

ULTRA-LOW GWP REFRIGERANT MIXTURES AS WORKING FLUIDS IN ORC FOR WASTE HEAT RECOVERY

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ABSTRACT

The F-gases regulations of the European Union have introduced restrictions and bans on refrigerants with global warming potential (GWP) above 150 in order to reduce the use of fluorinated gases (such as HFCs) by two-thirds compared to 2014 levels. As a result, significant research efforts have been lately oriented towards ultra-low GWP refrigerants in Vapor Compression and Organic Rankine Cycles (ORC). Meanwhile, the use of zeotropic mixtures in ORCs has been suggested as a promising second law efficiency improvement strategy in ORC applications. Considering the above, in the present study binary zeotropic mixtures of R32 and 6 ultra-low GWP fluids (R1234yf, R1234ze(E), n-pentane, propylene, isobutane and CO₂) at variable molar concentration ratios, corresponding to a total of 21 working fluid combinations, are evaluated as working fluids in ORCs for waste heat recovery at heat source temperatures ranging from 100 to 300 °C. In each case, the cycles are optimized with respect to the molar concentration ratio of the mixture components and the evaporation pressure. The relative exergetic efficiency improvement attained by the use of mixture fluid ORCs (ZORCs) compared to the optimized pure fluid ORCs (PORCs) running with their constituent components strongly depends on the mixture and the heat source temperature and typically ranges from a minimum of 0.56 % to a maximum of 62.92 %. For each binary mixture, ZORCs are mostly favourable compared to the PORCs of its components within a region between the critical high critical temperature component (HTC) and LTC critical temperatures. The application of ZORCs running with ultra-low GWP fluids is primarily appealing at very low heat source temperatures (100 and 120 °C), for which the relative exergetic efficiency benefits are maximized. Among the mixtures examined, n-pentane/isobutane exhibits the highest exergetic efficiency within a broad range of heat source temperatures.

1. INTRODUCTION

Organic Rankine Cycle (ORC) is a mature technology, which is considered as one of the most competitive solutions for power generation from low temperature heat sources such as geothermal and solar energy, biomass and industrial waste heat. In the case of the latter, the maximization of the exergetic or second law efficiency is typically the guiding design principle of ORC systems applications from a thermodynamic standpoint.

In this context, several methods have been proposed, such as the implementation of transcritical (or supercritical) cycles, which has been extensively investigated (Schuster *et al.*, 2010; Vetter *et al.*, 2013; Yağlı *et al.*, 2016) in the literature. An additional method is the use of zeotropic mixtures as working fluids, which can lead to improved matching of the working fluid and heat source and sink temperature profiles in the evaporator and the condenser, respectively, owing to the variable-temperature phase change (glide) of these working fluids in these heat exchange processes (Heberle *et al.*, 2012; Liu *et al.*, 2014). Numerous studies have been carried out concerning a wide range of refrigerants as components of the mixtures. Lecompte *et al.* (2014) performed exergy analysis of seven zeotropic mixtures with cyclohexane, hexane, isobutane, isopentane, pentane, R245fa and R365mfc as constituent components.

They concluded that, at heat source temperature of 150 °C, an exergetic efficiency increase within the range of 7.1 and 14.2% can be achieved compared to pure working fluids, while the maximum efficiency is attained by the isobutane/isopentane mixture at 0.81/0.19 molar fraction. Feng *et al.* (2015) conducted a techno-economic optimization procedure for an R245fa/R227ea mixture, based on genetic algorithms. They claimed that a second law efficiency of 59.23% can be reached at 120 °C heat source temperature. This high value resulted from the low pinch point temperature difference that was assumed in the evaporator. According to Wu *et al.* (2016), who studied the performance of R227ea/R245fa, butane/R245fa and RC318/R245fa mixtures, the maximum energetic and exergetic efficiencies occur in the fraction in which the temperature glide in the condenser approaches the temperature increase of the cooling source. Satanphol *et al.* (2017) examined the subcritical and supercritical cycles of binary, ternary and quaternary zeotropic mixtures of various refrigerants for waste heat recovery and reported an 8% increase in electrical power output. Finally, Zhai *et al.* (2018) proposed a mixture design method that attributes to the mixture similar critical temperature and environmental behavior with the optimum pure working fluid and matches the glide in the condenser with the temperature profile of the cooling medium. The exergetic efficiency improvement was estimated at 6.4% relative to the optimal pure working fluid R236ea.

However, besides efficiency improvement, environmental issues related to the Global Warming Potential (GWP) and Ozone Depletion Potential (ODP) indexes of the constituent components have to be addressed. Within this framework, a legislative context has been developed, including the Montreal (European Parliament, 2000) and Kyoto Protocol (United Nations, 1997), leading to the prohibition of fluids with non-zero ODP and very high GWP, respectively. In addition, the European Union has enacted regulations regarding fluorinated gases (F-gases) (European Parliament, 2014) aiming to reduce their use by two thirds compared to 2014 levels. Specifically, perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) are addressed and, among others, a maximum GWP limit of 150 is set concerning the use of HFCs in various equipment, such as domestic and commercial refrigerators and freezers and movable room air-conditioning units. This fact effects significantly the availability of common fluids for Vapor Compression and ORC systems.

Consequently, focus is currently given to alternatives, including hydrofluoroolefins (HFOs) and natural hydrocarbons (HCs), which have low GWP and zero ODP values. As it was mentioned above, Lecompte *et al.* (2014) examined mixtures with cyclohexane, hexane, isobutane, isopentane and pentane as components. Liu *et al.* (2014) studied the effect of condensation temperature glide on geothermal and cogenerative biomass ORCs for mixtures comprising natural HCs and siloxanes. It was concluded that isobutane/n-pentane and octane/decane mixtures were the optimal in terms of exergetic efficiency, respectively. Braimakis *et al.* (2015) investigated the binary mixtures of five natural HCs in subcritical and supercritical ORC for waste heat recovery. It was stated that zeotropic mixtures lead to better performance than pure fluids, especially in supercritical cycles. Other researches have emphasized on the use of HC-based mixtures for waste heat recovery from engines (Shu *et al.*, 2014; Song and Gu, 2015). Lastly, the optimization of a subcritical cycle with heat source temperature from 80 to 180 °C and mixtures containing pentane, isopentane, neopentane, butane, isobutane and propane was conducted by Sanchez *et al.* (2018). Apart from the exergetic efficiency, the net power output and the overall conductance of the heat exchangers were considered for the optimization.

The present work focuses on the use of natural HCs and HFOs with ultra-low GWP for a subcritical waste heat recovery ORC, as both pure working fluids and binary mixtures. In addition, carbon dioxide (CO₂) is evaluated as mixture component. The performance assessment is conducted based on the exergetic efficiency and possible improvements are pointed out. The scope of the research arises from the fact that no investigation has been conducted in the literature regarding the mixtures examined in this paper.

2. METHODOLOGY

2.1 System description

The study aims to provide insight into the exergetic performance of ORC with pure working fluids of very low environmental impact, as well as with their mixtures. Hence, the system consists of a conventional subcritical ORC system without additional features, such as a recuperator between the expander outlet and pump inlet or double stage expansion. As far as the heat source is considered, the waste heat carrier is simulated by a 2 bar dry atmospheric air stream of temperature ranging from 100 to 300 °C and maximum capacity of 1000 kW_{th}.

In particular, the working fluid at saturated liquid state enters the pump, where its pressure increases through the consumption of mechanical power. Next, it is transferred into the heater (preheater, evaporator and superheater) where it absorbs heat from the heat source and evaporates. The superheated steam then expands in the expander and the mechanical work produced is converted into electricity by means of an electric generator. Afterwards, the low-pressure superheated steam flows through the condenser where it releases heat and condenses so that the cycle is repeated.

2.2 Working fluids

The working fluids that are investigated constitute of six ultra-low GWP (below 10) fluids with zero ODP, in conjunction with the refrigerant R32. More specifically, two HFOs, three HCs, CO₂ and one HFC are considered. The mixtures derived from them are zeotropic at all concentration ratios. The examined pure fluids and their basic properties (critical pressure and temperature, ODP, GWP, type) are summarized in Table 1, while their saturation curves in the T - s diagram are presented in Figure 1.

Table 1: Basic properties of the evaluated pure fluids.

Working fluid	p_{cr} (bar _a)	T_{cr} (°C)	ODP	GWP	Type
n-pentane (R601)	33.7	196.6	0	4	HC
Isobutane (R600a)	36.5	134.7	0	3	HC
R1234ze(E)	33.4	109.4	0	6	HFO
R1234yf	33.8	94.7	0	4	HFO
Propylene (R1270)	46.2	91.9	0	1.8	HC
R32	57.8	78.1	0	675	HFC
CO ₂ (R744)	73.8	31.0	0	1	–

As it can be observed, the critical temperature varies substantially, namely from approximately 30 °C for CO₂ to 200 °C for n-pentane. This fact enables the assessment of a wide range of heat source temperatures without transition from subcritical to supercritical cycle. With regard to the type of fluids, n-pentane is slightly dry, CO₂ and R32 are wet and the others tend to be isentropic. Additionally, HFOs and CO₂ have lower latent heat of vaporization. Finally, it is noted that, although R32 has a very high GWP index compared to the others, it is included in the study because it is currently widely used in commercial products as a substitute of other refrigerants with higher GWP, like R410A.

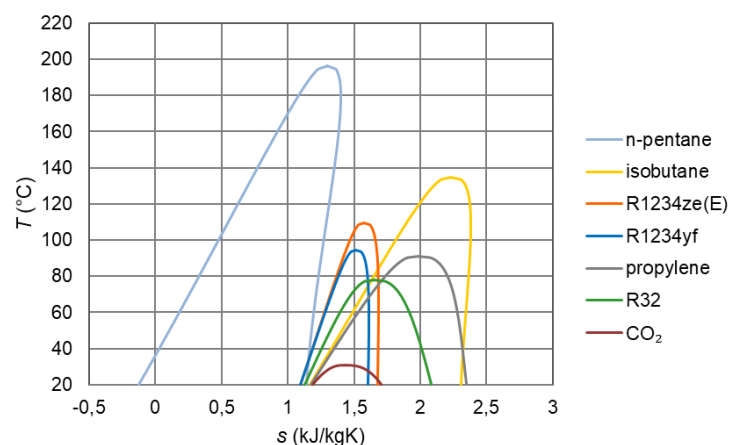


Figure 1: Saturation curves of the evaluated fluids in T - s diagram.

2.3 Modeling and assumptions

Regarding the modeling of the system, calculations were performed in steady-state conditions using simple numerical models of the components and their corresponding processes. Namely, typical efficiencies for the expander, the pump, the motor of the pump and the generator were assumed. In addition, the analysis was carried out using specific pinch point temperature differences in the heat exchangers, which operate with countercurrent streams. Moreover, a maximum superheating of 10 K and certain cooling water inlet temperature and temperature increase were imposed. Concerning the heat source, no limit was set for its outlet temperature. Eventually, pressure drops and heat losses across the system were neglected, whereas changes in the mixture composition due to the two-phase hold-up (Zhao and Bao, 2014) were also not taken into consideration. The main model assumptions are listed in Table 2.

The optimization procedure aims at the maximization of the exergetic efficiency for each working fluid (pure or mixture) at different heat source temperatures. For each heat source temperature between 100 and 300 °C, with increments of 20 K, different evaporation pressures between 2 and 42 bar_a with 10 bar_a steps, were evaluated for each mixture in different compositions in order to find the optimal composition and evaporation pressure. With regard to the mixtures, molar fractions ranging from 0.9/0.1 to 0.1/0.9, in steps of 0.1, were investigated. It is noted that only binary mixtures were taken into account since multi-component mixtures increase complexity with negligible efficiency benefits (Chys *et al.*, 2012; Abadi and Kim, 2017). The simulations were conducted with the Aspen Plus™ software and the properties of the working fluids were calculated through the Peng-Robinson equation of state with Boston-Mathias alpha property method (2011).

Table 2: Model assumptions.

Parameter	Value
Expander isentropic efficiency (-)	0.75
Pump isentropic efficiency (-)	0.80
Pump motor isentropic efficiency (-)	0.85
Generator efficiency (-)	0.95
Cooling water inlet temperature (°C)	20
Cooling water temperature increase (K)	15
Evaporator pinch point (K)	10
Condenser pinch point (K)	10
Maximum superheating (K)	10

In order to evaluate the performance of pure fluids and their mixtures in terms of exergetic efficiency, relevant performance indicators are specified. Firstly, the exergetic or second law efficiency is defined as the ratio of the net generated power $P_{e,net}$ to the exergy rate input \dot{E}_{hs} of the heat source:

$$\eta_{ex} = \frac{P_{e,net}}{\dot{E}_{hs}} \quad (1)$$

where the exergy rate of the heat source expresses the maximum work that could be done if the system was brought into equilibrium with its surroundings (reference conditions):

$$\dot{E}_{hs} = \dot{m}_{hs} \left[\left(h_{hs,in} - h_{hs,ref} \right) - T_{ref} \left(s_{hs,in} - s_{hs,ref} \right) \right] \quad (2)$$

In addition to the exergetic efficiency, the system performance can be also assessed based on the energetic and heat utilization efficiency of the system. Energetic or first law efficiency represents the ratio of the net produced power to the heat input, while heat utilization efficiency expresses the amount of the maximum heat input that is absorbed by the working fluid. The maximum possible heat input could be attained if the heat source was cooled to the reference temperature. As a result, the aforementioned indexes are described by the following equations, respectively:

$$\eta_{en} = \frac{P_{e,net}}{\dot{Q}_{hs}} \quad (3)$$

$$\eta_{hs,u} = \frac{\dot{Q}_{hs}}{\dot{Q}_{hs,max}} \quad (4)$$

According to Braimakis *et al.* (2015), the exergetic efficiency can be expressed as a function of the energetic and heat utilization efficiencies:

$$\eta_{ex} = \eta_{en} \eta_{hs,u} \frac{h_{hs,in} - h_{ref}}{h_{hs,in} - h_{hs,ref} - T_{ref} (s_{hs,in} - s_{hs,ref})} \quad (5)$$

Thus, if the heat source properties (specific enthalpy and entropy) are defined, the exergetic efficiency depends entirely on the product of these factors. This relationship facilitates the interpretation of the following results.

3. RESULTS AND DISCUSSION

Based on the aforementioned optimization process, the maximum exergetic efficiency of the cycle with each pure working fluid (PORC) and their zeotropic binary mixtures (ZORC) is depicted in Figure 2. In the case of ZORCs, each curve corresponds to all the mixtures whose high critical temperature component (HTC) is the same fluid. The points of each line represent the mixture of the particular HTC, with the optimal molar fraction and evaporation pressure, that achieves the maximum second law efficiency in the respective heat source temperature. It is noted that the curves of PORCs with propylene and R32 stop in a low driving temperature. This happens because, at higher heat source temperatures, the pinch point in the evaporator may not be met without transition to supercritical state or due to the fact, that in this temperature range the stream exiting the expander may be in the two-phase region. The latter is caused from the saturation curves of these fluids (Figure 1).

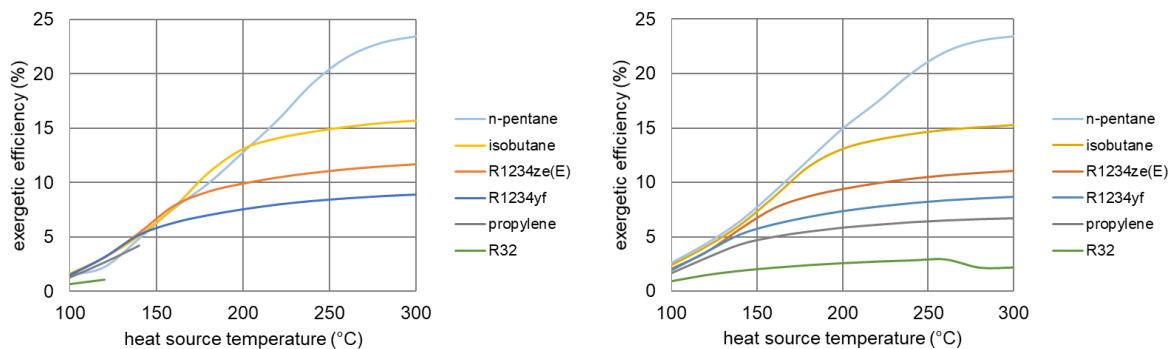


Figure 2: Maximum exergetic efficiency of the optimized PORCs (left) and ZORCs (right) of each HTC with respect to heat source temperature.

Regarding the form of the figures, it is observed that the exergetic efficiency increases proportionally with respect to the heat source temperature, but in a declining rate. As the heat source temperature increases, the evaporation temperature and pressure rise. In this way, the energetic efficiency is improved due to the greater enthalpy drop in the expander and thus, the higher produced power. Also, at low heat source temperatures (100-150 °C), the evaporator pinch point is located at the preheater outlet and so, higher temperature leads to better heat utilization. As a result, second law efficiency is enhanced. However, a further increase in temperature leads to a constant, maximum evaporation pressure and to the shift of the pinch point position in the preheater inlet. Hence, energetic and heat utilization efficiencies begin to stabilize, resulting in the exergetic efficiency stall. The turning point

depends on the critical temperature of the working fluid and its relation to the driving temperature. For higher critical point temperature fluids, as in the case of isobutane and n-pentane, the heat source temperature, in which exergetic efficiency improvement rate begins to decline, is higher.

As far as PORCs are considered, n-pentane is the most favourable fluid for temperatures above 200 °C, while at lower temperatures its performance is deteriorated. This is mainly attributed to the low energetic efficiency because of the low operating evaporation pressures in the low temperature region. Additionally, propylene and R32 cycles are technically feasible only for temperatures below 140 and 120 °C respectively, whereas CO₂ subcritical PORC cannot be implemented at all.

In the context of ZORCs, the same pattern is followed. However, mixtures containing n-pentane as HTC exhibit the highest efficiency within the whole range of heat source temperatures. Furthermore, ZORCs of propylene and R32 are plausible, but are the least effective among the other mixtures. Compared to the PORCs, ZORCs running with a specific HTC achieve, in general, higher exergetic efficiencies than the PORCs with the same working fluid. This is more clearly concluded from Figure 3, in which the relative exergetic efficiency difference between the optimized PORCs and ZORCs of each HTC, as well as the relative difference between their global optimal cycles is presented, with respect to the driving temperature. In particular, the efficiency improvement for the ZORC of each fluid is maximized at lower heat source temperatures, up to 96.85 % for n-pentane at 120 °C and is eliminated as the temperature increases, which implies that at high temperatures, PORCs are preferred in terms of second law efficiency. The temperature, above which ZORCs of a HTC become inefficient, compared to their PORCs, varies from 140 °C for R1234yf to 280 °C for n-pentane. However, for the global optimal ZORCs, in general, efficiency enhancement is attained within the whole range of heat source temperatures, except for the temperature of 300 °C. Similarly, it has a declining trend with respect to driving temperature and the maximum improvement is 62.44 % and occurs at 100 °C.

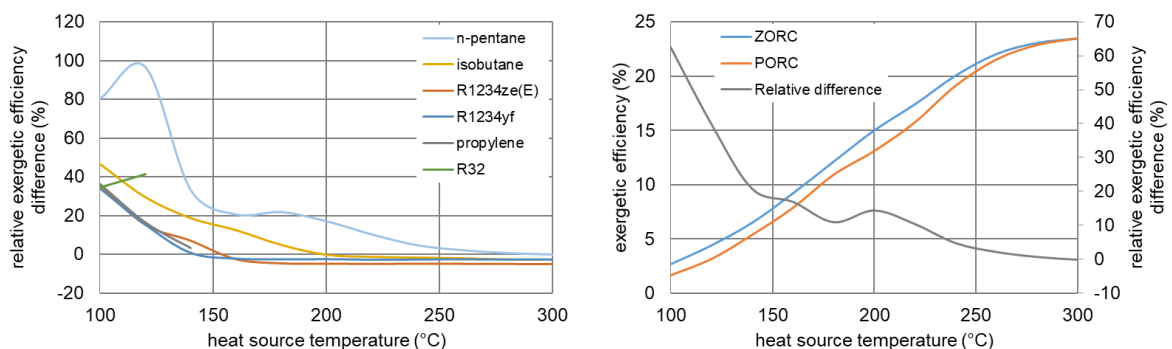


Figure 3: Relative exergetic efficiency difference between the optimized PORCs and ZORCs of each HTC (left) and their global optimal cycles (right) with respect to heat source temperature.

The previous results compare the efficiency of ZORCs to the PORC of only one component of each mixture. For this purpose, a more detailed analysis is presented below in which the comparison is conducted with the PORC of the optimal component of each mixture. In this context, the relative exergetic efficiency difference between the optimized ZORCs of each HTC and the optimized PORCs running with their constituent components is illustrated in Figure 4. From these figures, the curves with propylene and R32 as HTC are excluded, given that their cycles are feasible only for temperatures below 140 °C. Initially, it can be established that the efficiency benefit is maximized, in most cases, at temperatures of 100 and 120 °C, while above 280 °C all ZORCs lead to poor performance relative to PORCs of their most efficient component. The relative efficiency improvement in this temperature range varies from a minimum of 0.56 to a maximum of 62.92 %, corresponding to the n-pentane/isobutane and n-pentane/R1234ze(E) mixture, respectively. However, the benefit for all HTC mixtures is substantially reduced above the critical temperature of the HTCs. Also, it is observed that, although the low critical temperature components (LTC) R32 and CO₂ lead, in principle, to infeasible PORCs, they can enhance exergetic efficiency if they are combined with HTCs and especially with HTCs of lower critical temperature, regarding CO₂. The above can be explained based on the optimal composition e.g. the molar concentration of the components of each mixture, which is analyzed subsequently.

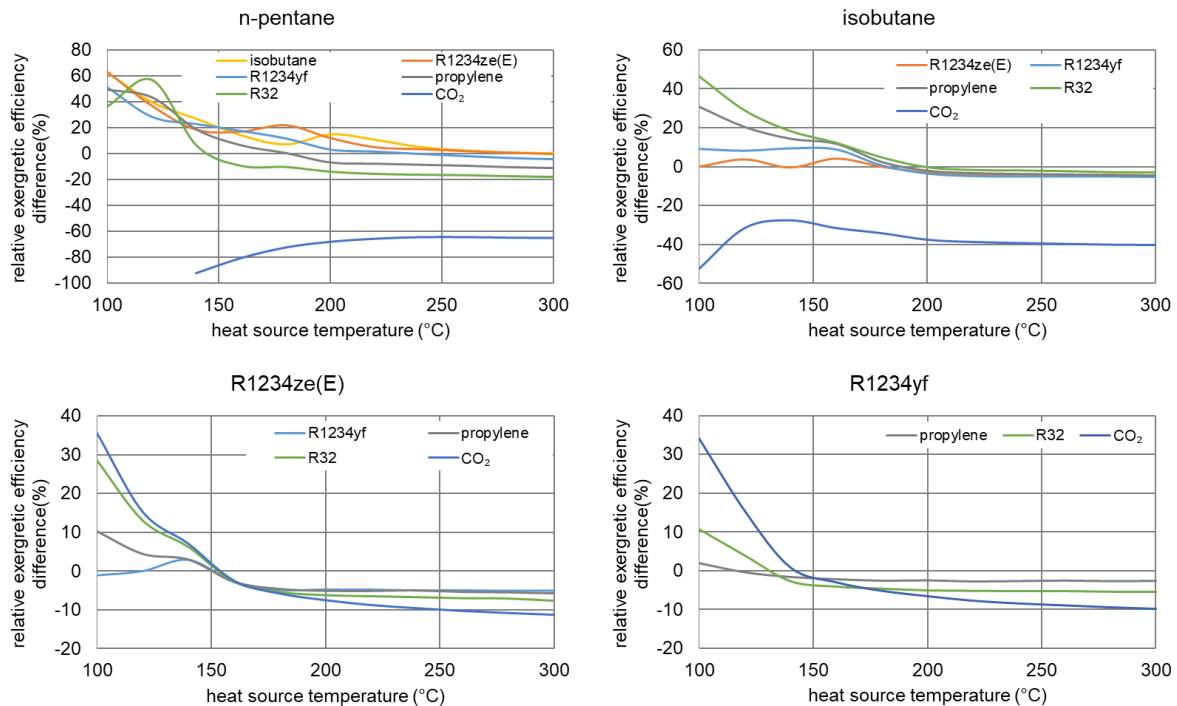


Figure 4: Relative exergetic efficiency difference between the optimized ZORCs of each HTC and the PORCs of their constituent components as a function of heat source temperature.

The aggregated results are summarized in Tables 3, 4. Namely, the exergetic efficiency, the working fluid, the molar composition (for ZORCs) and the evaporation pressure of the optimized ZORCs and PORCs are listed in Table 3, whereas the optimal LTC and HTC molar concentration for the ZORCs of each HTC are presented in Table 4, with respect to driving temperature. Concerning the composition, it is worth noting that it determines the temperature glides in the heat exchangers, which lead, in principle, to exergetic efficiency benefits. Thus, for each HTC, the optimal LTCs have significantly lower critical temperatures. This stems from the effect of the temperature glide, since it is diminished for mixtures with components of similar critical temperature. In addition, it is shown that, apart from n-pentane, the optimal ZORCs tend to be transformed into PORCs (no LTC and HTC molar concentration equal to 1.0 for the corresponding HTCs in Table 4) within a wide range of heat source temperatures. In order to understand the impact of the mixture composition, n-pentane mixtures are considered since they exhibit the greatest variability in terms of LTCs and concentration ratios.

At heat source temperatures up to 140 °C, the driving temperature approaches the critical temperature of the LTC (isobutane) and is much lower than the critical temperature of n-pentane. As a result, the PORC of isobutane would have relatively high evaporation pressure compared to the PORC of n-pentane and thus, higher energetic efficiency. However, although the mixture of these components leads to a lower evaporation pressure and consequently lower energetic efficiency, the temperature glides enhance heat utilization, which compensates the reduced energetic efficiency. At 140 °C, the heat source is above the critical temperature of isobutane, leading to increased evaporation pressure. This fact, along with the smaller impact of the corresponding temperature glides at this temperature, causes an increment in isobutane composition. For temperatures of 160 and 180 °C, the driving temperature is sufficiently higher than the critical temperature of R1234ze(E) resulting in high evaporation pressure in its PORC. Hence, minimum concentrations of n-pentane occur. Between 200 and 220 °C, the PORCs of n-pentane and isobutane have lower exergetic performance than the optimized mixture. Concerning isobutane, this happens due to the high exergy destruction in the evaporator at 220 °C, because of the much higher heat source temperature. Regarding n-pentane, it has sufficient exergetic performance, but it cannot surpass the positive impact of the temperature glides. Thus, the optimal fluid is a mixture. Lastly, at temperatures higher than 240 °C, n-pentane is superior to other fluids and therefore, it is the dominant component of the optimized mixtures, whereas its PORC exhibits the highest efficiency at 300 °C.

Table 3: Exergetic efficiency, working fluid, molar composition (for ZORCs) and evaporation pressure of the optimized ZORCs and PORCs as a function of heat source temperature.

T_{hs} (°C)	ZORCs				PORCs		
	η_{ex} (%)	Working fluid	C_{opt}	p_{ev} (bar)	η_{ex} (%)	Working fluid	p_{ev} (bar)
100	2.66	n-pentane/isobutane	0.4/0.6	6	1.64	isobutane	10
120	4.39	n-pentane/isobutane	0.6/0.4	6	3.14	isobutane	14
140	6.48	n-pentane/isobutane	0.3/0.7	10	5.36	R1234ze(E)	26
160	9.19	n-pentane/R1234ze(E)	0.1/0.9	30	7.86	R1234ze(E)	34
180	12.11	n-pentane/R1234ze(E)	0.2/0.8	34	10.91	isobutane	30
200	14.99	n-pentane/isobutane	0.2/0.8	30	13.11	isobutane	34
220	17.40	n-pentane/isobutane	0.3/0.7	30	15.77	n-pentane	14
240	20.05	n-pentane/isobutane	0.8/0.2	26	19.14	n-pentane	18
260	22.03	n-pentane/isobutane	0.8/0.2	30	21.55	n-pentane	26
280	23.05	n-pentane/R1234ze(E)	0.9/0.1	30	22.88	n-pentane	30
300	23.46	n-pentane/isobutane	0.9/0.1	30	23.48	n-pentane	30

Table 4: Optimal LTC and HTC molar concentration for the ZORCs of each HTC as a function of heat source temperature.

T_{hs} (°C)	n-pentane	isobutane	R1234ze(E)	R1234yf	propylene	R32
100	isobutane (0.4)	R32 (0.6)	CO ₂ (0.9)	CO ₂ (0.9)	CO ₂ (0.9)	CO ₂ (0.9)
120	isobutane (0.6)	R32 (0.7)	CO ₂ (0.9)	CO ₂ (0.9)	CO ₂ (0.9)	CO ₂ (0.9)
140	isobutane (0.3)	R32 (0.8)	CO ₂ (0.9)	CO ₂ (0.9)	CO ₂ (0.9)	CO ₂ (0.9)
160	R1234ze(E) (0.1)	R32 (0.7)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.9)
180	R1234ze(E) (0.2)	R32 (0.8)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.9)
200	isobutane (0.2)	– (1.0)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.9)
220	isobutane (0.3)	– (1.0)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.9)
240	isobutane (0.8)	– (1.0)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.9)
260	isobutane (0.8)	– (1.0)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.9)
280	R1234ze(E) (0.9)	– (1.0)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.8)
300	– (1.0)	– (1.0)	– (1.0)	– (1.0)	CO ₂ (0.9)	CO ₂ (0.8)

4. CONCLUSIONS

This paper investigates the use of ultra-low GWP binary refrigerant mixtures as working fluids in ORC for waste heat recovery. Seven environmentally friendly pure fluids of various critical temperatures and pressures were included. The study revealed the design versatility provided by zeotropic mixtures, as well as their exergetic efficiency benefits. In general, n-pentane appears to be superior to other fluids, both in PORC and ZORC operation, whereas ZORCs appear to have better exergetic performance at low driving temperatures. The increase in second law efficiency at low temperatures amounts to almost 60 %, in the case of n-pentane/isobutane mixture, which constitutes the most favourable mixture within a wide range of heat source temperatures, outperforming fluorinated mixtures.

Moreover, two factors were identified as decisive for the exergetic efficiency. On the one hand, the relation between the heat source temperature and the critical temperature of the working fluid defines the evaporation pressure affecting energetic efficiency and on the other hand, the temperature glide in the heat exchangers influences heat utilization. The optimal combination of them determines the

composition of the mixture, regarding not only its constituent components, but also their concentration ratio.

Ultimately, some future work recommendations are made. In order to enhance the efficiency at high heat source temperatures, the use of a recuperator is proposed, exploiting the temperature glide in the condenser. In this way, lower heat input is provided and energetic efficiency is enhanced leading potentially to an increase in exergetic efficiency. Nonetheless, despite the efficiency improvements due to ultra-low GWP mixtures, a more holistic analysis should be carried out to examine their feasibility in techno-economic terms. Regarding this, technical issues such as the size of the heat exchangers, the pressure drops and the change in mixture composition during operation should be evaluated.

NOMENCLATURE

C	molar concentration ratio	(–)
\dot{E}	exergy rate	(kW)
h	specific enthalpy	(kJ/kg)
\dot{m}	mass flow rate	(kg/s)
p	absolute pressure	(bar _a)
P	power	(kW)
\dot{Q}	heat flux	(kW)
s	specific entropy	(kJ/kgK)
T	temperature	(°C)

Greek symbols

η	efficiency	(–)
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Subscripts

cr	critical
e	electric
en	energetic
ev	evaporator
ex	exergetic
hs	heat source
in	inlet
max	maximum
net	net
opt	optimal
ref	reference
u	utilization

Abbreviations

GWP	Global Warming Potential
HC	hydrocarbon
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
HTC	high critical temperature component
LTC	low critical temperature component
ODP	Ozone Depletion Potential
ORC	Organic Rankine Cycle
PORC	Organic Rankine Cycle with pure fluid as working fluid
PFC	perfluorocarbon
ZORC	Organic Rankine Cycle with zeotropic mixture as working fluid

REFERENCES

- Aspen Technology Inc. Aspen one V7, process optimization for Engineering Manufacturing and Supply Chain. Aspen Plus V 7.3 ed. Burlington, ON, Canada: Aspen Technology; 2011.
- Abadi, G.B., Kim, K.C., 2017, Investigation of organic Rankine cycles with zeotropic mixtures as a working fluid: Advantages and issues, *Renew. Sust. Energ. Rev.*, vol. 73, p. 1000-1013.
- Braimakis, K., Preißinger, M., Brüggemann, D., Karellas, S., Panopoulos, K., 2015, Low grade waste heat recovery with subcritical and supercritical Organic Rankine Cycle based on natural refrigerants and their binary mixtures, *Energy*, vol. 88, p. 80-92.
- Chys, M., van den Broek, M., Vanslambrouck, B., De Paepe, M., 2012, Potential of zeotropic mixtures as working fluids in organic Rankine cycles, *Energy*, vol. 44, no. 1, p. 623-632.
- European Parliament, Council of the European Union. Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer. 2000.
- European Parliament, Council of the European Union. Regulation (EU) No 517/2017 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006. 2014.
- Feng, Y., Hung, T., Greg, K., Zhang, Y., Li, B., Yang, J., 2015, Thermoeconomic comparison between pure and mixture working fluids of organic Rankine cycles (ORCs) for low temperature waste heat recovery, *Energy Convers. Manage.*, vol. 106, p. 859-872.
- Heberle, F., Preißinger, M., Brüggemann, D., 2012, Zeotropic mixtures as working fluids in Organic Rankine Cycles for low-enthalpy geothermal resources, *Renew. Energ.*, vol. 37, no. 1, p. 364-370.
- Lecompte, S., Ameel, B., Ziviani, D., van den Broek, M., De Paepe, M., 2014, Exergy analysis of zeotropic mixtures as working fluids in Organic Rankine Cycles, *Energy Convers. Manage.*, vol. 85, p. 727-739.
- Liu, Q., Duan, Y., Yang, Z., 2014, Effect of condensation temperature glide on the performance of organic Rankine cycles with zeotropic mixture working fluids, *Appl. Energy*, vol. 115, p. 394-404.
- Sanchez, C.J.N., Gosselin, L., da Silva, A.K., 2018, Designed binary mixtures for subcritical organic Rankine cycles based on multiobjective optimization, *Energy Convers. Manage.*, vol. 156, p. 585-596.
- Satanphol, K., Pridasawas, W., Suphanit, B., 2017, A study on optimal composition of zeotropic working fluid in an Organic Rankine Cycle (ORC) for low grade heat recovery, *Energy*, vol. 123, p. 326-339.
- Schuster, A., Karellas, S., Aumann, R., 2010, Efficiency optimization potential in supercritical Organic Rankine Cycles, *Energy*, vol. 35, no. 2, p. 1033-1039.
- Shu, G., Gao, Y., Tian, H., Wei, H., Liang, X., 2014, Study of mixtures based on hydrocarbons used in ORC (Organic Rankine Cycle) for engine waste heat recovery, *Energy*, vol. 74, p. 428-438.
- Song, J., Gu, C.-w., 2015, Analysis of ORC (Organic Rankine Cycle) systems with pure hydrocarbons and mixtures of hydrocarbon and retardant for engine waste heat recovery, *Appl. Therm. Eng.*, vol. 89, p. 693-702.
- United Nations. Kyoto, Japan: Kyoto Protocol. 1997.
- Vetter, C., Wiemer, H.-J., Kuhn, D., 2013, Comparison of sub-and supercritical Organic Rankine Cycles for power generation from low-temperature/low-enthalpy geothermal wells, considering specific net power output and efficiency, *Appl. Therm. Eng.*, vol. 51, no. 1-2, p. 871-879.
- Wu, Y., Zhu, Y., Yu, L., 2016, Thermal and economic performance analysis of zeotropic mixtures for Organic Rankine Cycles, *Appl. Therm. Eng.*, vol. 96, p. 57-63.
- Yağlı, H., Koç, Y., Koç, A., Görgülü, A., Tandiroğlu, A., 2016, Parametric optimization and exergetic analysis comparison of subcritical and supercritical organic Rankine cycle (ORC) for biogas fuelled combined heat and power (CHP) engine exhaust gas waste heat, *Energy*, vol. 111, p. 923-932.
- Zhai, H., An, Q., Shi, L., 2018, Zeotropic mixture active design method for organic Rankine cycle, *Appl. Therm. Eng.*, vol. 129, p. 1171-1180.
- Zhao, L., Bao, J., 2014, The influence of composition shift on organic Rankine cycle (ORC) with zeotropic mixtures, *Energy Convers. Manage.*, vol. 83, p. 203-211.