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## **Thermodynamic analysis of a marine-type ORC waste heat recovery system using zeotropic mixtures of HCFO and HFO refrigerants**

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# Thermodynamic analysis of a marine-type ORC waste heat recovery system using zeotropic mixtures of HCFO and HFO refrigerants

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**Abstract:** This study aims to investigate the energetic and exergetic performance of an exhaust gas-driven recuperative ORC waste heat recovery system using zeotropic mixtures. Working fluids with zero ozone depletion potential and very low global warming potential ( $<10$ ), including R1234ze (Z), R1336mzz (Z), R1224yd (Z), and R1233zd (E), are selected and mixed in various compositions. The effects of temperature glide, mass fraction, and evaporation pressure on thermodynamic performance are explored. Results show that using mixtures instead of pure fluids can enhance thermal and exergy efficiency by 5.1% to 9.4%, with a 7.2% reduction in exergy destruction when using an R1336mzz (Z)/R1233zd (E) (0.9/0.1) mixture.

**Keywords:** organic rankine cycle; ORC; waste heat recovery; WHR; ship energy efficiency; exergy; zeotropic mixture.

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This paper is a revised and expanded version of a paper entitled 'Energetic and exergetic analysis of a marine-type ORC WHRS using zeotropic mixtures' presented at 12th International Exergy, Energy and Environment Symposium (IEEES-14), Tuzla, Istanbul, Türkiye, 24–27 December 2023.

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## 1 Introduction

Seaborne trade accounts for about 3% of global greenhouse gas emissions (GHGs), and without intervention, the percentage may exceed 130% of their 2008 levels by 2050 (IMO, 2020). To address the problem, the International Maritime Organization (IMO) has put strict measures into force and developed a strategy focusing on reducing the maritime carbon footprint by 20% by 2030 and 70% by 2040 (IMO, 2023). Complying with the IMO targets is still challenging and adopting dual-fuel using alternative fuels such as methanol (MeOH), has been considered one of the key solutions to mitigate the environmental impact of ships. Methanol as a marine fuel can reduce SOX and PM emissions by over 90%, the NOX between 30–50% and CO<sub>2</sub> by about 11% compared to those of heavy fuel oil (HFO) tier II (MAN, 2021). However, much like traditional two-stroke marine diesel engines, these engines lose about half of the fuel energy via exhaust gas and cooling fluids (MAN, 2020), underlining the importance of waste heat recovery (WHR).

Organic rankine cycle (ORC) WHR systems, on the other hand, have recently been a challenging choice to enhance ships' energy efficiency and reduce emissions. Recent studies on ORC WHRS for ships concentrate on optimising thermodynamic and thermo-economic performance as well as assessing environmental impacts. Konur et al. (2023) investigated the performance of ORC recovering the exhaust gas of marine engines and they stated that ORC WHRS can provide about a 5% reduction in overall fuel consumption. Pesyridis et al. (2023) proposed an exhaust gas ORC WHRS using R245fa as the working fluid, which decreases fuel consumption by 2.9% to 5.1%. Song and Gu (2015) used R141b (ODP > 0, GWP = 700) as a retardant in the mixtures and found that the system's net power could be enhanced by 13.3% when this specially designed mixture is employed instead of a pure working fluid. Kang et al. (2015) investigated the performance of mixtures made from hydrocarbons (HCs), hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs) for a geothermal ORC WHRS. They stated that R245fa/R600a (0.9/0.1) was the most favourable mixture among working fluids. Wu et al. (2016) examined the thermal and economic performance of an ORC system driven by hot air and various zeotropic mixtures, including R227ea/R245fa, Butane/R245fa, and RC318/R245fa. According to their results, optimal thermal performance is achieved when the cooling water temperature difference aligns closely with the temperature glide of the mixture in the condenser.

Research on zeotropic mixtures for marine WHR is limited and the studies mainly focus on working fluids and increasing the thermodynamic performance of mixtures made from HCs or hydrofluorocarbons HFCs. However, high GWP (>2,500) and ODP

(>0), highly flammable and toxic working fluids should not be used in a marine-type ORC WHR system that is expected to comply with maritime regulations. Therefore, this study investigates the energetic and exergetic performance of an exhaust gas-driven ORC WHR system using eco-friendly HFO and HCFO-based zeotropic mixtures in comparison with the existing studies. The primary objectives and scientific contributions are summarised as follows:

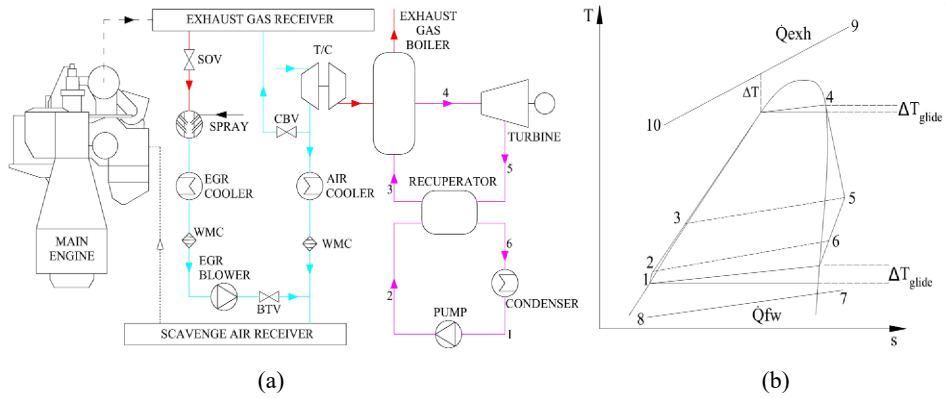
- Exhaust gas waste heat of a methanol-fuelled dual-fuel engine is analysed under different operating conditions for the modelled recuperative ORC WHR system using zeotropic mixtures, addressing the limited research in this area.
- Low environmental impact working fluids with very low GWP (<2) and zero ODP from hydrochlorofluoroolefins (HCFOs) and HFOs are selected instead of commonly used hydrofluorocarbons or hydrocarbons.
- The working fluids are mixed to analyse the energetic and exergetic performances under various mass fractions and temperature glides as well as evaporation pressures to reveal the superiorities of zeotropic mixtures.
- The improvement of the ORC WHRS performance by the temperature glide matching with the evaporator and condenser in certain conditions is evaluated.

## 2 Modelling of the ORC WHR system

### 2.1 ORC WHR system

The recuperative ORC WHR system and T-s diagram are schematically shown in Figures 1(a)–1(b). The ORC WHR system is integrated into the exhaust gas boiler of a methanol-fuelled engine. The evaporation occurs in the boiler and working fluid is sent to the turbine for power generation. After the expansion process, the fluid is sent to the recuperator to enhance the enthalpy of the fluid coming from the pump. Following the recuperator, the fluid is cooled in a condenser using fresh water, and then the liquid mixture is recirculated. In the condenser and evaporator, a temperature glide happens due to the zeotropic mixture's composition, which has varying boiling and dew point temperatures.

The main engine used in this study is a two-stroke dual-fuel engine which can burn MeOH and marine diesel oil (MDO) fuels, has five cylinders with 50 cm bore, and produces 7,860 kW brake power (@104 rpm and full load). The primary fuel is MeOH, and MDO is used as the pilot fuel to control knocking and misfiring (Babicz, 2015). The engine is operable in tiers II and III NOX control mode where the exhaust gas recirculation (EGR) unit is activated. The exhaust gas bypass (EGB) valve in the EGR system manages the switch between tiers II and III modes. In the EGR system, some of the exhaust gas is directed for cleaning, cooling, and blending with scavenge air before combustion. This method reduces the oxygen content by using CO<sub>2</sub> and enhances the heat capacity of the air, thereby lowering the peak temperature of combustion, which significantly contributes to thermal NOX formation (MAN, 2022). When both the EGR valve and the blower throttle valve are opened in tier III, the conditioned exhaust gas passes to the cooler then the mist catcher ensuring that no liquid water enters the cylinders.

**Figure 1** (a) The diagrams of the ORC WHR system (b) Temperature-entropy (see online version for colours)

The fuel consumption and exhaust gas properties are obtained using the computerised engine application system (CEAS) (MAN, 2020). According to the obtained data, the main engine's fuel consumption ranges from 344.8 to 368.2 g/kWh for MeOH as the primary fuel and from 13.9 to 8.8 g/kWh for MDO as the pilot fuel at 50–100% MCR, respectively. The exhaust gas mass flow rate ranges from 7.9 to 15.2 kg/s, while the exhaust temperature ranges from 211 to 219°C at 50–100% MCR, respectively. It is worthy of note that the exhaust temperatures are about 10–15°C lower at medium loads (70–80% MCR) compared to those of low or high loads.

## 2.2 Selection of working fluid for the ORC WHRS

The determination of the working fluid for an ORC WHR system is substantial in achieving high thermal efficiency and power output while keeping costs low. However, the selection must also consider regulatory and environmental frameworks, especially for marine-type ORC WHRS. The Montreal Protocol has phased out substances with high ODP, and the Council of the European Union and the European Parliament have gradually enacted regulations to eliminate fluorinated substances (EU, 2014). For an onboard ORC system, the selection of a working fluid is regulated by MARPOL Annex VI, which has banned chlorofluorocarbons and phased out hydrochlorofluorocarbons since January 2020. Additionally, EU-flagged ships must use fluids with a low GWP, set to be below 2,500 GWP, have started on 1 January 2020 (Glavan et al., 2022). Although natural hydrocarbons, siloxanes, and some hydrofluorocarbons meet the ODP and GWP limits, their flammability, toxicity, cost, and the need for a large heat transfer area are generally high (Mondejar et al., 2018). Besides, hydrofluoroolefins, are identified as one of the best substitutes due to their safe, eco-friendly physical properties and favourable thermo-economic performances (Mondejar et al., 2018; Akman and Ergin, 2023). Considering both thermo-economic parameters and regulations three working fluids, two from hydrofluoroolefins and one from hydrochlorofluoroolefin are selected, as given in Table 1. The working fluid selection criteria are as follows (Mondejar et al., 2018; Zhai et al., 2018):

- Fluids will have very low GWP (<10) and zero ODP.
- Fluids will be safe; lower or no flame propagation and low toxicity (A1 or A2L).
- The critical temperature will be as close to the source temperature as possible (>150°C).
- Normal boiling point (NBP) will be as close to heat sink temperature as possible.
- Normal boiling temperature difference between fluid compositions in the zeotropic mixtures will be between 1°C and 45°C.

**Table 1** Main features of the selected working fluids

| Working fluids | Type | Normal boiling point (°C) | Critical temperature (°C) | Critical pressure (kPa) | GWP | ODP | ASHRAE class*, ** |
|----------------|------|---------------------------|---------------------------|-------------------------|-----|-----|-------------------|
| R1336mzz (Z)   | HFO  | 33.453                    | 171.35                    | 2903                    | 2   | 0   | A1                |
| R1233zd (E)    | HCFO | 18.263                    | 166.45                    | 3623                    | 1   | 0   | A1                |
| R1224yd (Z)    | HFO  | 14.617                    | 155.54                    | 3337                    | 1   | 0   | A1                |
| R1234ze (Z)    | HFO  | 9.728                     | 150.12                    | 3530                    | 7   | 0   | A2L               |

Notes: \*A1 safety group classification: no flame propagation and lower toxicity.

\*\*A2L safety group classification: lower flammability and lower toxicity.

Source: NIST (2020), ASHRAE (2024) and Kondou et al. (2014)

### 3 Methodology

The workflow of the thermodynamic analysis is summarised in Figure 2. The whole process starts with obtaining the properties of the selected working fluids and zeotropic mixtures using the Refprop 10 database (NIST, 2020). The properties of each state of the ORC model are determined by writing a MATLAB code integrated with the Refprop. The coding algorithm is based on the iterative loops where the properties of each state are defined for each working fluid under different engine loads, evaporation and condensation pressures and temperatures, and assumptions. Properties like enthalpy, entropy and density are obtained as outputs of this process. The written code is capable of mixing and estimating the thermophysical properties of mixtures in case it complies with the predefined criteria explained in the previous section.

The system's main engine operates with a brake power ranging from 3,930 to 7,860 kW, within a load range of 50 to 100% of the maximum continuous rating (MCR) (MAN, 2020). The condenser maintains a sink temperature of 40°C, while the freshwater inlet temperature is set at 25°C. The turbine exhibits an isentropic efficiency ( $\eta_t$ ) of 0.75, similar to the pump's isentropic efficiency ( $\eta_p$ ) (Akman and Ergin, 2023; Yang and Yeh, 2015). The recuperator effectiveness is 0.8 and the recuperator outlet temperature is 47°C. The evaporation temperature of the working fluids is between 109°C and 169°C. In terms of the zeotropic mixture, the mass fraction varies between 0.1 and 0.9. The system also experiences a pressure drop of 2% of the maximum pressure across the lines, while the heat exchangers incur a heat loss of 2%.

Heat input to the system ( $\dot{Q}_m$ ) is calculated as follows,

$$\dot{Q}_{in} = \dot{m}_f (h_4 - h_3) \quad (1)$$

where  $\dot{m}_f$  is the mass flow rate of the working fluid and  $h$  is the enthalpy of the state. The thermal efficiency of the ORC ( $\eta_{th,ORC}$ ) is calculated as follows,

$$\eta_{th,ORC} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_t - \dot{W}_p}{\dot{Q}_{in}} = \frac{\dot{m}_f (h_4 - h_{5a}) \cdot \eta_t - \dot{m}_f (h_{2a} - h_1) / \eta_p}{\dot{Q}_{in}} \quad (2)$$

where  $\dot{W}_{net}$  is the net power output of ORC WHRS, which is calculated using the turbine power output ( $\dot{W}_t$ ) and pump power ( $\dot{W}_p$ ). Besides, the thermal efficiency of the power generation system ( $\eta_{th,PGS}$ ) is calculate as follows,

$$\eta_{th,PGS} = \frac{P_{br} + \dot{W}_{net}}{Q_{LHV} \dot{m}_{fuel}} \quad (3)$$

where  $P_{br}$  is the brake power output of main engine,  $Q_{LHV}$  is the lower heating value of fuel which is 19,900 kJ/kg for methanol, and  $\dot{m}_{fuel}$  is the mass flow rate of the exhaust gas at corresponding engine load. Exergy of states ( $x_i$ ) can be calculated using the enthalpy and entropy differences relative to the dead state conditions, where the dead state temperature ( $T_0$ ) and pressure ( $P_0$ ) are taken as 293.15 K and 101.15 kPa, respectively.

$$x_i = (h_i - h_0) - T_0 (s_i - s_0) \text{ state number } i \in \{1, 2, \dots, 9\} \quad (4)$$

Then, the exergy efficiency ( $\eta_{ex}$ ) of ORC WHRS is calculated as follows,

$$\eta_{ex} = \frac{\dot{W}_{net}}{\dot{Q}_{in} \left( 1 - \frac{T_0}{T_{hs}} \right)} \quad (5)$$

where  $T_{hs}$  is the heat source temperature which is calculated for each engine load. The exergy destruction in ORC components are calculated as follows,

$$\dot{X}_{des,p} = \dot{m}_f (x_1 - x_2) + \dot{W}_p \quad (6)$$

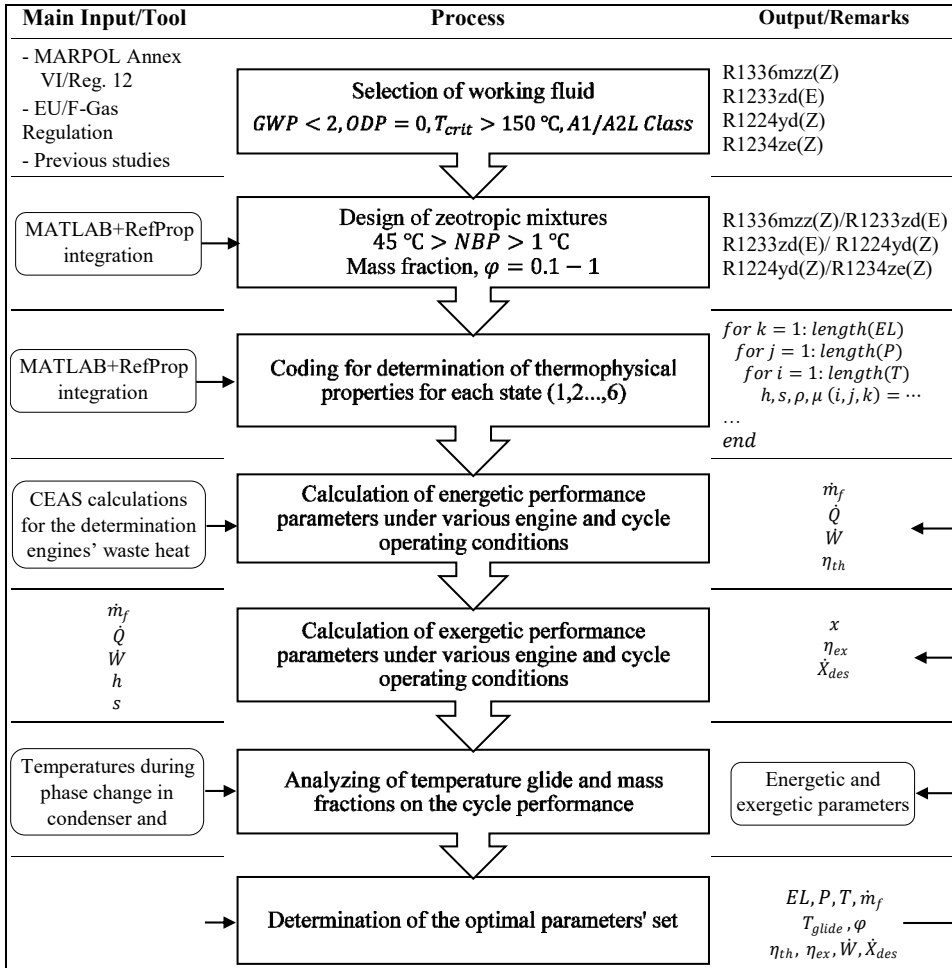
$$\dot{X}_{des,r} = \dot{m}_f (x_3 - x_2) + \dot{Q}_{in,r} \left( 1 - \frac{T_0}{T_{hs,r}} \right) \quad (7)$$

$$\dot{X}_{des,b} = \dot{m}_f (x_3 - x_4) + \dot{Q}_{in,b} \left( 1 - \frac{T_0}{T_{hs,b}} \right) \quad (8)$$

$$\dot{X}_{des,t} = \dot{m}_f (x_4 - x_5) - \dot{W}_t \quad (9)$$

$$\dot{X}_{des,c} = \dot{m}_f (x_6 - x_1) - \dot{Q}_{out,c} \left( 1 - \frac{T_0}{T_{hs,c}} \right) \quad (10)$$

where  $\dot{X}_{des,p}$ ,  $\dot{X}_{des,r}$ ,  $\dot{X}_{des,b}$ ,  $\dot{X}_{des,t}$  and  $\dot{X}_{des,c}$  are the exergy destruction in pump, recuperator, boiler, turbine and condenser, respectively.

**Figure 2** Workflow of the energetic and exergetic analyses

## 4 Results and discussion

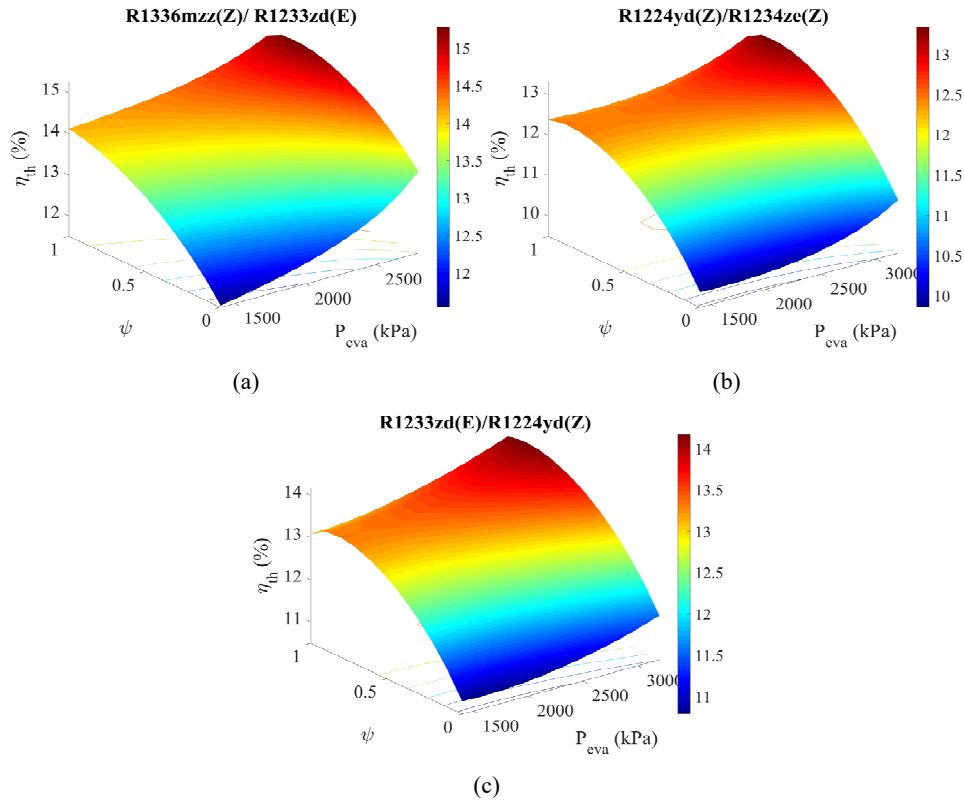
### 4.1 Analysis of thermal performance

Parametric analysis shows that increasing the evaporation pressure and engine load also increases the net power output. R1336mzz (Z)/R1233zd (E) (0.5/0.5) mixture shows the best net power output and up to 186 kW net power can be produced at 85% MCR. Using the same mixture, 252.9 kW net power output is obtained at full load. Besides, R1233zd (E)/R1224yd (Z) shows the poorest net power output performance among other mixtures. It is worthy of note that the critical temperature of the mixture is one of the primary factors in achieving high thermodynamic performance. The critical temperatures are 166.4°C for the R1336mzz (Z)/R1233zd (E) mixture, 149.8°C for the R1224yd

(Z)/R1234ze (Z) mixture, and 159.0°C for the R1233zd (E)/R1224yd (Z) mixture, each with a 0.5/0.5 mass fraction.

On the other hand, the integration of the ORC system remarkably increases the PGS brake thermal efficiency. The brake thermal efficiency of PGS without the ORC system ranges between 49.06% and 50.92% depending on the engine load. When the ORC WHR system is integrated, the PGS brake thermal efficiency increases to the approximate range of 50.3% and 52.4% when the R1336mzz (Z)/1233zd (E) mixture is used as the working fluid. It is worth noting that the ORC system operated at high loads (>85% MCR) and high evaporation pressure, generates more power, resulting in a greater increase in PGS brake thermal efficiency.

**Figure 3** ORC thermal efficiency with, (a) R1336mzz (Z)/R1233zd (E), (b) R1224yd (Z)/R1234ze (Z) (c) R1233zd (E)/R1224yd (Z) according to mass fraction and evaporation pressure (see online version for colours)



The effects of mass fraction and evaporation pressure on the thermal efficiency of ORC WHR systems using different zeotropic mixtures are presented in Figures 3(a)–3(c). As expected, R1336mzz (Z)/1233zd (E) has the best thermal performance yielding with a 14.94% efficiency. According to the surface plots, ORC with pure working fluids ( $\varphi = 1$ ) with a high critical temperature in the zeotropic mixture group has the highest thermal efficiency. For instance, pure R1336mzz (Z) has the highest thermal efficiency with 15.2% at 2520 kPa while R1224yd (Z) with 13.2% at 2,520 kPa has the lowest among the working fluids. Besides, as can be seen on the plots, it is also possible to have higher

thermal efficiency with zeotropic mixtures. The ORC WHRS thermal efficiency can be increased up to 9.7% using zeotropic mixtures compared to that of the ORC WHRS operated with pure working fluid.

#### 4.2 Exergetic performance analysis

The exergy performance of the zeotropic mixtures is analysed at various operating conditions for each mixture. According to the results, 70–80% MCR is the most suitable load range in terms of exergy efficiency. This is based on the higher net power output per exergy input to the system, along with the heat source temperature being close to the evaporation pressure, resulting in less entropy generation. The mass fraction, on the other hand, has a significant effect on the temperature glide which decreases the exergy destruction in the condenser. The R1336mzz (Z)/R1233zd (E) with 0.7/0.3 mass fraction has a 2.18°C glide highest among the other mixtures. The same mixture has also the highest temperature glide in the boiler calculated to be 1.15°C. The temperature glide allows for a more efficient alignment between the temperature profiles of the fluid and the heat source or sink. This matching decreases the irreversibilities during heat transfer, thus enhancing the exergy efficiency.

Besides, Figures 4(a)–4(c) shows the exergy destruction of zeotropic mixtures changing with evaporation pressure and mass fraction at 85% MCR. According to the results, the lower the evaporation pressure, the higher the exergy destruction. However, increasing the mass fraction of the working fluid with a higher critical temperature in the mixture decreases the exergy destruction. The R1336mzz (Z)/R1233zd (E) mixture has the lowest exergy destruction between 0.6/0.4–1/0 mass fraction range and above 2,700 kPa.

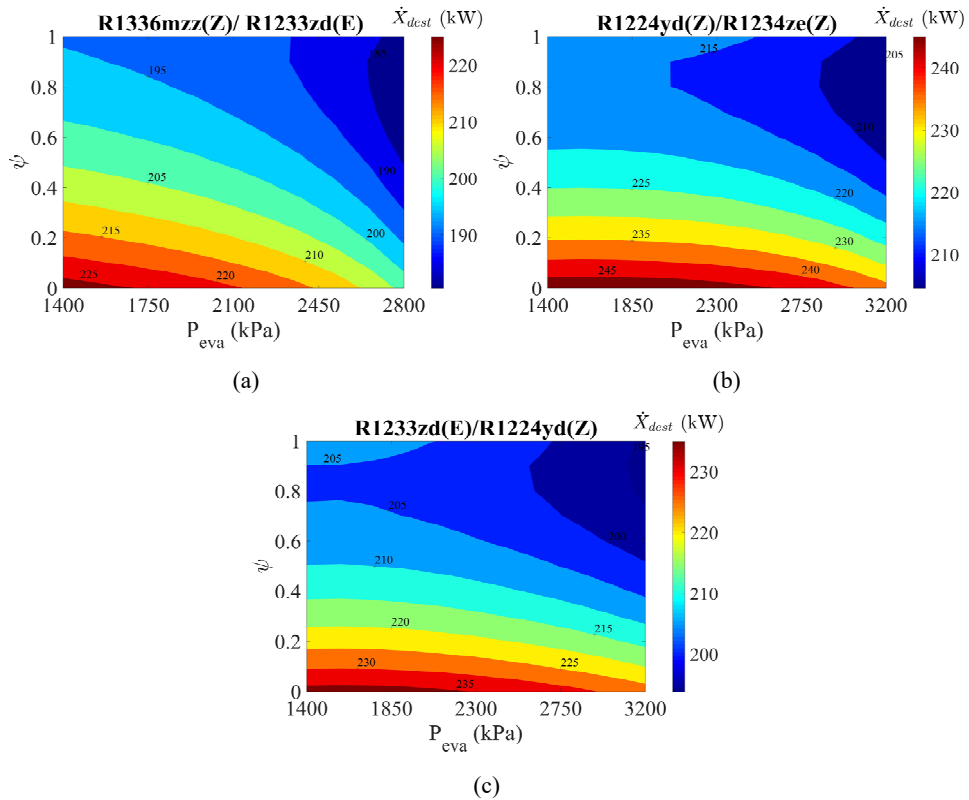
The evaluation criteria are selected to be the exergy efficiency and net power output. The optimal parameters are obtained using the max and min functions of the calculation matrixes in MATLAB. R1336mzz (Z)/R1233zd (E), has an evaporation pressure of 2,520 kPa and an evaporation temperature of 163.3°C, with a mass flow rate of 5.75 kg/s and a mixture ratio of 0.9/0.1. It produces a net power output of 164.6 kW, with a thermal efficiency of 14.9% and an exergy efficiency of 49.7%. Besides, R1224yd (Z)/R1234ze (Z), operates at a higher evaporation pressure of 2840 kPa and a lower evaporation temperature of 144.3°C, resulting in a net power output of 144.1 kW. It has a thermal efficiency of 13.1% and an exergy efficiency of 43.5%. On the other hand, R1233zd (E)/R1224yd (Z), operates at an evaporation pressure of 3020 kPa and a temperature of 154.5°C, producing 154.4 kW of net power. This mixture achieves a thermal efficiency of 14.0% and an exergy efficiency of 46.6%. The comparison of these mixtures provides insights into their relative efficiencies and performance under varying conditions. The exergy efficiency is maximum at 75% MCR where the entropy generation is the lowest. At this load point, the maximum net power output and the parameters dependent on these criteria are obtained. According to the evaluations, R1336mzz (Z)/R1233zd (E) exhibits the most favourable performance among other mixtures.

#### 4.3 Validation

The ORC model results are validated using the results of Zhai et al. (2018) who proposed a mixture design methodology for ORC systems. They used HCs, HFCs and HFOs for

mixtures and R1234ze (E)/R245fa is one of the mixtures they used for the ORC system. There is no recuperator in the ORC model in the reference study; therefore, the states in the configuration and the operating conditions used in this study are modified accordingly. The heat source in the reference study is hot air and water at 210°C and 150°C, respectively. According to the comparison results, at the same mass fraction of 0.3/0.7 and an evaporation temperature of 405.17 K, the difference between exergy efficiencies is less than 1%.

**Figure 4** Change of exergy destruction with respect to evaporation pressure and mass fraction, (a) R1336mzz (Z)/R1233zd (E) (b) R1224yd (Z)/R1234ze (Z) (c) R1233zd (E)/R1224yd (Z) (see online version for colours)



## 5 Conclusions

This study evaluates the energy and exergy performance of an exhaust gas-driven ORC WHR system using zeotropic mixtures in a methanol-fuelled engine, leading to the following conclusions:

- Using zeotropic mixtures instead of pure fluids increases thermal and exergy efficiency by 5.1% to 9.4%.

- Medium engine loads favour higher exergy efficiency and reduced fuel consumption, enhancing overall energy efficiency.
- The environmentally friendly and safe R1336mzz (Z)/R1233zd (E) mixture ( $GWP < 2$ ,  $ODP = 0$ ) is suitable for ORC applications onboard ships.
- Temperature glide improves performance, reducing exergy destruction by about 7.2% with the R1336mzz (Z)/R1233zd (E) mixture.
- Methanol-fuelled engines play a significant role in the maritime energy transition, and integrating an ORC WHR system with eco-friendly fluids can accelerate this process.

## Acknowledgements

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