ANALYSIS OF LOW GLOBAL WARMING POTENTIAL ALTERNATIVES TO HFC-245FA IN MICRO SCALE LOW TEMPERATURE ORGANIC RANKINE CYCLES

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ABSTRACT

The Organic Rankine Cycle is a power cycle for the valorisation of low-temperature heat sources, being similar to a conventional Rankine cycle, but using an organic working fluid instead of water. Focusing on micro-scale low-temperature applications up to 100ºC, HFC-245fa and HFC-134a are the most common working fluids, which stands out for its suitable thermodynamic and security properties. Nevertheless, due to new legislations, finding a low global warming potential working fluid is becoming increasingly necessary. New HFOs and HCFOs have been recently presented as potential low GWP alternatives for their use in low-temperature micro-scale ORC technology. The purpose of the present study is to analyse the behaviour of these low-GWP substitutes in typical configurations, basic cycle and regenerative cycle, under generation and cogeneration operating conditions. The different working fluids will be tested in a theoretical model, which has been computed taking as a reference real installation with similar features. Finally, the main conclusions about the main strategies in order to design a new installation or to face a drop-in replacement with these low GWP working fluids are commented.

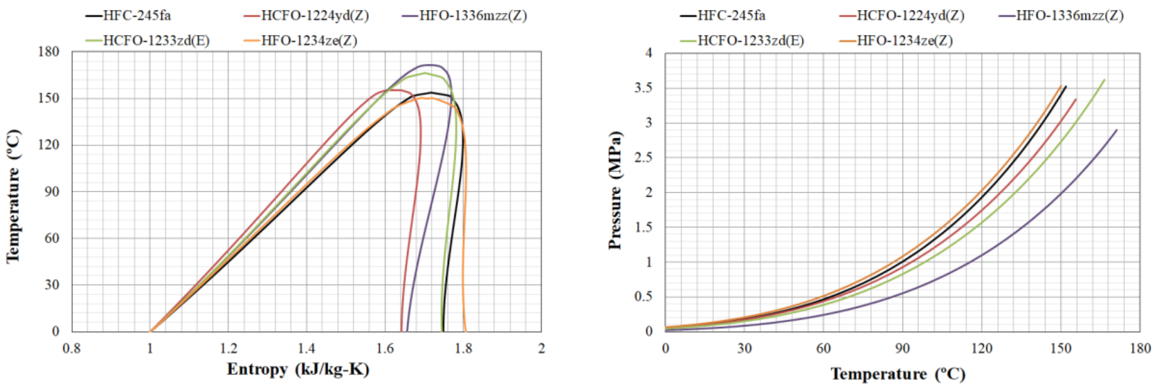
1. INTRODUCTION

Our planet is changing because of human practices, and now the environmental situation is alarming. This issue, added to the depletion of natural resources, has led to a search for heat recovery technologies. At low temperature range, Organic Rankine Cycle (ORC) stands out as a suitable option due to its performance and, especially, its simplicity. The use of an ORC allows upgrading low-grade heat into electrical power; it is even possible to employ this technology as a Combined Heat and Power (CHP) system, by using the exhaust heat from the condenser to meet heating demands.

Working fluid selection is an essential topic in the ORC research field. Among ORC working fluids, HFC-245fa is widely used at low temperatures as it has attractive thermodynamic and safety properties and a zero Ozone Depletion Potential (ODP) (Petr and Raabe, 2015). However, HFC-245fa has a high Global Warming Potential (GWP) value. New regulations and legislation, such as the Kyoto Protocol (Naciones Unidas, 1998) and the fluorinated gases European Regulation (Off. J. Eur. Union, 2014), and increasing environmental awareness have encouraged searching for working fluids with low GWP. However, the decreasing availability is the fact that has led to search for alternative working fluids with low GWP. Therefore, at best, the acquisition cost of these working fluids will be increased meanwhile in another case they might no longer be available. This makes it necessary to search for new working fluids to replace HFC-245fa.

Juhasz and Simoni (2015) study the thermal stability and material compatibility of HFCF-123, HFC-245fa, HFO-1336mzz(Z), DR-12 and HCFO-1233zd(E). They affirm that HFO-1336mzz(Z) has a good thermal stability up to 250ºC. Kontomaris et al. (2016) use an un-optimized regenerative ORC prototype system in order to analyses the behaviour of HFO-1336mzz(Z). Navarro-Esbrí et al. (2017) test experimentally HFO-1336mzz(Z), where the net electrical efficiency obtained was 5.5-8.3%. Molés et al. (2014) compare HCFO-1233zd(E) and HFO-1336mzz(Z) with HFC-245fa, where the net cycle efficiency increases by a 10.6% and 17%, respectively. Regarding to the turbine size, it would be incremented between 30.9%-41.5% with HFO-1336mzz(Z), while similar results are obtained using HCFO-1233zd(E), with 7.5%-10.2% larger than HFC-245fa. Ziviani et al. (2016) analyse a drop-in replacement of HFC-245fa by HFO-1234ze(Z), obtaining a reasonable performance comparison, and they conclude that HFO-1234ze(Z) and HCFO-1233zd(E) were suitable alternatives to HFC-245fa. Datla and Brasz (2014) analyse the possibility of a drop-in replacement of HFC-245fa by HCFO-1233zd(E) in a 75 kW ORC system, confirming its feasibility, where the net cycle efficiency was 8.7% higher. Eyerer et al. (2016) provided an experimental comparison between HFC-245fa and HCFO-1233zd(E). The thermal efficiency increased a 6.92% using HCFO-1233zd(E) and, perhaps the maximal gross power output was up to 12.17% lower, they concluded the suitability of the drop-in replacement of HFC-245fa by HCFO-1233zd(E). Molés et al. (2016) also compares experimentally HCFO-1233zd(E) with HFC-245fa. They obtain that electrical and thermal efficiency are slight lower, nevertheless it could be improved.

To sum up, HFO-1336mzz(Z), HCFO-1233zd(E) and HFO-1234ze(Z) have been presented by various authors as potential alternatives to HFC-245fa, due to its low GWPs and suitable thermodynamic and safety properties, similar to those of the reference fluid, HFC-245fa. Interestingly, HFO-1234ze(Z) does not seem to be commercially available despite its attractive predicted cycle performance. New promising working fluids continue to be identified by ongoing research and development efforts. HCFO-1224yd(Z) is another potential alternative to HFC-245fa, which provides great efficiencies (Fukushima, 2016) and has a GWP lower than 1 (Saito and Sundaresan, 2017). HCFO-1224yd(Z) was proposed by Fukushima et al. (2016a) as a replacement for HCFC-123 and HFC-245fa in high-temperature heat pumps and low-pressure centrifugal chillers due to its non-flammability and low-toxicity.



(a) (b)

Figure 1: (a) Temperature-Entropy diagram, **(b)** Pressure-Temperature curve for HFC-245fa, HCFO-1224yd(Z), HFO-1336mzz(Z), HCFO-1233zd(E) and HFO-1234ze(Z).

So, focusing on heat sources up to 150ºC and small-scale applications, the low-GWP alternatives selected for the present analysis are HCFO-1224yd(Z), HFO-1336mzz(Z), HCFO-1233zd(E) and HFO-1234ze(Z). The safety, health, environmental and thermo-physical properties of these candidates are compared to the properties of the reference fluid, namely HFC-245fa, in Table 1 and Fig. 1. As it can be observed, the main differences between the reference fluid and its potential alternatives are the GWP reduction and a change in safety class from B1 to A1 or to A2L for HFO-1234ze(Z), that would have to be considered in the ORC design procedure. The thermo-physical properties of the low-GWP candidates are quite similar to those of the reference fluid. It might be noted that the ODP values for HCFO-1224yd(Z) and HCFO-1233zd(E) are non-zero but almost negligible (Fukushima et al., 2016b).

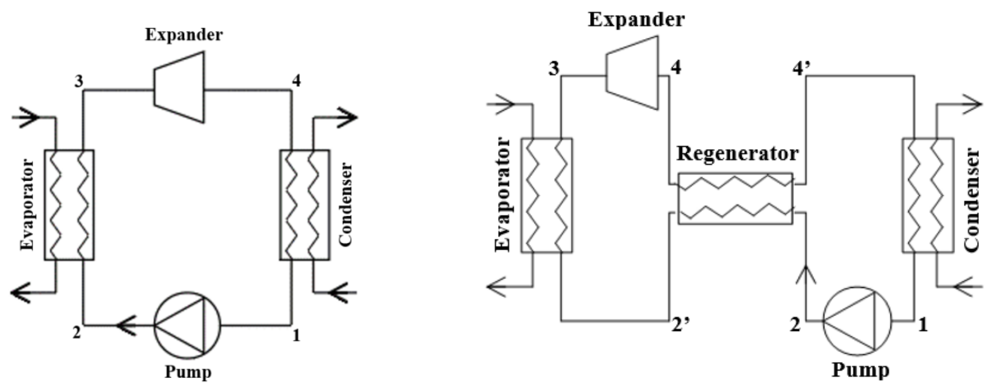
Table 1: Thermo-physical and safety properties of HFC-245fa, HCFO-1224yd(Z), HFO-1336mzz(Z), HCFO-1233zd(E) and HFO-1234ze(Z).

Parameters	HFC-245fa	HCFO-1224yd(Z)	HFO-1336mzz(Z)	HCFO-1233zd(E)	HFO-1234ze(Z)
$T_{critical}$ (ºC)	153.86	155.5	171.27	166.45	150.12
$P_{critical}$ (MPa)	3.65	3.34	2.90	3.62	3.53
Mol. w. (kg/kmol)	134.05	148.49	164.05	130.5	114.04
Slope	Dry	Dry	Dry	Dry	Dry
OEL (ppm)	300	1000	500	800	-
Flammability	No	No	No	No	Low
ASHRAE Standard 34 Safety Class	B1	A1	A1	A1	A2L
ALT (days)	2.811	20	22.6	26	10
ODP	0.0	0.00023	0	0.00034	0
GWP	858	<1	2	1	1
Boiling point (ºC)	15.05	14.00	33.38	18.26	9.73

After the literature review, it can be seen that some low-GWP alternative working fluids as HFO-1336mzz(Z) and HCFO-1233zd(E) have been previously compared. There is no previous study evaluating under the same operating conditions the performance of all potential HFC-245fa substitutes for small-scale, low-temperature applications at the same time. Therefore, the present paper offers an evaluation of a comprehensive set of prospective recently developed alternatives. It will identify the leading candidates to use as HFC-245fa low-GWP alternatives according to the heat source and heat sink temperatures. The aim of this paper is to evaluate the suitability of these potential substitutes.

2. ORC MODEL AND SIMULATIONS

A liquid pump, evaporator, expander and condenser, as shown in Figure 2(a), compose the Basic Organic Rankine Cycle (BORC). Among a large number of possible ORC configurations, the Regenerative Organic Rankine Cycle (RORC), Figure 2(b), is one of the most popular due to its low complexity and cost.



(a) (b)

Figure 2: (a) BORC layout, **(b)** RORC layout.

In order to estimate the cycle performance of HFC-245fa, HCFO-1224yd(Z), HFO-1336mzz(Z), HCFO-1233zd(E) and HFO-1234ze(Z) at different operating conditions, a computational model has been developed. This paper analyses four study cases; the heat source temperature has been varied from

90 ºC to the critical temperature of each working fluid, representing low-temperature heat sources, and keeping constant heat sink at two different temperatures: 20 ºC and 40 ºC. Considering that temperatures at the heat sink outlet are 30 ºC and 50 ºC respectively, this latter case is particularly interesting since the temperature supplied is sufficiently high to be used in another process, conforming a CHP system. These conditions have been fixed for the BORC as well as for the RORC analysis. A simplified model developed with REFPROP 10.0 (Lemmon et al., 2018) provide the fluid thermophysical data required to analyse cycle performance.

For all the analysis net cycle efficiency is maximized, this optimization has been achieved by adjusting between 2.5 ºC and 20 ºC the degree of superheat at the expander inlet; meanwhile, the maximum cycle pressure has been limited at 30 MPa and the evaporating temperature limited at the critical temperature minus 5 ºC of each fluid, which would assure not to be working in an unstable operating zone. Table 2 contains all the initial necessary values to realize the simulations, which have been stated according to previous works (Molés et al., 2017). In addition, Table 3 summarizes the basic equations used to model the cycle.

Table 2: Cycle operating parameters.

Parameters	Value	
Heat source temperature	90ºC to $T_{critical}$	
Heat sink inlet temperature	Low temperature: 20 ºC	CHP system: 40 ºC
$T_{heat\ source}$ - T_{max} T_{min} - $T_{heat\ sink}$	2.5 ºC	
Superheating	2.5 ºC - 20 ºC (maximizing the net cycle efficiency)	
Subcooling	5 K	
Regenerator effectiveness (ε_{rege})	80 %	
Expander isentropic efficiency ($\eta_{x,is}$)	85 %	
Expander overall efficiency ($\eta_{x,ov}$)	70 %	
Pump overall efficiency ($\eta_{p,is}$)	45 %	
Pump isentropic efficiency ($\eta_{p,ov}$)	85 %	
Q_{evap}	100 kW	

Table 3: Basic equations for each element design and cycle evaluation.

Element	Equation	
Pump	$W_p = \dot{m} \cdot (h_{2,is} - h_1)/\eta_{ov,p}$ $\eta_{is,p} = (h_{2,is} - h_1)/(h_2 - h_1)$	(1) (2)
Expander	$W_x = \dot{m} \cdot \left(h_3 - h_{4,is}\right) \cdot \eta_{ov,x}$ $\eta_{is,x} = (h_4 - h_3)/(h_{4,is} - h_3)$	(3) (4)
Condenser	$Q_{cond} = \dot{m} \cdot (h_{4`} - h_1)$	(5)
Evaporator	$Q_{evap} = \dot{m} \cdot (h_3 - h_{2`})$	(6)
Regenerator	$\varepsilon_{reg} = Q_{real}/Q_{max}$	(7)
Cycle	$\eta_n = (W_x - W_p)/Q_{evap}$ $\eta_g = W_x/Q_{evap}$	(8) (9)

3. RESULTS AND DISCUSSION

In this section, the main results are presented. The information has been analysed from the point of view of designing a new installation. The variation of the expander power output, net cycle efficiency and volumetric flow rate at the expander inlet with the heat sink and heat source temperature have been computed for the selected working fluids in order to determine their suitability in a low-temperature and small-scale ORC. The different working fluids have been analysed optimizing the net cycle efficiency.

Figure 3 shows the computed power provided by the expander; as expected, there is an increase of the power expander output by increasing the heat source temperature and lowering the heat sink temperature; in fact, the expander power output decreases between 13.49% and 32.58% by growing 20 ºC the heat sink temperature. In addition, with the RORC configuration the cycle increases up to 15.6 % the expander power output. Focusing on the comparison between the working fluids, Figure 3(a) and Figure 3(b) show how those fluids with higher critical temperatures, such as HFO-1336mzz(Z) and HCFO-1233zd(E), allow to achieve higher power at the expander output for high activation temperatures. By contrast, when using a BORC, Figures 3(c) and Figure 3(d), the results obtained by using HFO-1336mzz(Z) become worse in comparison with the use of an intermediate heat exchanger; and HCFO-1233zd(E) allows getting the maximal expander power output values for the BORC configuration. HFC-245fa and HCFO-1224yd(Z) show almost the same behaviour for all tested temperatures.

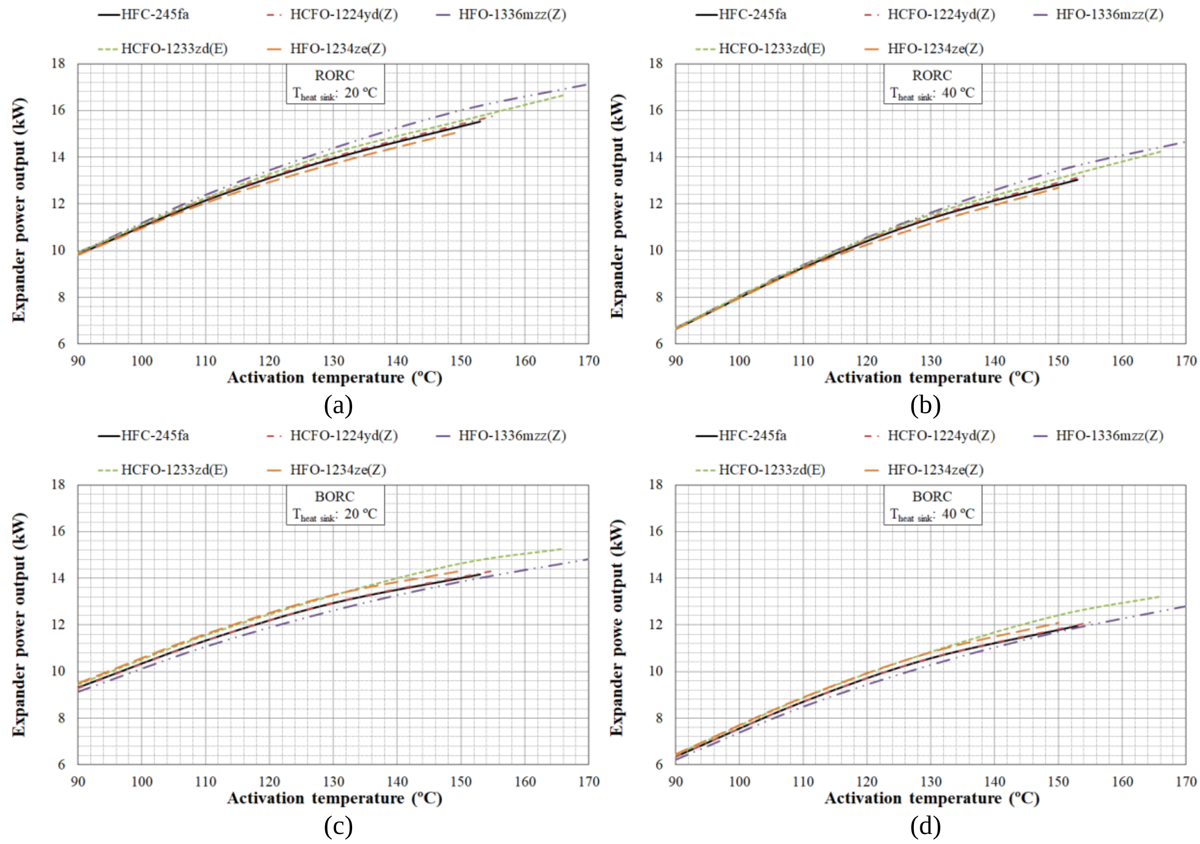


Figure 3: Expander power output varying the heat source temperature: **(a)** heat sink temperature at 20 ºC with a RORC configuration, **(b)** heat sink temperature at 40 ºC with a RORC configuration, **(c)** heat sink temperature at 20 ºC with a BORC configuration, **(d)** heat sink temperature at 40 ºC with a BORC configuration.

Figure 4 shows the net cycle efficiency, defined as the net power extracted from the cycle (i.e. the difference between the power generated at the expander and the power consumed by the liquid pump) over the heat rate supplied to the evaporator. Since the thermal power provided to the evaporator is constant, these figures show also the net power output trends. Figure 4 shows, as expected, that the higher the heat source temperature is, the greater the net power is. Conversely, a comparison between Figures 4(a)and 4(b), and Figures 4(c) and 4(d), shows a significant reduction in net power when the heat sink temperature rises. The RORC configuration provides highest net cycle efficiency, especially when the activation temperature increases. Focusing on working fluid behaviour, Figure 4 shows that all the analysed working fluids provide similar net cycle efficiencies for low activation temperatures; when the heat source temperature grows these differences set to increase. Figure 4 also shows that HFC-

245fa and HCFO-1224yd(Z) lead to almost identical net cycle efficiency over the cycle conditions examined. The highest net cycle efficiency results have been obtained by using HFO-1336mzz(Z) in a RORC, with relative differences up to 8.16 %, taking HFC-245fa as a reference.

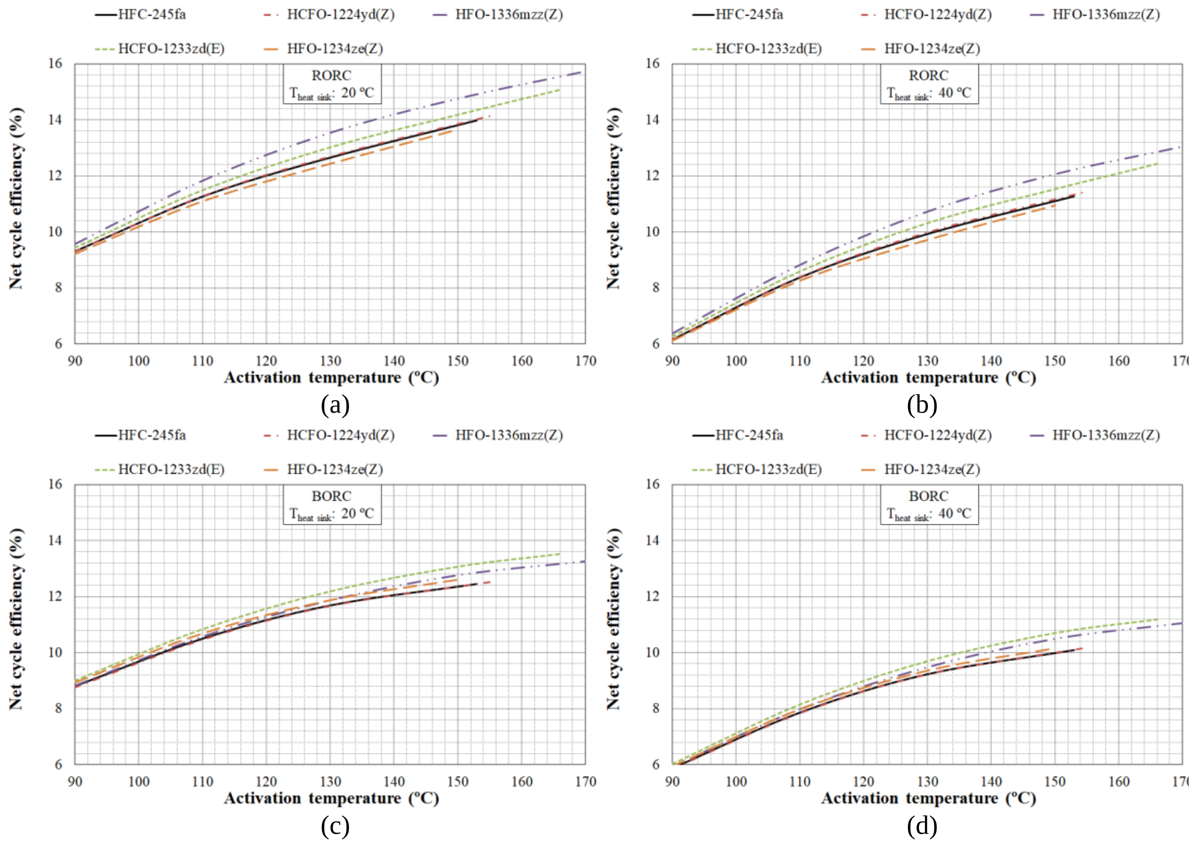


Figure 4: Net cycle efficiency varying the heat source temperature: **(a)**heat sink temperature at 20 ºC with a RORC configuration, **(b)**heat sink temperature at 40 ºC with a RORC configuration, **(c)** heat sink temperature at 20 ºC with a BORC configuration, **(d)** heat sink temperature at 40 ºC with a BORC configuration.

Finally, a fast analysis of the volumetric flow rate at the expander inlet has been developed in order to approach to a drop-in replacement case, since it is an indicator of the expander size. An increase in the maximum cycle temperature is associated with a reduction in the volumetric flow rate. Focusing on working fluid behaviour, data shows the importance of determining the temperature working range, since the volumetric flow rate is highly affected by the operating temperatures. The highest volumetric flow rates at this temperature range have been obtained using HFO-1336mzz(Z), followed by HCFO-1233zd(E) and HCFO-1224yd(Z), and therefore the highest required expander size. With regard to the expander size, the closest results to the use of HFC-245fa have been obtained by using HFO-1234ze(Z). The volumetric flow rate is reduced and the difference between working fluids dismissed at higher heat source temperature.

4. CONCLUSIONS

In this paper, the possibility of using HCFO-1224yd(Z), HFO-1336mzz(Z), HCFO-1233zd(E) and HFO-1234ze(Z) as potential replacements for HFC-245fa in small-scale, low-temperature Organic Rankine Cycle has been evaluated. A RORC and a BORC model maximizing the net cycle efficiency were developed, using REFPROP 10.0, and employed to compare the cycle performance of the working fluids, under conditions reflecting real installations.

Based on this theoretical comparison, the following conclusions can be drawn. The net cycle efficiency increases for higher thermal sources and lower heat sink temperature values. Focusing on the effect of working fluid choice, the highest net cycle efficiencies can be reached by using HFO-1336mzz(Z) in a

RORC, up to 8.16 % higher than HFC-245fa. HCFO-1224yd(Z) offers almost the same net cycle efficiency that HFC-245fa. In case of a CHP application, where the heat sink temperature has been increased 20 ºC, there is a decrease between 13.49 % and 32.58 % for the expander power output and between 16.62 % and 33.89 % for the net cycle efficiency. Finally, it has been shown that HFO-1336mzz(Z) leads to the largest expander sizes and HFO-1234ze(Z) and HFC-245fa to the lowest, with close volumetric rates.

To conclude, the use of a RORC with HFO-1336mzz(Z) and HCFO-1233zd(E) is recommended in case of design a new installation since, these working fluids, with higher critical temperatures, offer better cycle efficiencies. On the other hand, the use of HFO-1234ze(Z) could be an appropriate choice as HFC-245fa alternative in a drop-in replacement case, due to its low volumetric flow rate, especially with low heat source temperatures; however, its reduced availability makes it less attractive. The use of HCFO-1224yd(Z) also could be an interesting alternative due to its similar cycle behaviour; nevertheless, it should be considered that its volumetric flow rate is between 10 % and 16% higher than HFC-245fa.The chemical stability and compatibility with materials of equipment construction of the candidate fluids were not tested.

NOMENCLATURE

h	specific enthalpy	(kJ/kg)
$\dot{m}$	mass flow rate	(kg/s)
P	pressure	(MPa)
$\dot{Q}$	heat rate	(kW)
T	temperature	(ºC)
$\dot{W}$	electrical power	(kW)

Greek symbols

ε	effectiveness	(-)
η	efficiency	(-)

Subscripts

cond	condensation
evap	evaporation
g	gross
is	isentropic
max	maximum
min	minimum
n	net
ov	overall
reg	regenerator
p	pump
x	expander

Acronyms

ALT	Atmospheric Life Time
BORC	Basic Organic Rankine Cycle
CHP	Combined Heat and Power
GWP	Global Warming Potential
HCFO	HydroChloroFluoroOlefin
HFC	HydroFluoroCarbon
HFO	HydroFluoroOlefin
OEL	Occupational Exposure Limit
ODP	Ozone Depletion Potential
ORC	Organic Rankine Cycle

RORC Regenerative Organic Rankine Cycle

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