangers; (3) The heat losses in system are neglected; (4) The organic fluid at outlet of the condenser is saturated liquid; (5) The leaking of working fluid in ORC is an isothermal process and only vapor phase leak during the leak process; and (6) The liquid receiver is at the vapor-liquid equilibrium state.

2.2. Selection of working fluid

The selection of organic fluids used in ORC system is crucial because the difference in boiling points will affect the matching relations with heat source. Among these organic fluids, zeotropic mixtures are more attractive because of its non-isothermal phase change, which possesses less irreversibility and better matching performance between exothermic process of heat sources and the endothermic process of working fluids. However, in order to control the emissions of F-gases and HFCs, selecting environmental friendly organic fluids is of great significance, especially for fluids with zero ODP. For zeotropic mixtures, flame retardants are used to suppress of the flammability for another fluid by blending them together, meanwhile, the mixed organic fluids could decrease the GWP relatively to the flame retardants. In this study, HCs, including R600, R600a and R290, with GWP being lower than 150, and R134a, R245fa and R227ea with higher GWP are chosen as environmental-friendly fluids and inert fluids, respectively. The thermal properties of pure organic fluids are listed in Table 2.

2.3. Thermodynamic model

The equations of energy analysis for ORC system are presented as follows:

The heat transferred to organic fluid in evaporator can be calculated by Eq. 1.

$$Q_{evap} = m_{hs} \times (h_{hs,in} - h_{hs,out}) = m_{wf} \times (h_1 - h_5) \quad (1)$$

where Q_{evap} is the heat absorption rate of organic fluid in the evaporator, m_{hs} is the mass flow rate of flue gas, m_{wf} is the mass flow rate of organic fluid, and h_i is the specific enthalpy of fluid at state point *i* (as shown in Fig. 1b).

The power produced by the expander can be determined by Eq. 2.

$$W_{exp} = m_{wf} \times (h_1 - h_2) = m_{wf} \times (h_1 - h_{2s}) \times \eta_{exp} \quad (2)$$

where W_{exp} is the power output by expander, η_{exp} is the isentropic efficiency of expander and subscript 2s is the ideal case of 2.

The heat transfer in the condenser can be expressed as:

$$Q_{cond} = m_{cs} \times (h_{cs,out} - h_{cs,in}) = m_{wf} \times (h_2 - h_4) \quad (3)$$

where Q_{cond} is the heat released from organic fluid in condenser and m_{cs} is the mass flow rate of cooling air.

The power consumed in the pump can be determined by Eq. 4.

$$W_p = m_{wf} \times (h_5 - h_4) = m_{wf} \times (h_{5s} - h_4) / \eta_p \quad (4)$$

where W_p is the power of pump, and η_p is the isentropic efficiency of pump.

The electricity produced by ORC system can be calculated by Eq. 5.

$$W_{elec} = W_{exp} \times \eta_{elec} \quad (5)$$

where W_{elec} is the power output of generator and η_{elec} is the generator efficiency.

The net power output can then be determined by Eq. 6.

$$W_{net} = W_{elec} - W_p \quad (6)$$

where W_{net} is the net power output of ORC system without leak.

2.4. Heat exchangers area calculation

The heat exchanger area calculation is crucial for estimating the mass of heat exchangers. To determine the areas of evaporator and condenser, the heat transfer coefficient should be determined first. The types of heat and cooling sources are waste flue gas and air, respectively. The convective heat transfer coefficient of organic fluid side is more than 2000 W/($m^2 \cdot K$) which is much bigger than that of flue gas side (Xi et al., 2017). Thus, the overall heat transfer coefficient in the heat exchanger mainly depends on the flue gas side. Thus, the Kern formula (Kern, 1950) is employed to determine the total heat transfer coefficient in evaporator and condenser:

$$k_{sp} = k_{tp} = 0.36 \times (\lambda / d_e) \times Re_g^{0.55} \times Pr^{1/3} \times (\mu / \mu_{wall})^{0.14} \tag{7}$$

where k_{sp} and k_{tp} are the heat transfer coefficients during the single-phase flow and two-phase flow, respectively. d_e is the equivalent diameter of tube. *Re* and *Pr* are the Reynolds number and Prandtl number. μ and λ are the dynamic viscosity of air and heat conductivity coefficient, respectively.

In the heat exchanger model, the logarithmic mean temperature difference (LMTD) method is selected during the design and calculation processes. The fouling heat resistance is ignored in heat transfer process. During the calculation process of evaporator, the model can be divided into three regions including preheating, evaporation and superheating regions, while the model of condenser is divided into two regions, and they are cooling and condensing regions. For each region, the process is then divided into 30 finite small elements so that constant properties are able to be assumed in each element (Zhang et al., 2017).

2.5. Leak model of ORC system

The leak of working fluid is a possible phenomenon in ORC system. The influence of leak in liquid receiver of ORC on mass fraction of zeotropic mixture and system thermodynamic performance has been evaluated by Wang et al., (2018). It is found that the vapor leak would influence the mass fraction of zeotropic mixture and then further change the net power output of ORC. Meanwhile, the calculation of leak is a continuous iterative process. Thus, the equation for mole fraction calculation of working fluid after the leak process is presented in Eq. 8.

$$z_i' = [x_i \times n_l + y_i \times (n_v - \Delta n_v)] / (n - \Delta n) \tag{8}$$

where z, x and y are the total mole fraction, liquid and vapor mole fraction, respectively. n represents the moles in liquid receiver. The subscripts l and v represent liquid and vapor, respectively, and i represents the i-th component.

The leak in the liquid receiver is an isothermal and slow process, and the unit step of leak rate is 0.001 (MinSooKim and Didion, 1995). The total leak rate and operation time of ORC during life-time can be discretized into each small step based on the unit of leak rate, which can be defined as:

$$(1 - \varepsilon_{step})^j = (1 - \varepsilon) \tag{9}$$

where ε is the annual leak rate of organic fluid, ε_{step} is the unit step of leak rate, which is 0.001 and j is the steps of operation time.

Thus, the operation time can be divided into j-th small sections:

$$t_{op,step} = t_{op} / j \tag{10}$$

where t_{op} is the annual operation time of ORC, and $t_{op,step}$ is the operation time for each small region of leak process.

Similarly, the power of pump and generator can be calculated based on the thermodynamic model under different mass fraction of zeotropic mixture and the value of power during each j-th time can be assumed as the same. The total electricity generated by ORC system can be represented as follow:

$$TEG = LT \times \sum_j [(W_{elec,j} - W_{pump,j}) \times t_{op,step}] \tag{11}$$

where *TEG* is total electricity generated by ORC system during life-time considering the leak phenomenon (kWh), LT is the life cycle time of ORC system, $W_{elec,j}$ is the power output of generator after j-th leak process (kW) and $W_{pump,j}$ is the power of pump after j-th leak process (kW).

3. Life cycle and carbon footprint analysis of ORC

3.1. Life cycle boundary of ORC system

The life cycle boundary of ORC system is shown in Fig. 2. The whole life-cycle is made up of three phases, the construction phase, the operation phase and the decommissioning phase. In the construction phase, the main considerations are the raw material processing and transportation. The consumption of major devices was converted into the steel consumption (Liu et al., 2013). In addition, the usage of different kinds of pipes and valves are all classified into the materials consumption, which are steel, aluminum, plastic and copper consumptions based on the estimated percentage of 46%, 12%, 23% and 19%, respectively (ILW, 2015). The road transportation distances for materials and equipment are taken from the statistics mean in China, which is 187 km (China Statistics Press, 2013). During the operation phase, the ORC system driven by waste flue gas generates electricity. There are no any other materials consumed but the leak of organic fluid should also be considered. In the decommissioning phase, the disposal and recycling of equipment and working fluid, and transportation for the waste are considered.

3.2. Carbon footprint model

$CO_{2,eq}$ emissions calculation is applied to determine the total greenhouse-gas emission of ORC system across its life-time. The calculation model is comprised of direct emissions and indirect emissions. The direct emissions mainly consist of annual leak of fluids under operation phase and the loss at the end of life emissions, and it can be determined by Eq. 12.

$$CF_{\mathrm{direct}} = M_{\mathrm{fluid}} \times (\varepsilon \times LT + \varphi) \times GWP \tag{12}$$

where CF is carbon footprint, M_{fluid} is the mass of organic fluid in ORC system (kg), φ is the end of life refrigerant leakage, which is 15% based on the reference (ILW, 2015), GWP is the global warming potential of working fluid (kg $CO_{2,eq}$/kg).

The indirect emissions are all the emissions from transportation, manufacture and disposal of working fluids and materials. The indirect emissions can be determined by Eq. 13.

$$CF_{\mathrm{indirect}} = M_{\mathrm{tot}} \times S_{\mathrm{trans}} / e_{\mathrm{CO_{2,trans}}} + M_{\mathrm{equip,v}} \times e_{\mathrm{mv,p}} + M_{\mathrm{equip,m}} \times e_{\mathrm{mm,p}} + M_{\mathrm{equip}} \times e_{\mathrm{m,r}} + M_{\mathrm{fluid}} \times (1 + LT \times \varepsilon) \times e_{\mathrm{f,p}} + M_{\mathrm{fluid}} \times (1 - \varphi) \times e_{\mathrm{f,d}} \tag{13}$$

where M_{tot} is the total mass of ORC system, including organic fluid and equipment (kg), S_{trans} is the transport distances by truck, $e_{\mathrm{CO2,trans}}$ is the emission of $CO_{2,eq}$ for 1 kg·km transportation discharge by truck, which is 2.377×10^{-2} kg $CO_{2,eq}$ (Wang et al., 2015), $M_{\mathrm{equip,v}}$ is the virgin material mass of equipment in ORC system (kg), $e_{\mathrm{mv,p}}$ is the $CO_{2,eq}$ produced unit virgin material mass (kg $CO_{2,eq}$/kg), $M_{\mathrm{equip,m}}$ is the mass of mixed material (kg), $e_{\mathrm{mm,p}}$ is the $CO_{2,eq}$ produced unit mixed material mass (kg $CO_{2,eq}$/kg), M_{equip} is the total material mass of equipment in ORC system (kg), $e_{\mathrm{m,r}}$ is the $CO_{2,eq}$ produced by unit material recycling (kg $CO_{2,eq}$/kg), $e_{\mathrm{f,p}}$ is the $CO_{2,eq}$ produced by manufacturing of organic fluid (kg $CO_{2,eq}$/kg), $e_{\mathrm{f,d}}$ is the $CO_{2,eq}$ produced by fluid disposal (kg $CO_{2,eq}$/kg).

The total $CO_{2,eq}$ emissions (CF_{tot}) of ORC system during the life cycle time can be determined by Eq. 14.

$$CF_{\mathrm{tot}} = CF_{\mathrm{direct}} + CF_{\mathrm{indirect}} \tag{14}$$

The $CO_{2,eq}$ emissions for per electricity production (CF_{pep}) of ORC system can be determined by Eq. 15.

$$CF_{pep} = CF_{tot} / TEG \quad (15)$$

In addition, the $CO_{2,eq}$ emission reductions (*ER*) of ORC during life-time can be determined by Eq. 16.

$$ER = TEG \times e_{elec} - CF_{tot} \quad (16)$$

where e_{elec} is the $CO_{2,e}$ produced for 1 kWh electricity production by coal-fired power plant, which is 0.968 kg $CO_{2,eq}$/kWh (Aminyavari et al., 2014).

3.3. Data sources

The charging mass of organic fluid is 5.57 kg/kW based on the power output generated by generator, and the mass of steel required by expander is 31.22 kg/kW based on the power production while the mass of pump is 14 kg/kW depending on the power consumption (Wang et al., 2019). Nowadays, the raw materials are made with the mixture of recycled materials and virgin materials. The emissions for material manufacturing and recycling are listed in Table 3. Similarly, the emissions of organic fluid are also divided into two parts, i.e. manufacturing and disposal processes. The emissions of fluid during disposal process are calculated from the combustion equation which is assumed to be fully burned (Weckert, 2008). The detailed data is listed in Table 4.

With respect to different zeotropic mixtures consisting of inert organic fluids and flammable organic fluids, the mass fractions of fluids are different based on security, thermodynamic and environmental criteria. As presented in Eq. (17), the mass fraction of binary mixture under the security criterion is determined by its explosion limit, which majorly concerns the flammable limits of leaked zeotropic mixtures mixed with air. The mass fractions of mixtures considering explosion limit are obtained from the work of Yang et al., (2012), Yang et al., (2013) and Zhao et al., (2004). The environmental criterion is based on 'MAC Directive' and the mass fractions of mixtures are calculated on the critical GWP of 150 as presented in Eq. (18). The mass fractions of zeotropic mixtures under thermodynamic criterion are selected by its calculation conditions corresponding to the optimal W_{net}, as presented in Eq. 19.

$$M_{wf,SC} = M_{explosionlimit} \quad (17)$$

where $M_{wf,SC}$ is the mass fraction of zeotropic mixture based on the security criterion and $M_{explosionlimit}$ is explosion-limited mass fraction of zeotropic mixture obtained from the experiment data.

$$M_{wf,EC} = M_{GWP_{wf1}+GWP_{wf2}=150} \quad (18)$$

where $M_{wf,EC}$ is the mass fraction of zeotropic mixture based on the environmental criterion and $M_{GWPwf1+GWPWF2=150}$ is the mass fraction of zeotropic mixture with the 150 GWP.

$$M_{wf,TC} = M_{Wnet,max} \quad (19)$$

where $M_{wf,TC}$ is the mass fraction of zeotropic mixture based on the thermodynamic criterion and $M_{Wnet,max}$ is the mass fraction of zeotropic mixture with the maximum net power output.

3.4. Calculation process

The thermal physics properties of working fluids can be obtained from REFPROP 9.1 software (Lemmon et al., 2013). In the model, the optimization algorithm is carried out by using

PSO. Evaporating pressure, pinch-point temperature differences in evaporator and condenser, outlet temperature of flue gas, mass flow rates of working fluid and cooling source can be obtained according to the corresponding maximum *ER*. The calculation flow chart is shown in Fig. 3. The orange section represents the calculation process of the leak model while the PSO process is shown in the red section. The blue section represents three criteria of zeotropic mixtures, including environmental criterion, security criterion and thermodynamic criterion. In addition, the main calculating process of carbon footprint is shown in black.

4. Results and discussion

4.1. Model validation

In order to verify the proposed model of ORC using zeotropic mixtures, the data reported in literatures is used. Since there is no report on the carbon footprint calculation of ORC using mixtures, this work validates three models, including the thermodynamic model of ORC using zeotropic mixtures, leak model of ORC with mixtures, and the carbon footprint calculation model of ORC. Table 5 compares the obtained results from present model and those reported by Wu et al., (2016) for the ORC using zeotropic mixtures. Table 6 shows the results of comparison with leak phenomenon in ORC with zeotropic mixtures reported by Wang et al., (2018). In addition, Table 7 gives the comparison between present model and those from Zhang et al., (2019). Referring to Tables 5-7, there presents good agreements between the obtained results in proposed model and those reported in the literatures.

4.2. Optimization results of thermodynamic calculation

The mass fractions of working fluids and optimized working conditions are listed in Table 8. The optimal pinch point temperatures in the evaporator and condenser are 5 K and 8 K, respectively. The mass fractions of zeotropic mixtures based on different criteria are completely different. When considering the security criterion, the composition of inert organic fluid is the largest. For example, the mass ratio of R134a/R600a is 0.8785/0.1215 with the fraction of inert fluid R134a being 87.85%, and the fraction of inert fluid in this mixture is the lowest among all the compositions of mixtures investigated under security criterion. But the fraction 87.85% of this inert fluid is quitely higher than the other mixtures under the other two criteria. When considering the environmental criterion, the component of flammable organic fluids would be the majority, because the GWPs of inert organic fluids are much higher than flammable fluids. When the thermodynamic criterion is taken into consideration, the mass fraction of inert fluid is bigger than the one under environmental criterion and smaller than another operated under security criterion. These proposed mixtures under the same mass fractions can't satisfied both security and environmental-friendly requirement, and it means that the searching and development on safe and environmental refrigeration fluids are still important for researchers. Based on security criterion, the highest evaporating pressure is about 4.00×10^6 Pa for ORC using R134a/R290 as working fluids. For other systems, the ranges of evaporating pressure are from 0.98×10^6 Pa to 3.70×10^6 Pa, and system using R245fa/R600a exhibits the lowest evaporating pressure of 0.98×10^6 Pa. Under the thermodynamic criterion, the highest evaporating pressure is about 4.10×10^6 Pa for ORC using R245fa/R290 while the lowest pressure of ORC using R245fa/R600a is about 1.37×10^6 Pa. The evaporating pressures of other systems are between the ranges of 2.89×10^6 – 3.90×10^6 Pa. In addition, the highest evaporating pressure is about 4.05×10^6 Pa for ORC with R134a/R290 under environmental criterion but the ORC using R134a/R600 operates at the lowest evaporating pressure of 1.24×10^6 Pa under giving conditions.

Under different criteria, the relations between the W_{net} and the evaporating pressure are shown in Fig. 4. It should be noted that, for systems using certain mixtures, the W_{net} monotonously increases with the increase of evaporating pressure under giving mass fractions, such as R227ea/R600a, R227ea/R290 and R134a/R290 under security and thermodynamic criteria. But it shows the optimal W_{net} for majority mixtures under environmental criterion. Moreover, the maximum W_{net} is also different for the same mixture under different criteria. The net power output of ORC operated under thermodynamic criterion is bigger than that operated under the other two criteria. For example of ORC using R245fa/R600a, the optimal W_{net} based on security criterion is 36.16 kW and the relative decrease is 16.81% than the result based on thermodynamic criterion, which is 42.24 kW. Analogously, there is also a further small decrease of 0.37 kW on W_{net} based on environmental criterion and the net power output is 41.87 kW. After the thermodynamic calculations, the consumptions of material and organic fluid can be further calculated. The results of mass calculation about ORC are shown in Appendix A.

4.3. Carbon footprint results

4.3.1. Results of $CO_{2,eq}$ emission

The $CO_{2,eq}$ emissions and the total electricity produced by ORC using zeotropic mixtures considering leak are shown in Fig. 5. The annual leak rate is assumed as 5% (ILW, 2015) and the organic fluid would be recharged into system every year to keep the initial composition constant (Wang et al., 2018). It could be observed that the $CO_{2,eq}$ emissions of ORC during different phases are quite different. Meanwhile, the total electricity productions during life-time by different ORC systems are also different. As shown in Fig. 5a, based on security criterion, the emission during operation phase accounts for the most and the minimum emission occur in the decommissioning phase. ORCs using R245fa as inert fluid produce less $CO_{2,eq}$ emissions than the other ORC systems. The system using R227ea/R600a products the highest $CO_{2,eq}$ emission during life-time. But it also should be noted that the total electricity produced by this system is higher than the others. The minimum electricity production, 2042.18 MWh, is achieved by the ORC using R245fa/R290 within its life-time. As for thermodynamic criterion, similarly, ORC with R227ea/R600a produces both the highest emission about 1367.16 tons $CO_{2,eq}$ and the highest electricity production, 7193.10 MWh, as shown in Fig. 5b. But the $CO_{2,eq}$ emissions of ORCs using R245fa as the inert fluid show that the proportion of construction phase is the largest, followed by the operation phase and then the decommissioning phase. Among these ORCs, the minimum $CO_{2,eq}$ emission comes from system using R245fa/R290 about 145.59 tons, and the total electricity production of the system using R245fa/R600a is the smallest, about 4752.34 MWh. Fig. 5c reflects the $CO_{2,eq}$ emissions and total electricity production under environmental criterion. It could be noted that the $CO_{2,eq}$ emissions during life-time are much less than the other two criteria and the emission of construction phase occupies the most while that of decommissioning phase is the minimum. In addition, the total $CO_{2,eq}$ emission of different ORC is relatively close, and this phenomenon is different from the system under other criteria. System using R134a/R600 produces both minimum $CO_{2,eq}$ emissions, 116.41 tons, and electricity production, 4019.82 MWh, during life-time. Moreover, systems using R134a/R290, R245fa/R290 and R227ea/R290 produce the $CO_{2,eq}$ emissions about 145.09 tons, 143.81 tons and 144.03 tons, respectively, which are higher than the other systems. It can be concluded that the $CO_{2,eq}$ emissions and total electricity produced by each ORC have their own merits when system selects different zeotropic mixtures as the working fluid under different criteria. Thus in order to facilitate comparison, the $CO_{2,eq}$ emission for 1 kWh electricity production by ORC is calculated and listed in Table 9.

Table 9 shows that the ORC, based on environmental criterion, produces less $CO_{2,eq}$ emission for 1 kWh electricity production. The minimum one of ORC is 26.30 g $CO_{2,eq}$/kWh during life-time and the corresponding working fluid is R245fa/R600a. With respect to the other mixtures, the $CO_{2,eq}$ emissions of ORC for 1 kWh electricity production are sharply different under different criteria. Based on security criterion, ORC with R245fa/R600a produces the minimum $CF_{sc,pep}$, 66.48 g $CO_{2,eq}$/kWh, followed by ORCs with R134a/R600, R134a/R600a and R134a/R290, and the corresponding emissions are 83.45, 85.49 and 99.32 g $CO_{2,eq}$/kWh, respectively. ORC using R227ea/R290 possesses the highest $CF_{sc,pep}$, which is 189.28 g $CO_{2,eq}$/kWh. However, the maximum and minimum emissions produced by ORCs operated under thermodynamic criterion are 190.07 and 29.30 g $CO_{2,eq}$/kWh, respectively, with organic fluids of R227ea/R600a and R245fa/R290. This phenomenon is quitely different from the $CF_{ec,pep}$ under environmental criterion. It could be observed that the $CO_{2,eq}$ emissions of ORCs for 1 kWh electricity production range from 26.30 to 29.14 g $CO_{2,eq}$/kWh. That means the restriction on GWP of organic fluid could reduce the CF_{pep} efficiently and it has significant meaning to select environmental criterion for ORC using zeotropic mixture as working fluid to realize low carbon production.

As discussed above, imposing restrictions on fluid could reduce the CF_{pep} efficiently. Thus, we calculated the values of $CO_{2,eq}$ emissions and the proportion of each individual part during life-time, as shown in Fig. 6. Here, the emissions could be classified into three sections, i.e. the emissions of organic fluid, the emissions of equipment and the transportation emissions. It is observed that the maximum transportation emissions account for about 0.5% during the whole life-time which is much smaller than the others. Based on the security criterion, the $CO_{2,eq}$ emission proportion of organic fluid accounts about 58.22 - 84.4% of the total $CO_{2,eq}$ emissions in all the ORCs with zeotropic mixtures investigated in this work, followed by the equipment emissions ranging from 15.51% to 41.52%. Moreover, it also can be found that the emissions of equipment are almost the same for all the ORC with mixtures considered in this work. The reason for systems with R227ea/R600a and R227ea/R290 having higher $CO_{2,eq}$ emissions is that the fluid R227ea has a higher GWP than R134a and R245fa. Thus, there are more emissions during the leaking of organic fluid. Analogously, when the ORCs operate under the thermodynamic criterion, the $CO_{2,eq}$ emissions of fluids are larger than that of equipment and transportation, except for ORC with R245fa/R290. The fluid emissions of ORC using working fluids, i.e. R134a/R600, R134a/R600a, R134a/R290, R227ea/R600a and R227ea/R290, account for 64.04%-84.17% of the total $CO_{2,eq}$ emissions while the shares of emissions from equipment range from 15.73% to 35.74%. For R245fa/R600a, the proportions of $CO_{2,eq}$ emissions of equipment, fluid and transportation are 50.05%, 49.64% and 0.31%, respectively. However, for the environmental criterion, the proportions of fluid emissions are significantly reduced, ranging from 25.33% to 29.85%. It is clearly observed that the environmental criterion places great constraints on fluid emissions.

4.3.2. $CO_{2,eq}$ emission proportions of components and fluids during life-time

Fig. 7 shows the emissions and proportions of device components during life-time under different criteria. It could be found that, for equipment, the main $CO_{2,eq}$ emissions root in the emissions of heat exchangers, followed by the emissions form expander and the last one from the pump. Based on security criterion, when systems use different mixtures, the proportions of evaporator range from 43.87% to 63.42% while that of condenser is about 31.52%-47.37%. With respect to expander and pump, the $CO_{2,eq}$ emissions proportions are 4.47-9.01% and 0.13-0.66%, respectively. As for ORCs operating under thermodynamic criterion, the ranges of proportions are 40.31-69.15%, 25.95-51.75%, 4.52-9.13% and 0.24-0.78% for evaporator, condenser, expander and pump, respectively. Similarly, there exists the same phenomenon for ORCs running under environmental criterion.

As shown in Fig. 8, it should be noted that the primary source of $CO_{2,eq}$ emissions from different zeotropic mixtures is leak during operation and decommission phase, which accounts for about 96.60-99.50%. The $CO_{2,eq}$ emissions even exceed over 950 tons for systems using R227ea/R600a and R227ea/R290 due to leak. Based on security criterion and thermodynamic criterion, R227ea/R600a shows the maximum $CO_{2,eq}$ emission, which is over 1000 tons and leak accounts for more than 96% of the total emission of fluid. It mainly results from the high GWP of this mixture. With respect to environmental criterion, the mass fractions of zeotropic mixtures are calculated based on a uniform standard, which is 150 GWP. Thus, the emissions of fluid charging and disposal are about 1.42-4.09% and 1.58-1.92%, respectively. Moreover, the total emission of fluid is also much less than the others two criteria.

4.3.3. $CO_{2,eq}$ emission reductions of different systems during life-time

The discussion above is focused on direct and indirect $CO_{2,eq}$ emissions of ORCs using zeotropic mixtures and the emissions of 1 kWh electricity production is also analyzed. However, ORC as a waste heat power generation technology, the emission reductions could be more comprehensive to evaluate the environmental benefits. Thus, the emission reductions of ORC during life-time are taken into account. Fig. 8 shows the $CO_{2,eq}$ emission reductions for ORC systems using different organic fluids under different criteria. It should be noted that ORC with R227ea/R600a operated under the thermodynamic criterion exhibits the maximum $CO_{2,eq}$ emission reduction, which is 5595.76 tons, among all the proposed systems. The other two emission reductions under the environmental criterion and security criterion are about 4375.09 and 5356.92 tons, respectively. Analogously, ORC system with R134a/R290 operated under the thermodynamic criterion shows the larger $CO_{2,eq}$ emission reduction, which is 5158.80 tons $CO_{2,eq}$, than the other criteria. Thus, under given conditions, the mass fraction selections of R227ea/R600a and R134a/R290 should firstly consider thermodynamic criterion. For ORCs with R134a/R600 and R245fa/R290, the emission reductions under thermodynamic criterion also present the biggest, followed by those under the environmental and security criteria. However, for R134a/R600, the emission reduction under security criterion is 4460.37 tons $CO_{2,eq}$, which is very closely to that under thermodynamic criterion, 4499.49 tons $CO_{2,eq}$. Meanwhile, there also exists the nearly emission reductions for ORC with R245fa/R290 operated between the environmental and thermodynamic criteria, which are 4641.41 tons and 4663.69 tons, respectively. As for R245fa/R600a, the ORC system operated under environmental criterion represents the maximum emission reduction of 4434.82 tons $CO_{2,eq}$ while ORCs using R134a/R600a and R227ea/R290 operated under the security criterion exhibit the largest emission reductions among the three criteria, corresponding to 4716.00 tons $CO_{2,eq}$ and 4876.40 tons $CO_{2,eq}$, respectively. Therefore, the security criterion could be considered to replace thermodynamic criterion for the mass fractions selections of these three mixtures, including R134a/R600, R134a/R600a and R227ea/R290, when emphasizing the system security. As for the mass fractions selection of R245fa/R600a and R245fa/R290, the environmental criterion could be firstly considered to reach the maximum emission reductions. In a word, the system design and organic fluid selection depend on the decision makers, whether the system security should be firstly considered or obtained more $CO_{2,eq}$ emission reductions.

4.4. $CO_{2,eq}$ emission reductions of ORC under different leak rates

Fig. 10 shows the variations of $CO_{2,eq}$ emission reductions with the leak rates. It can be observed that the distribution of the $CO_{2,eq}$ emission reduction shows almost the linear behavior under the same inlet temperature of heat source. The correlations could be helpful to predict the emission reductions with good accuracy considering different leak rates, without the need of detailed calculation process. This method adopted in this work can be useful to compute correlations between emission reductions and the leak rates of fluid when the waste heat source is 120 ℃ and the working conditions of ORC system are confirmed. Under given conditions of this work, the correlations between emission reductions and the leak rates for selected 7 different mixtures are given as Eqs. (20)-(26):

ORC with R134a/R290 operated under thermodynamic criterion:

$$ER = -62.42306 \times \varepsilon + 5520.85506 \tag{20}$$

ORC with R227ea/R600a operated under thermodynamic criterion:

$$ER = -180.39049 \times \varepsilon + 6515.92214 \tag{21}$$

ORC with R134a/R600 operated under security criterion:

$$ER = -54.86503 \times \varepsilon + 4745.13841 \tag{22}$$

ORC with R134a/R600a operated under security criterion:

$$ER = -61.79874 \times \varepsilon + 5047.44996 \tag{23}$$

ORC with R227ea/R290 operated under security criterion:

$$ER = -135.69394 \times \varepsilon + 5376.64962 \tag{24}$$

ORC with R245fa/R600a operated under environmental criterion:

$$ER = -5.74906 \times \varepsilon + 4463.50882 \tag{25}$$

ORC with R245fa/R290 operated under environmental criterion:

$$ER = -7.69861 \times \varepsilon + 4683.61081 \tag{26}$$

It can be summarized from the above formulas that as the leak rates of the ORC system increase, the $CO_{2,eq}$ emission reductions monotonously decrease. That means the working fluid leak of ORC would induce the environmental degradation. In addition, the emission reductions under the environmental criterion are much less than those under security and thermodynamic criteria. This result is correct because the environmental criterion imposes strong restrictions on the $CO_{2,eq}$ emissions of working fluid. These formulas fit from the discussed results for emission reductions determination for the recommended 7 mixtures.

5. Conclusions

The carbon footprint model of ORC using zeotropic mixture was developed in this study. $CO_{2,eq}$ emissions and emission reductions of ORCs with zeotropic mixtures during its life-time are measured under different criteria. The PSO algorithm was employed to optimize the system conditions, and the emissions from different phases were also calculated and analyzed. The correlations between emission reductions of $CO_{2,eq}$ and the leak rates of ORCs with 7 mixtures were investigated. The results reveal that the ORC to operate under thermodynamic criterion will generate higher net power output and produce larger $CO_{2,eq}$ emissions during life-time compared with the cases which either the security or the environmental criteria was adopted. Under the given conditions, the ORC with R245fa/R600a operated under environmental criterion generates the least $CO_{2,eq}$ emissions, accounting to 26.30 g $CO_{2,eq}$/kWh, while the system with R227ea/R600a operated under thermodynamic criterion has the highest emission reduction, accounting to 5595.76 tons $CO_{2,eq}$. The result shows that the emissions of heat exchangers take up the largest proportion of the equipment emissions, followed by the expander and then the pump in the descending order. For the emissions from working fluid, the leak process accounts to about 96.60-99.50%, followed by the recharging process and then the disposal process. Moreover, for fluids of R134a/R600, R134a/R600a and R227ea/R290, in order to ensuring nearly the maximum emission reductions the mass fractions of mixtures under security criterion could be considered over those under thermodynamic and the environmental criteria when emphasizing the safety. Nevertheless, for the mixtures of R245fa/R600a and R245fa/R290, the environmental criterion is preferentially considered to guarantee the maximum emission reductions. The correlations between $CO_{2,eq}$ emission reductions and the leak rates for the selected 7 mixtures indicated that the environmental criteria would alleviate the influence of leak phenomenon.

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Nomenclature

A	heat exchanger area (m^2)
CF	Carbon footprint (kg $CO_{2,eq}$/kWh)
e	emission of CO_2 (kg $CO_{2,eq}$/unit)
ER	emission reduction (kg $CO_{2,eq}$)
LT	life-time (year)
k	heat transfer coefficient
M	mass (kg) / mass fraction
m	mass flow rate ($kg \cdot s^{-1}$)
n	mole
Nu	Nuselt number
Pr	Prandtl number
Q	absorbing or releasing heat rate (kW) / Quantity (t)
Re	Reynolds number
S	transport distance (km)
T	Temperature (K)
W	Power (kW)
x	liquid mole fraction
y	vapor mole fraction
z	total mole fraction

Abbreviations

GWP	Global warming potential
LMTD	Log mean temperature difference
ODP	Ozone depletion potential
MAC	Mobile air conditioning
OHE	Osmotic heat engine
ORC	Organic Rankine cycle

Greek letters

ΔT	Temperature difference (K)
ε	leak rate (%)
μ	dynamic viscosity ($N \cdot s \cdot m^{-2}$)
η	efficiency
φ	end of life refrigerant leak (%)
λ	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)

Subscripts/superscripts

c/cond	condenser
crit	critical
cs	cooling source
elec	electricity
e/evap	evaporator
equip	equipment
fluid	organic fluid
exp	expander
hs	heat source
i	i-th component
in	inlet
op	l
out	op
out	op
out	outlet
p/pump	pump
v	vapor
wf	working fluid

Appendix A

The mass of components and zeotropic mixtures in ORC is listed in Tables A.1-A.7.

The ORC systems exhibit different power output and heat exchanger areas based on different criteria. This will result in different consumptions of component's material and working fluid. The raw material mass of system based on thermodynamic criterion consumes the most among the three kinds of criteria. Meanwhile, the net power output is also higher. ORC system using R227ea/R600a exhibits the highest material consumption about 125.38 tons based on the thermodynamic criterion while system using R245fa/R600a consumes the minimum material of 38.78 tons for the environmental criterion. ORC using R245fa/R290 outputs the least net power of 26.71 kW based on the security criterion. However, the maximum net power output of 63.68 kW is obtained in system using R227ea/R600a based on the thermodynamic criterion. It is observed that there is no direct correspondence between the mass consumption and net power output. Thus, through the calculation above, the $CO_{2,eq}$ emissions during the construction phase can be obtained and integrated with operation phase and decommission phase to calculate the $CO_{2,eq}$ emission of 1 kWh electricity production by ORC, and further obtain the $CO_{2,eq}$ emission reduction of ORC system during the life-time.

Table A.1 Mass of components and organic fluid of ORC using R134a/R600.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R134a/R600	Security Criterion	Power(Heat) / kW	505.36	457.69	57.01	9.33	-	44.82
		Heat exchanger area / m^2	445.85	472.14	-	-	-	917.99
		Mass / kg	18830.93	19941.49	19941.49	283.77	301.67	42924.30
	Thermodynamic Criterion	Power(Heat) / kW	574.82	526.90	55.77	7.84	-	45.14
		Heat exchanger area / m^2	473.71	544.51	-	-	-	1018.25
		Mass / kg	20007.76	22999.46	3784.67	238.47	295.11	47030.36
	Environmental Criterion	Power(Heat) / kW	520.48	482.69	40.00	2.32	-	35.79
		Heat exchanger area / m^2	458.82	412.33	-	-	-	871.15
		Mass / kg	19378.99	17415.16	2721.47	70.12	211.66	39585.74

Table A.2 Mass of components and organic fluid of ORC using R134a/R600a.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R134a/R600a	Security Criterion	Power(Heat) / kW	564.15	513.42	60.47	10.19	-	47.67
		Heat exchanger area / m^2	513.49	531.54	-	-	-	1045.03
		Mass / kg	21687.94	22450.46	4146.05	315.28	319.98	48599.73
	Thermodynamic Criterion	Power(Heat) / kW	604.63	550.69	65.70	11.75	-	50.66
		Heat exchanger area / m^2	589.20	569.38	-	-	-	1158.58
		Mass / kg	24885.77	24048.47	4457.80	357.35	347.65	53749.40
	Environmental Criterion	Power(Heat) / kW	554.53	514.01	43.90	3.40	-	38.32
		Heat exchanger area / m^2	443.19	474.84	-	-	-	918.03
		Mass / kg	18718.80	20055.44	2980.16	103.37	232.30	41857.76

Table A.3 Mass of components and organic fluid of ORC using R134a/R290.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R134a/ R290	Security Criterion	Power(Heat) / kW	603.58	556.26	52.10	8.83	-	44.40
		Heat exchanger area / m^2	572.78	557.79	-	-	-	1130.57
		Mass / kg	24192.00	23559.14	3953.95	332.99	275.69	52038.09
	Thermodynamic Criterion	Power(Heat) / kW	781.85	725.46	70.29	14.98	-	52.80
		Heat exchanger area / m^2	1238.87	765.15	-	-	-	2004.02
		Mass / kg	52325.42	32317.34	4886.95	475.08	371.94	90004.79
	Environmental Criterion	Power(Heat) / kW	546.52	498.04	60.34	11.82	-	45.46
		Heat exchanger area / m^2	490.21	510.15	-	-	-	1000.36
		Mass / kg	20704.72	21546.79	4090.25	358.84	319.29	46700.60

Table A.4 Mass of components and organic fluid of ORC using R245fa/R600a.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R245fa /R600a	Security Criterion	Power(Heat) $W(Q)$ / kW	522.81	484.66	38.96	1.52	-	36.16
		Heat exchanger area A / m^2	417.99	434.94	-	-	-	852.93
		Mass / kg	17654.36	18370.41	2703.71	51.29	206.16	38779.76
	Thermodynamic Criterion	Power(Heat) $W(Q)$ / kW	550.74	506.11	47.91	3.26	-	42.24
		Heat exchanger area A / m^2	402.59	516.92	-	-	-	919.51
		Mass / kg	17003.90	21832.91	3250.81	99.36	253.52	42186.98
	Environmental Criterion	Power(Heat) $W(Q)$ / kW	551.66	507.42	47.25	3.06	-	41.87
		Heat exchanger area A / m^2	398.60	517.83	-	-	-	916.42
		Mass / kg	16835.29	21871.14	3210.50	93.26	250.02	42010.20

Table A.5 Mass of components and organic fluid of ORC using R245fa/R290.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R245fa /R290	Security Criterion	Power(Heat) $W(Q)$ / kW	512.19	483.97	17.83	0.90	-	26.71
		Heat exchanger area A / m^2	691.73	348.70	-	-	-	1040.43
		Mass / kg	29216.11	14727.98	2059.52	64.44	94.35	46068.05
	Thermodynamic Criterion	Power(Heat) $W(Q)$ / kW	502.68	455.61	58.16	11.10	-	44.16
		Heat exchanger area A / m^2	449.70	473.10	-	-	-	922.80
		Mass / kg	18993.62	19981.93	3948.23	337.93	307.75	43261.72
	Environmental Criterion	Power(Heat) $W(Q)$ / kW	567.35	520.58	55.95	9.25	-	43.96
		Heat exchanger area A / m^2	463.67	539.78	-	-	-	1003.45
		Mass / kg	19583.77	22798.20	3802.53	281.91	296.06	46466.41

Table A.6 Mass of components and organic fluid of ORC using R227ea/R600a.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R227ea /R600a	Security Criterion	Power(Heat) $W(Q)$ / kW	785.15	720.09	79.56	14.60	-	61.08
		Heat exchanger area A / m^2	1490.38	749.66	-	-	-	2240.05
		Mass / kg	62948.48	31663.11	5411.19	446.18	420.99	100468.96
	Thermodynamic Criterion	Power(Heat) $W(Q)$ / kW	809.84	741.99	84.26	15.76	-	63.68
		Heat exchanger area A / m^2	2052.72	770.43	-	-	-	2823.14
		Mass / kg	86699.36	32540.09	5663.93	474.87	445.86	125378.26
	Environmental Criterion	Power(Heat) $W(Q)$ / kW	545.04	501.40	46.70	3.07	-	41.30
		Heat exchanger area A / m^2	398.93	503.80	-	-	-	902.73
		Mass / kg	16849.40	21278.59	3170.10	93.50	247.11	41391.59

Table A.7 Mass of components and organic fluid of ORC using R227ea/R290.

Fluids	Criteria	Items	Evaporator	Condenser	Expander	Pump	Fluid	System
R227ea /R290	Security Criterion	Power(Heat) $W(Q)$ / kW	754.72	696.04	74.48	14.59	-	55.03
		Heat exchanger area A / m^2	1173.64	707.94	-	-	-	1881.58
		Mass / kg	49570.35	29900.89	4955.58	436.38	394.11	84863.19
	Thermodynamic Criterion	Power(Heat) $W(Q)$ / kW	825.96	761.35	81.43	16.82	-	60.53
		Heat exchanger area A / m^2	3105.90	797.06	-	-	-	3903.00
		Mass / kg	60343.76	15485.89	2542.10	235.50	430.86	78607.25
	Environmental Criterion	Power(Heat) $W(Q)$ / kW	545.04	501.40	46.70	3.07	-	41.30
		Heat exchanger area A / m^2	398.93	503.80	-	-	-	902.73
		Mass / kg	16849.40	21278.59	3170.10	93.50	247.11	41391.59

Reference

Abam, F., Ekwe, E., Effiom, S., Ndukwu, M., 2018. A comparative performance analysis and thermo-sustainability indicators of modified low-heat organic Rankine cycles (ORCs): An exergy-based procedure. Energy Reports 4, 110-118.

Aminyavari, M., Najafi, B., Shirazi, A., Rinaldi, F., 2014. Exergetic, economic and environmental (3E) analyses, and multi-objective optimization of a CO2/NH3 cascade refrigeration system. Applied Thermal Engineering 65(1-2), 42-50.

Ashouri M, Razi Astaraei F, Ghasempour R, et al. Thermodynamic and economic evaluation of a small-scale organic Rankine cycle integrated with a concentrating solar collector[J]. International Journal of Low-Carbon Technologies, 2015, 12(1): 54-65.

China Statistics Press, 2013. China statistical yearbook 2013 (in Chinese). http://www.stats.gov.cn/tjsj/ndsj/2013/indexch.htm (accessed 20 February 2019).

Clarke, J., McLeskey Jr, J.T., 2015. Multi-objective particle swarm optimization of binary geothermal power plants. Applied Energy 138, 302-314.

Collings, P., Yu, Z., Wang, E., 2016. A dynamic organic Rankine cycle using a zeotropic mixture as the working fluid with composition tuning to match changing ambient conditions. Applied Energy 171, 581-591.

Eberhart, R., Kennedy, J., 1995. A new optimizer using particle swarm theory, MHS'95. Proceedings of the Sixth International Symposium on Micro Machine and Human Science. Ieee, pp. 39-43.

Feng, B., Yang, Z., Zhai, R., 2018. Experimental study on the influence of the flame retardants on the flammability of R1234yf. Energy 143, 212-218.

Garg, P., Orosz, M.S., 2018. Economic optimization of Organic Rankine cycle with pure fluids and mixtures for waste heat and solar applications using particle swarm optimization method. Energy conversion and management 165, 649-668.

Heberle, F., Brüggemann, D., 2015. Thermo-Economic Evaluation of Organic Rankine Cycles for Geothermal Power Generation Using Zeotropic Mixtures. Energies 8, 2097-2124.

Hickenbottom, K.L., Miller-Robbie, L., Vanneste, J., Marr, J.M., Heeley, M.B., Cath, T.Y., 2018. Comparative life-cycle assessment of a novel osmotic heat engine and an organic Rankine cycle for energy production from low-grade heat. Journal of Cleaner Production 191, 490-501.

Huo, E., Liu, C., Xu, X., Dang, C., 2017. A ReaxFF-based molecular dynamics study of the pyrolysis mechanism of HFO-1336mzz (Z). International Journal of Refrigeration 83, 118-130.

ILW, G., 2015. Guideline for Life Cycle Climate Performance. International Institute of Refrigeration.

Kern, D.Q., 1950. Process heat transfer. Tata McGraw-Hill Education.

Le, V.L., Kheiri, A., Feidt, M., Pelloux-Prayer, S., 2014. Thermodynamic and economic optimizations of a waste heat to power plant driven by a subcritical ORC (Organic Rankine Cycle) using pure or zeotropic working fluid. Energy 78, 622-638.

Lemmon, E., Huber, M., McLinden, M., 2013. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg. See http://www. nist. gov/srd/nist23. cfm.

Liu, C., He, C., Gao, H., Xie, H., Li, Y., Wu, S., Xu, J., 2013. The environmental impact of organic Rankine cycle for waste heat recovery through life-cycle assessment. Energy 56(7), 144-154.

Long, R., Bao, Y., Huang, X., Liu, W., 2014. Exergy analysis and working fluid selection of organic Rankine cycle for low grade waste heat recovery. Energy 73, 475-483.

Miao, Z., Zhang, K., Wang, M., Xu, J., 2019. Thermodynamic selection criteria of zeotropic mixtures for subcritical organic Rankine cycle. Energy 167, 484-497.

MinSooKim, Didion, D., 1995. Simulation of a Leak/Recharge Process of Refrigerant Mixtures. Hvac & R Research 1(3), 242-254.

Rahbar, K., Mahmoud, S., Al-Dadah, R.K., Moazami, N., Mirhadizadeh, S.A., 2017. Review of organic Rankine cycle for small-scale applications. Energy Conversion and Management 134, 135-155.

Tian, H., Chang, L., Gao, Y., Shu, G., Zhao, M., Yan, N., 2017. Thermo-economic analysis of zeotropic mixtures based on siloxanes for engine waste heat recovery using a dual-loop organic Rankine cycle (DORC). Energy conversion and management 136, 11-26.

Wang, D., Ling, X., Peng, H., Liu, L., Tao, L., 2013. Efficiency and optimal performance evaluation of organic Rankine cycle for low grade waste heat power generation. Energy 50, 343-352.

Wang, H., Xu, J., Yang, X., Miao, Z., Yu, C., 2015. Organic Rankine cycle saves energy and reduces gas emissions for cement production. Energy 86, 59-73.

Wang, S., Liu, C., Liu, L., Xu, X., Zhang, C., 2019. Ecological cumulative exergy consumption analysis of organic Rankine cycle for waste heat power generation. Journal of Cleaner Production 218, 543-554.

Wang, S., Liu, C., Zhang, C., Xu, X., 2018. Thermodynamic evaluation of leak phenomenon in liquid receiver of ORC systems. Applied Thermal Engineering 141, 1110-1119.

Weckert, M., 2008. Comparative life cycle assessment of CFC-replacement compounds in different technical applications.

Wu, Y., Zhu, Y., Yu, L., 2016. Thermal and economic performance analysis of zeotropic mixtures for Organic Rankine Cycles. Applied Thermal Engineering 96, 57-63.

Xi, H., Li, M.-J., He, Y.-L., Zhang, Y.-W., 2017. Economical evaluation and optimization of organic Rankine cycle with mixture working fluids using R245fa as flame retardant. Applied Thermal Engineering 113, 1056-1070.

Yang, M.-H., Yeh, R.-H., 2015. Thermodynamic and economic performances optimization of an organic Rankine cycle system utilizing exhaust gas of a large marine diesel engine. Applied Energy 149, 1-12.

Yang, Z., Liu, H., Wu, X., 2012. Theoretical and experimental study of the inhibition and inert effect of HFC125, HFC227ea and HFC13I1 on the flammability of HFC32. Process Safety and Environmental Protection 90(4), 311-316.

Yang, Z., Wu, X., Peng, J., 2013. Theoretical and experimental investigation on the flame-retarding characteristic of R245fa. Experimental Thermal and Fluid Science 44, 613-619.

Yi, Z., Luo, X., Chen, J., Chen, Y., 2017. Mathematical modelling and optimization of a liquid separation condenser-based organic Rankine cycle used in waste heat utilization. Energy 139, 916-934.

Zhang, C., Liu, C., Wang, S., Xu, X., Li, Q., 2017. Thermo-economic comparison of subcritical organic Rankine cycle based on different heat exchanger configurations. Energy 123, 728-741.

Zhang, C., Liu, C., Xu, X., Li, Q., Wang, S., 2019. Energetic, exergetic, economic and environmental (4E) analysis and multi-factor evaluation method of low GWP fluids in trans-critical organic Rankine cycles. Energy 168, 332-345.

Zhao, Y., Bin, L., Haibo, Z., 2004. Experimental study of the inert effect of R134a and R227ea on explosion limits of the flammable refrigerants. Experimental Thermal and Fluid Science 28(6), 557-563.

Zhu Y, Li W, Sun G, et al. Thermo-economic analysis based on objective functions of an organic Rankine cycle for waste heat recovery from marine diesel engine[J]. Energy, 2018, 158:343-356.

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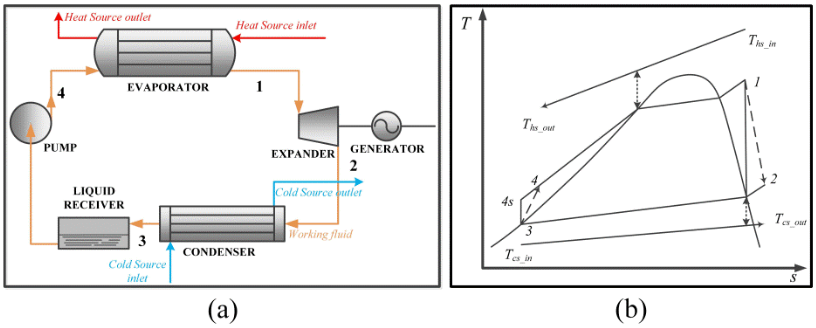
Fig. 9. Emission reductions of CO_2 equivalent of different systems during life-time based on different criteria.



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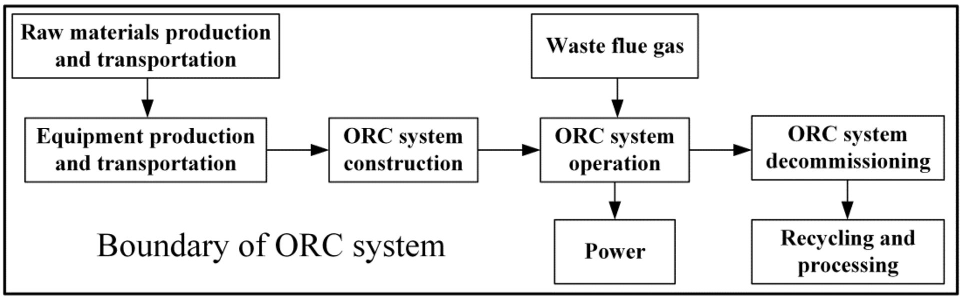
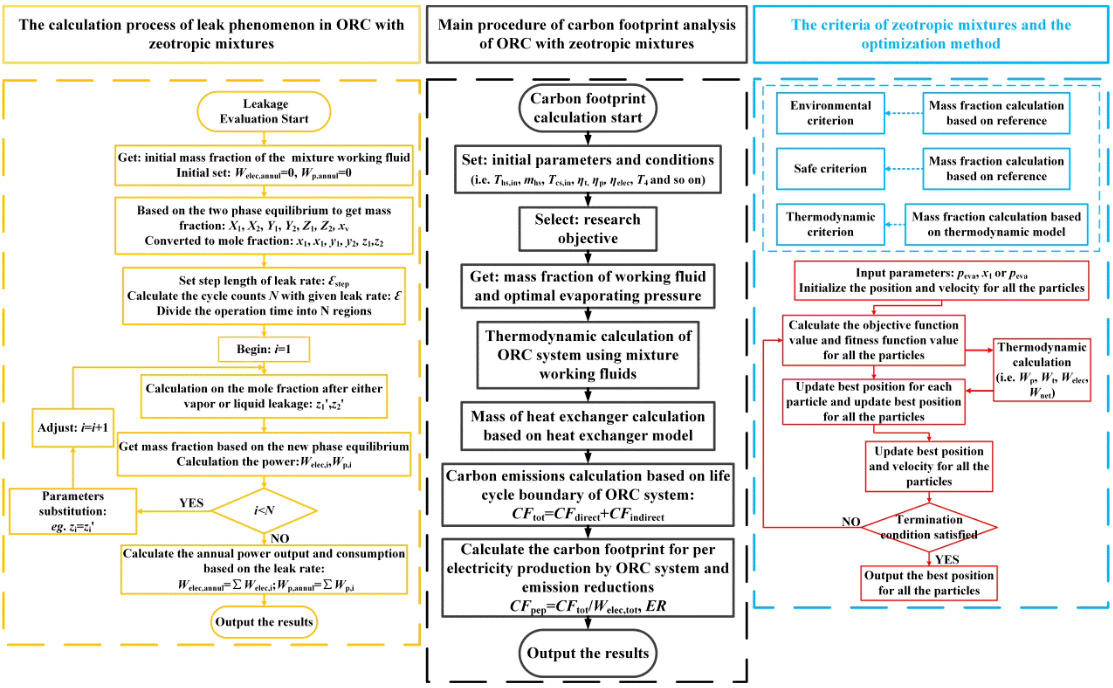


Fig. 2. Life cycle boundary of ORC system.



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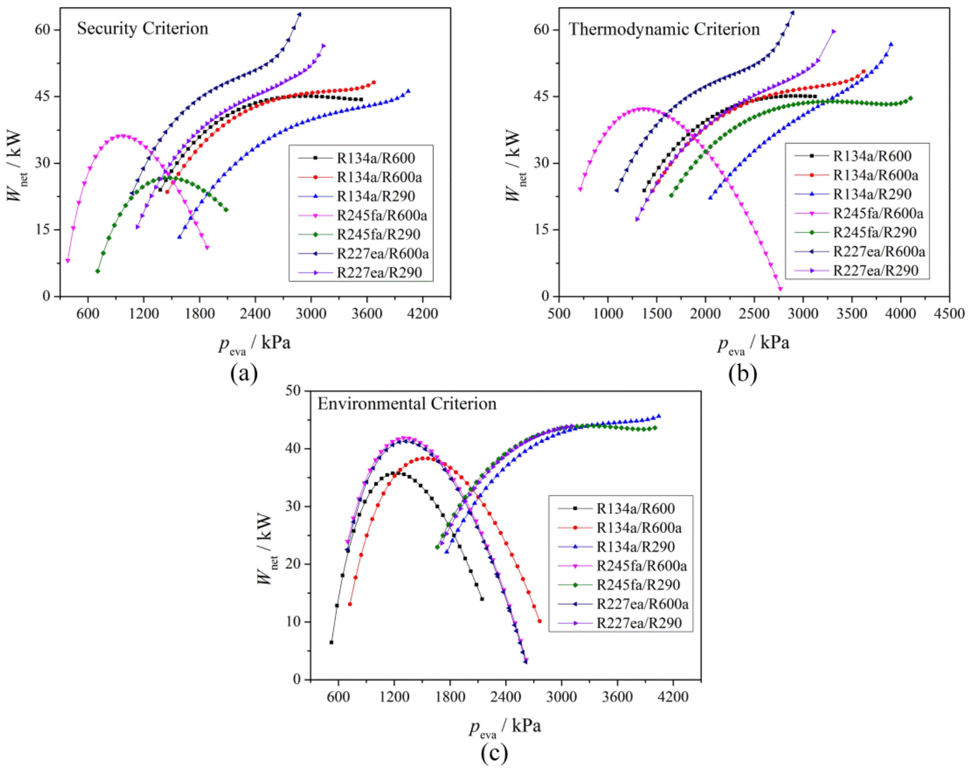
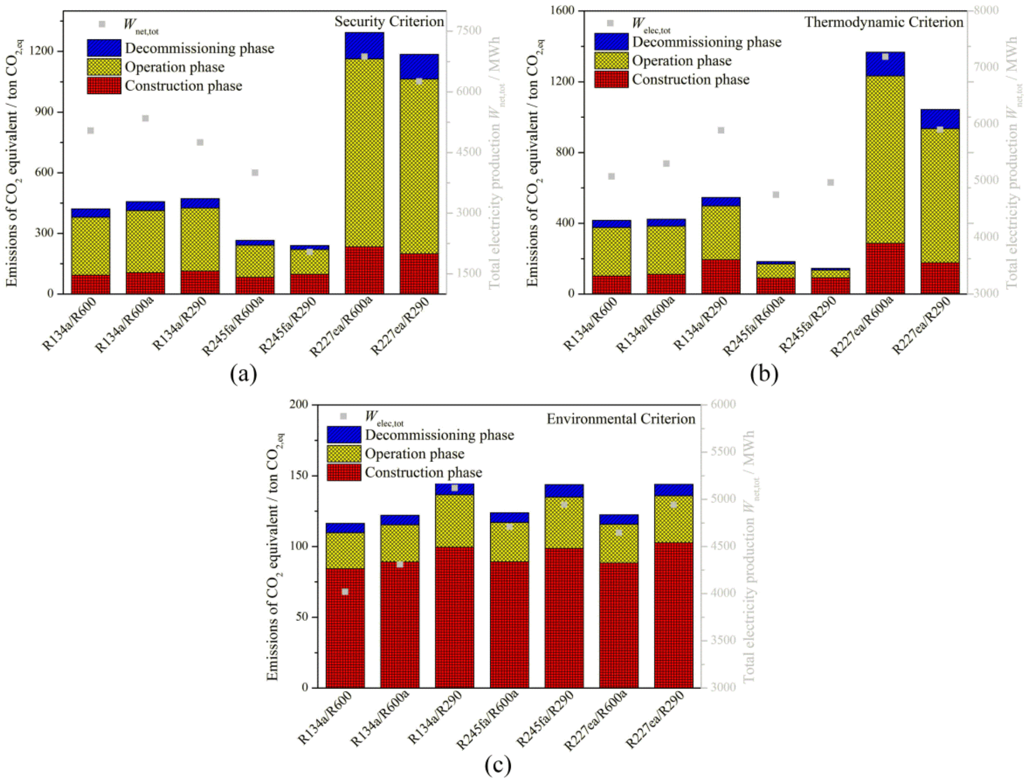


Fig. 4. Variations of the net power output of ORCs using zeotropic mixtures with evaporating pressures based on (a) security criterion, (b) thermodynamic criterion and (c) environmental criterion.



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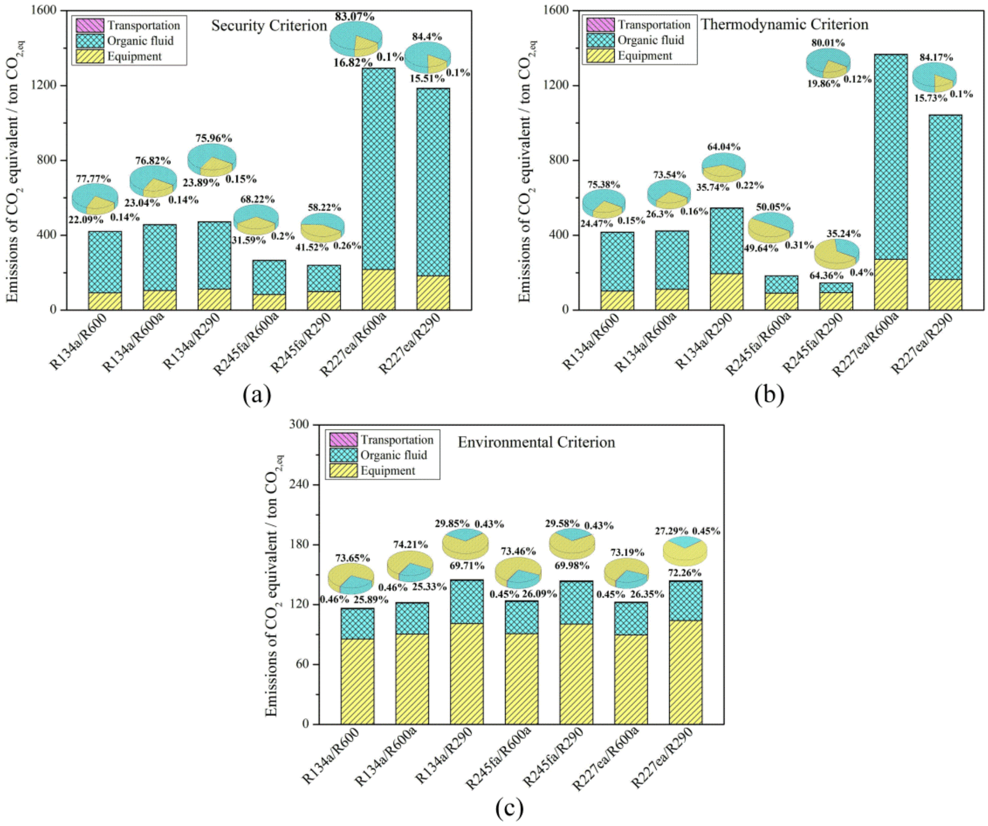

Fig. 6. Emissions of CO_2 equivalent and the proportions of organic fluid, equipment and transportation during life-time based on (a) security criterion, (b) thermodynamic criterion and (c) environmental criterion.

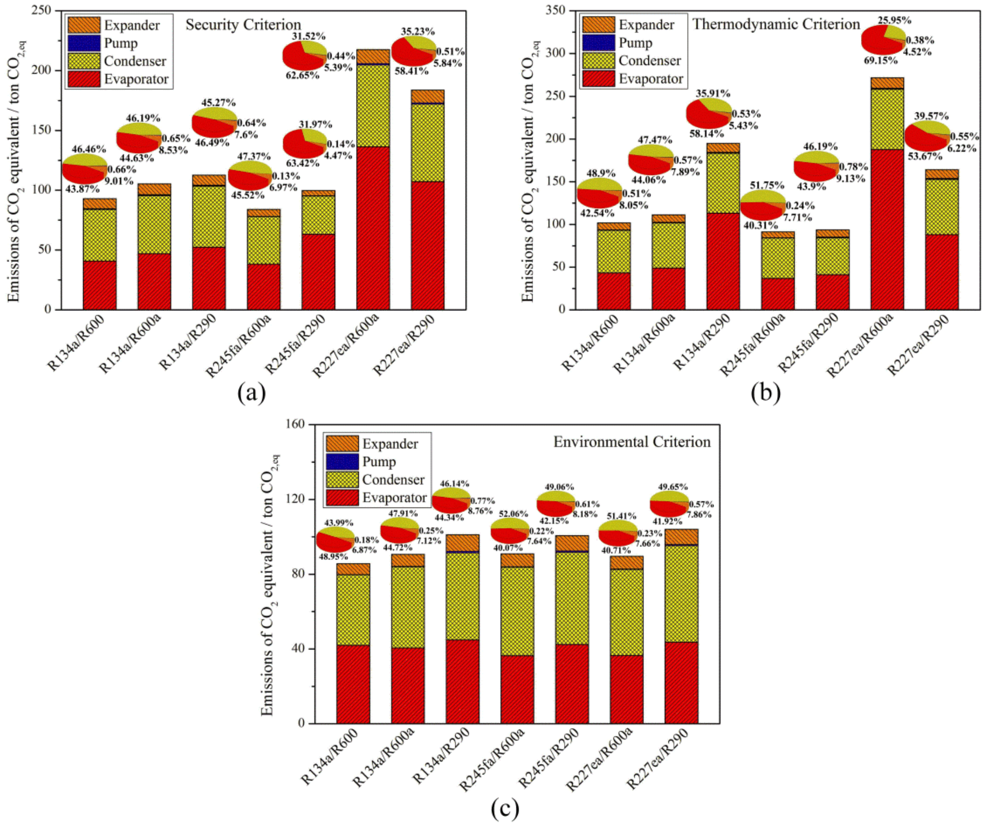

Fig. 7. Emissions of CO_2 equivalent of equipment during life-time and the proportions of evaporator, condenser, pump and expander based on (a) security criterion, (b) thermodynamic criterion and (c) environmental criterion.

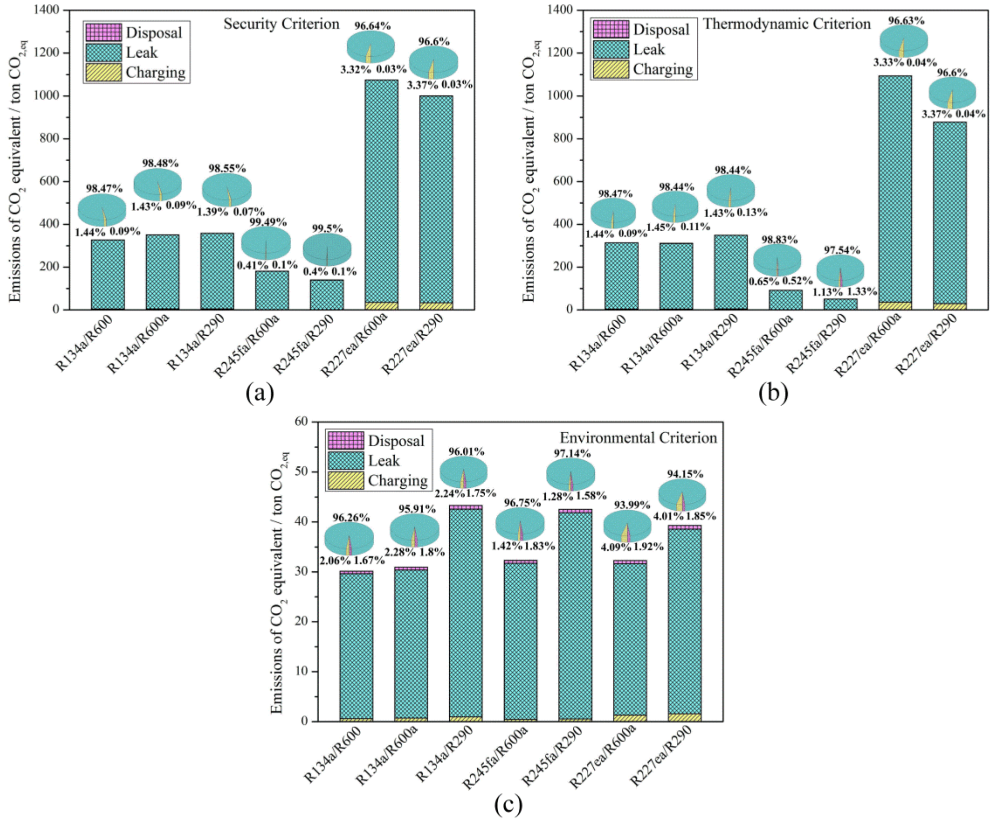

Fig. 8. Emissions of CO_2 equivalent of working fluids during life-time and the proportions of charging, leak and disposal processes based on (a) security criterion, (b) thermodynamic criterion and (c) environmental criterion.

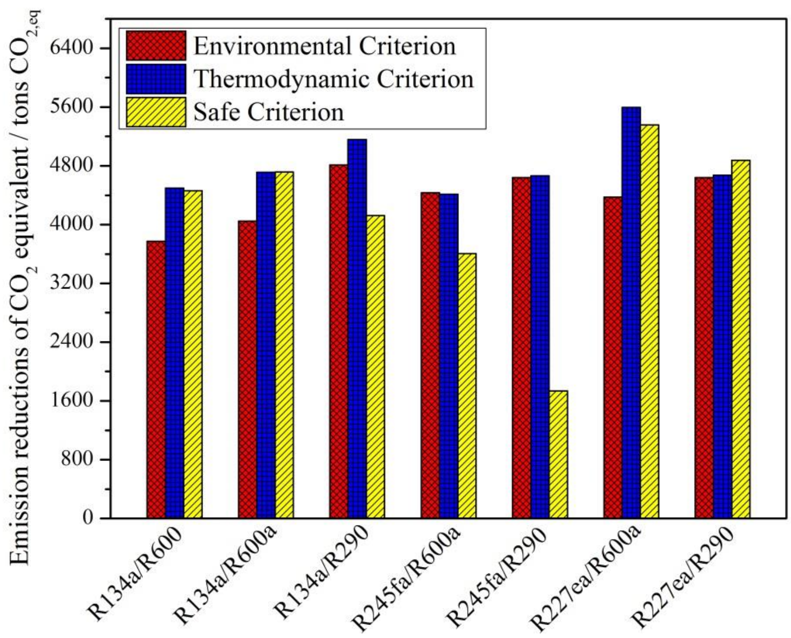

Fig. 9. Emission reductions of CO_2 equivalent of different systems during life-time based on different criteria.

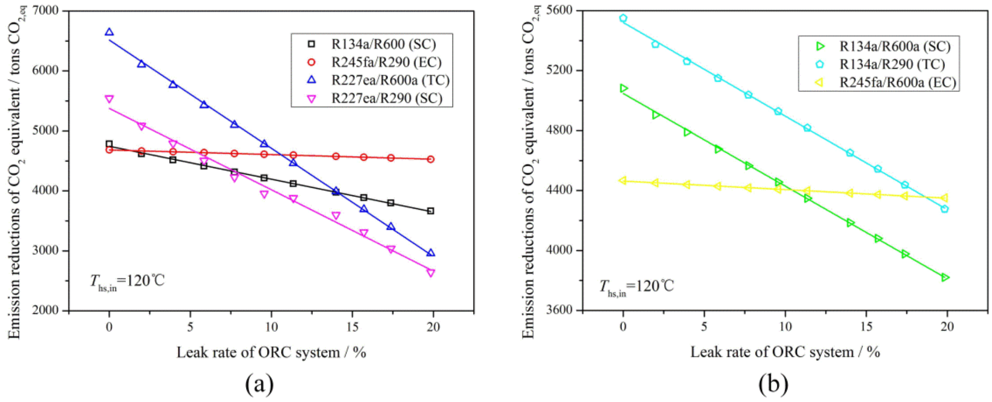

Fig. 10. CO_2 equivalent emission reductions of ORC under different leak rates using (a) R134a/R600, R245fa/R290, R227ea/R600a and R227ea/R290; and (b) R134a/R600a, R245fa/R600a and R134a/R290.

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Table 1 Calculation conditions.

Parameters	Units	Values
Flue gas inlet temperature / $T_{hs,in}$	K	393.15
Temperature constraint of discharged flue gas	K	355.15
Mass flow rate of flue gas / m_{hs}	kg/s	10
Condensing temperature / T_4	K	308.15
Pinch point temperature difference in evaporator / ΔT_e	K	5-30
Pinch point temperature difference in condenser / ΔT_c	K	5-8
Inlet temperature of cooling air / $T_{cs,in}$	K	293.15
Expander isentropic efficiency / η_{exp}	%	80
Pump isentropic efficiency / η_p	%	75
Generator efficiency / η_{elec}	%	95
Operating time of each year / t_{op}	hours	7500
Life cycle time / LT	years	15

Table 2 Thermal properties of pure organic fluids (Lemmon et al., 2013).

ASHRAE 34 [a]	Classification	Molecular mass / g·mol^{-1}	T_{crit} / ℃	p_{crit} / Pa	GWP 100 yr	ODP
R600	HC	58.12	152.00	3.80×10^6	20.00	0
R600a	HC	58.12	134.70	3.63×10^6	20.00	0
R290	HC	44.10	96.70	4.25×10^6	20.00	0
R134a	HFC	102.03	101.10	4.06×10^6	1430.00	0
R245fa	HFC	134.05	154.00	3.65×10^6	1030.00	0
R227ea	HFC	170.03	102.80	3.00×10^6	3220.00	0

[a] ASHRAE 34: American Society of Refrigerating Engineers: Standard 34 for designation and safety classification of refrigerants.

Table 3 Emissions of materials during manufacturing and recycling process (ILW, 2015).

Material	Emissions of mixed materials during manufacturing / kg $CO_{2,eq}$/kg	Emissions of materials during recycling / kg $CO_{2,eq}$/kg
Steel	1.43	0.07
Aluminum	4.50	0.07
Copper	1.64	0.07
Plastics	2.61	0.01

Table 4 Emissions of organic fluid during manufacturing and disposal process (ILW, 2015; Weckert, 2008).

Material	Emissions of organic fluid during manufacturing / kg $CO_{2,eq}$/kg	Emissions of organic fluid during disposal / kg $CO_{2,eq}$/kg
R134a	10.00	0.86
R245fa	2.05	0.99
R227ea	54.00	0.78
R600	0.83	3.03
R600a	0.90	3.03
R290	0.90	2.99

Table 5 Model validation for the ORC system with zeotropic mixtures using the date reported by Wu et al. (2016).

Decision and performance parameters		Wu et al. (2016)	Present work
Input values	Hot air inlet temperature	393.15 K	393.15 K
	Hot air inlet pressure	1×10^5 Pa	1×10^5 Pa
	Hot air flow rate	4000 m^3/h	4000 m^3/h
	Isentropic efficiency of pump	80 %	80 %
	Isentropic efficiency of expander	80 %	80 %
	Pinch point temperature in heat exchanger	5 K	5 K
Output values	Net power output of ORC using R227ea/R245fa	5.06 kW	5.20 kW
	Net power output of ORC using RC318/R245fa	4.78 kW	4.83 kW

Table 6 Model validation for the leak in ORC system with zeotropic mixtures using the date reported by Wang et al. (2018).

Decision and performance parameters		Wang et al. (2018)	Present work
Input values	Inlet temperature of heat source	433.15 K	433.15 K
	Flow rate of heat source	10 kg/s	10 kg/s
	Condensing temperature	303.15 K	303.15 K
	Pinch point temperature in evaporator	10 K	10 K
	Pinch point temperature in condenser	8 K	8 K
	Superheating temperature	2 K	2 K
Output values	Mass fraction of R152a/R600 after leak	9.88/90.12 %	9.79/90.21 %
	Net power output after leak	33.25 kW	33.21 kW

Table 7 Model validation for carbon footprint calculation of trans-critical ORC system with pure fluid using the date reported by Zhang et al. (2019).

Decision and performance parameters		Zhang et al. (2019)	Present work
Input values	Inlet temperature of heat source	423.15 K	423.15 K
	Flow rate of heat source	10 kg/s	10 kg/s
	Pump isentropic efficiency	75 %	75 %
	Expander isentropic efficiency	80 %	80 %
	Operating time	7000 h	7000 h
	Life cycle time	15 year	15 year
Output values	Emissions of CO_2 equivalent of ORC using R134a	665 tons $CO_{2,eq}$	663.89 tons $CO_{2,eq}$
	Emissions of CO_2 equivalent of ORC using R32	301 tons $CO_{2,eq}$	299.69 tons $CO_{2,eq}$

Table 8 Optimal working conditions of ORC based on different criteria.

Fluids	Security Criterion			Thermodynamic Criterion			Environmental Criterion		
	Mass fraction / %	Evaporating pressure $p_{sc,opt}$ / Pa	Mass flow rate of fluid / kg/s	Mass fraction / %	Evaporating pressure $p_{tc,opt}$ / Pa	Mass flow rate of fluid / kg/s	Mass fraction / %	Evaporating pressure $p_{ec,opt}$ / Pa	Mass flow rate of fluid / kg/s
R134a/R600	88.16/11.84	3.70×10^6	2.55	86.39/13.61	2.92×10^6	2.92	9.22/90.78	1.24×10^6	1.32
R134a/R600a	87.85/12.15	3.63×10^6	2.93	79.83/20.17	3.62×10^6	3.05	9.22/90.78	1.50×10^6	1.58
R134a/R290	91.27/8.73	4.00×10^6	3.20	72.52/27.48	3.90×10^6	4.05	9.22/90.78	4.05×10^6	1.63
R245fa/R600a	95.15/4.85	0.98×10^6	2.37	39.78/60.22	1.37×10^6	1.91	12.87/87.13	1.30×10^6	1.61
R245fa/R290	94.85/5.15	1.48×10^6	2.23	15.43/84.57	4.10×10^6	1.52	12.87/87.13	3.28×10^6	1.72
R227ea/R600a	89.39/10.61	2.88×10^6	6.18	87.10/12.90	2.89×10^6	5.98	4.06/95.94	1.32×10^6	1.52
R227ea/R290	92.28/7.72	3.13×10^6	5.77	84.89/15.11	3.32×10^6	5.61	4.06/95.94	3.11×10^6	1.73

Table 9 Carbon dioxide equivalent emissions for 1 kWh electricity produced by ORC using different zeotropic mixtures under calculated based on different criteria.

Fluids	**Security Criterion**	**Thermodynamic Criterion**	**Environmental Criterion**
	$CF_{sc,pep}$ / g $CO_{2,eq}$/kWh	$CF_{tc,pep}$ / g $CO_{2,eq}$/kWh	$CF_{ec,pep}$ / g $CO_{2,eq}$/kWh
R134a/R600	83.45	81.97	28.96
R134a/R600a	85.49	79.77	28.34
R134a/R290	99.32	92.57	28.33
R245fa/R600a	66.48	38.73	26.30
R245fa/R290	117.67	29.30	29.09
R227ea/R600a	188.29	190.07	26.36
R227ea/R290	189.28	176.66	29.14