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Original article

Optimal refrigerant mixture in single-stage high-temperature heat pumps based on a multiparameter evaluation

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A B S T R A C T

High-temperature heat pumps (HTHPs) are compression systems that convert residual heat to high-grade heat used in several industrial applications. Refrigerants for HTHPs are still not explored, and most studies consider only pure refrigerants. This study carries out a general screening of binary and ternary mixtures for HTHPs through a multiparameter optimization based on low global warming potential (GWP) refrigerants that are feasible for operating at higher temperatures. The proposed methodology considers several parameters such as coefficient of performance, volumetric heating capacity, flammability, GWP, and perfect glide matching. The blends were required to have a critical temperature above 150 °C and to provide high energy performance to diminish the indirect carbon footprint. No ideal mixture was found for every parameter, so a trade-off solution was required. The most critical variable was flammability, reducing the coefficient of performance significantly if the ASHRAE Std 34 A1 restriction had to be fulfilled. Finally, different mixtures are given as the bests based on the main optimizable parameter. The most promising ones which comply with the environmental restriction were R-1233zd(E) and R-1336mzz(Z) based mixtures.

Introduction

According to the International Energy Agency (IEA) [1], around 46% of the total energy used for heat is employed in the industry, which means approximately 79 EJ, and is increasing year to year. Moreover, up to 2.8% of the industrial energy consumption [2] is wasted as a low-grade heat below 100 °C. High-temperature heat pumps (HTHP) based on vapor compression cycles are useful for revalorizing this heat by converting it into a high-grade heat above 100 °C, useful for several industrial processes. These systems can be integrated into different heat sources as the requirements of temperature, pressures, and heat capacities can be adjusted thanks to different system configurations and fluids.

One of the most important factors that an engineer must consider when designing a heat pump compression system is the fluid employed. The election depends on the operational conditions and determines the performance of the cycle. Nowadays, the focus is on natural refrigerants [3], such as R-718 (water), R-744 (CO_2), R-717 (ammonia), and synthetic fluids, mainly hydrofluoroolefins (HFOs) [4]. Water presents 100 times higher latent than R-134a, making it an attractive option for temperatures higher than 150 °C. However, the low water vapor density is traduced on high-pressure ratio and swept volume, which sometimes makes the systems inviable.

On the other hand, HFOs have been studied as low GWP replacements of R-365mfc and R-245fa [5,6]. The attributes of R-1234ze (E) were presented by Mota-Babiloni et al. [7], concluding that it could work as a replacement of R-134a. R-1336mzz(E) has been studied as a novel working fluid for HTHP as it has zero ozone depletion potential (ODP), ultra-low global warming potential (GWP), high critical temperature, and it is nonflammable [8]. Other researchers, such as Yan et al. [9], predicted the energy performance of newer refrigerants R-1336mzz(Z) and R-1224yd(Z). Mateu-Royo et al. [10–13] also included R-1233zd(E) when looking for replacements to R-245fa in HTHP, showing promising results. Although the number of low GWP refrigerants is reduced [14,15], some fluids should be taken into deeper research as they can provide better performances at high condensation temperatures than R-134a [16]. However, a new topic is being discussed nowadays. Recent studies show that HFOs produce trifluoroacetic acids when they are decomposed, affecting some organisms [17–19]. While the impact of these refrigerants on nature is being evaluated and the methods for reducing leakages improved [20], HFOs still have to be explored as they are the newest low GWP option.

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Nomenclature

Variables

COP	coefficient of performance (-)
DX	variance (-)
EX	expected value (K)
F	fluorine
h	mole specific enthalpy (kJ mol^{-1})
H	hydrogen
$\dot{m}$	mass flow rate (kg s^{-1})
M	molecular weight (g mol^{-1})
p_r	reduced pressure (-)
p	pressure (bar)
prob	probability (-)
$\dot{Q}$	heat transfer (kW)
s	entropy (kJ mol^{-1} K^{-1})
T	temperature (°C)
VHC	volumetric heating capacity (kJ m^{-3})
x_v	vapor quality (-)
w	mass fraction (-)

Subscripts

ad	adiabatic flame temperature
cri	critical
dis	discharge
dsh	desuperheating
em	electromechanical
fg	heat of vaporization
i	intermediate
in	inlet
is	isentropic
k	condenser
mix	mixture
norm	normalized
o	evaporator
out	outlet
pp	pinch point
pb	pool boiling
r	refrigerant
suc	suction
vol	volumetric

Abbreviations

CS	carbon steel
FOM	figure of merit
GWP	global warming potential
HC	hydrocarbon
HFO	hydrofluoroolefin
HTF	heat transfer fluid
HTHP	high-temperature heat pump
IHX	internal heat exchanger
N/A	not available
NBP	normal boiling point
PGM	perfect glide matching
SC	subcooling
SH	superheating

Greek

E	effectiveness (-)
η	efficiency (-)
Π	flammability index (-)
ρ	density (kg m^{-1})
μ	viscosity (Pa s)

A method for obtaining the best fluid for a certain application is mixing different components on one blend. Mixtures such as R-410A, R-507A, or R-404A were widely used as they performed high but had to be replaced due to their high GWP. In the last years, different researchers showed the good effects of mixing components [21] as it is possible to reduce GWP, flammability [22] and increase the COP. Calleja-Anta et al. [23] found mixture replacements for R-290 and R-600a, resulting in a 13% COP increment. Yu et al. [24] concluded that for R-410A replacement in heat pump air condition system, the mildly flammable category could be achieved with a slight decrease in its COP. Then, Bell et al. [25] mixed different components for arriving at nonflammable and low-GWP replacements for R-134a.

This mixing method has been more used in refrigeration than in heat pumps, where few studies have been made [26–28]. In addition, no clear methodology for evaluating different kinds of mixtures has been found in the literature. This paper aims to provide a comprehensive methodology for estimating mixtures main parameters and applying it in HTHP application to prove the characteristics of the most promising mixtures generated. A multiparameter optimization of the mixtures is done based on COP, VHC, flammability, GWP, toxicity, showing the different tradeoffs between the parameters and providing the best mixtures depending on the safety requirement and the application.

Fluid selection

An optimal selection of the blend's components results in higher energy performances and decreases the computation time required in the screening. McLinden et al. [15] found a list of refrigerants able to be considered candidates for air conditioning and heat pump conditions (and they compared with R-410A). They also found that no perfect refrigerant is available, and mixtures are required for obtaining the most appropriate solution in each application. In this section, the different characteristics considered for the candidate fluids are exposed. All the thermodynamic properties for pure and mixed refrigerants were extracted from REFPROP v10.0 database [29], which was linked with the MATLAB R2018b platform [30].

Critical temperature

HTHPs achieve high condensation temperatures, so one of the main restricting parameters to be controlled is the critical temperature. This parameter is relatively restricting because most used fluids in other applications have critical temperatures around 100 °C, as shown in Fig. 1. No phase change occurs if the refrigerant achieves temperatures above the critical temperature, resulting in transcritical operation. For preventing this, a first screening of the new generation refrigerants and most used refrigerants in HTHP is required [10,15]. Fig. 1 presents all the refrigerants that could be considered for this work.

To assure condensation and temperature and pressure control, the minimum critical temperature of the resulting mixture is 150 °C (black dashed line). On the other hand, the minimum critical temperature for pure fluids is 100 °C (red dashed line). Fluids below this temperature are discarded for saving computation time.

According to this methodology, Fig. 1 shows that commonly used refrigerants like R-744, R-32, or R-1234yf are not valid for HTHP mixtures. However, some hydrocarbons (HCs) such as R-600, R-600a, and R-601 seem good candidates for our application. Then, except for particular refrigerants, most of them have critical pressures from 32 to 39 bar.

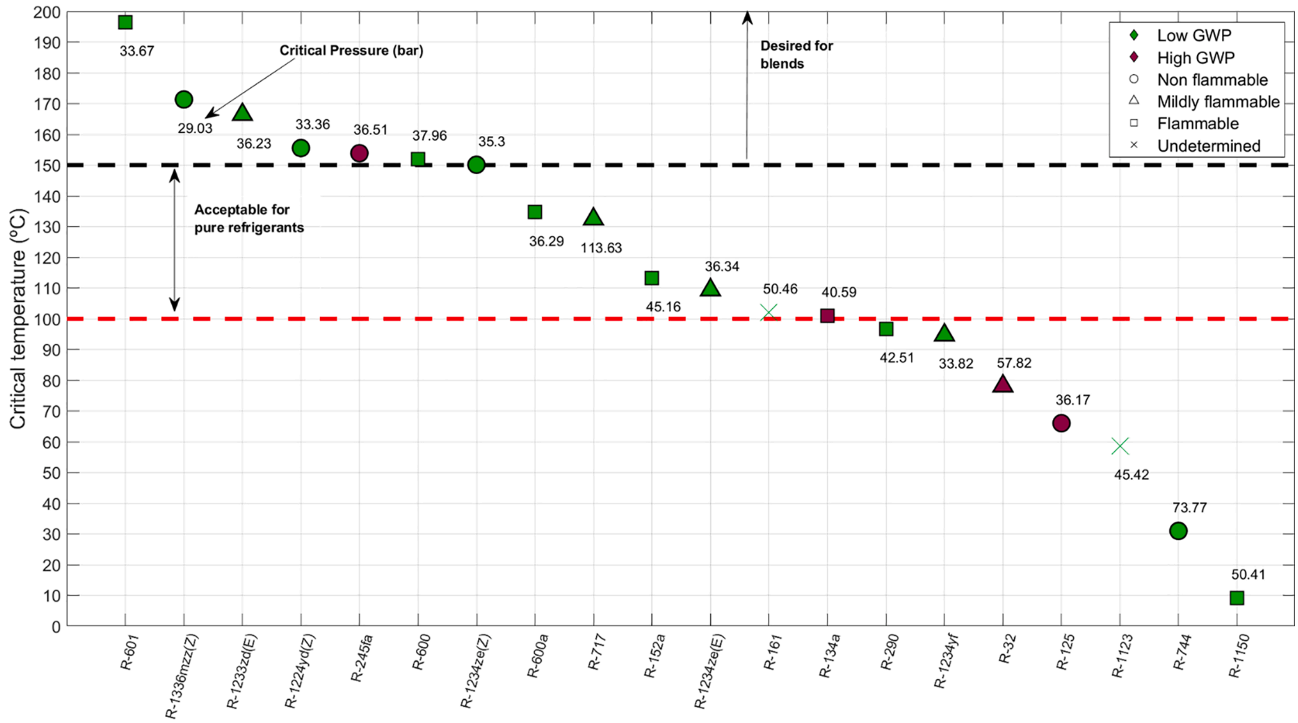

Fig. 1. Screening of the candidates by means of the critical temperature.

Global warming potential

In Fig. 1, the GWP and flammability of the fluids are also presented, as these are two of the other main parameters that will be optimized. Most of the GWPs (100 years' timeframe) are below 150 (green color), which is important for reducing the direct contribution to the carbon footprint. Most of the candidates belong to low-GWP groups like hydrocarbons or olefins (double-bound), and they meet this criterion. The only high GWP fluids considered are R-245fa and R-134a. Therefore, a low direct greenhouse gas contribution is expected for most of the mixtures because the GWP of the mixture is a weighted sum of the single fluids.

Flammability

Looking at flammability, it is important to have nonflammable fluids as they act as an inhibitor on blends [19]. The effect of adding a nonflammable refrigerant on a mixture with a flammable refrigerant is shown in a visual example presented in Fig. 2. The radial axis shows the percentage mole fraction of the nonflammable refrigerant in the mixture, and the angle axis shows the flammability.

As shown in the figures, a 60% R-125 mixture with R-600 and R-601 (highly flammable fluids) can push the mixture to the A2L class (ASHRAE Std 34 [31]), and with only a 15%, it can make the R-1234ze(E) (A2L, mildly flammable) mixture nonflammable. Similar conclusions

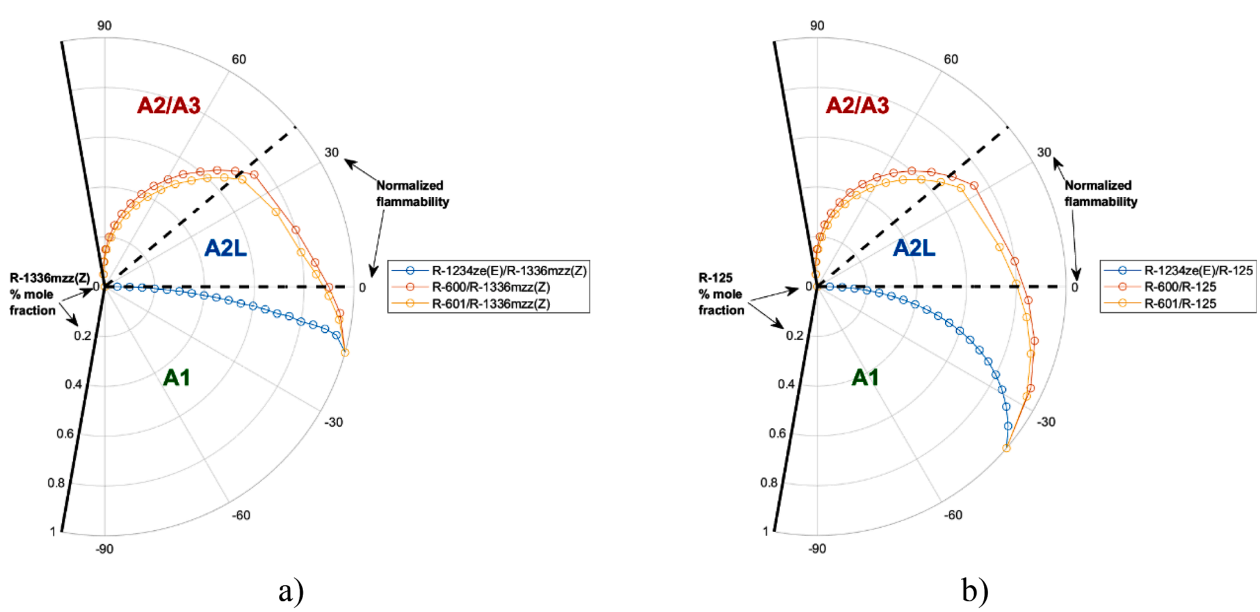

Fig. 2. Effect of nonflammable refrigerants on the flammability of flammable refrigerants: a) R-1336mzz(Z) and b) R-125.

can be obtained with R-1336mzz(Z), but this refrigerant has lower flame suppression characteristics because more than 85% of this fluid is required for a nonflammable mixture with R-601. This shows the importance of A1 refrigerants (no flame propagation) in mixtures for reducing hazards. All flammability definitions and parameters are according to the ASHRAE Std 34.

Compatibility

The mixture of different molecules may produce hazards as the interaction between two different elements is unknown from the start. The results obtained by CAMEO Chemicals can be used for checking if there is any known reaction between the selected fluids [32]. If this happens, the performed model should not calculate that blend. 10 of the 13 fluids considered for this paper are in this database. It shows that no known hazardous reaction is registered, which does not give us full reliability but can work as a first approximation. It can also be checked if the selected fluids are chemically stable and other parameters like autoignition temperature.

For HTHPs, it is also important to check the autoignition temperature as high temperatures are achieved at the compressor's discharge. As a general condition, it can be set that the minimum autoignition temperature of the selected fluids must be above 250 °C and the maximum discharge temperature be less than 175 °C for assuring chemical stability with lubricant. It is also worth noting that this temperature at the compressor discharge depends on the fluid's specific heat capacity, being higher for lower heat capacities. For preventing this, temperatures at the discharge have to be validated.

The possible hazards of the selected fluids are taken from the literature. Firstly, R-601 (R-601) has a lower autoignition temperature of 260 °C, but this is acceptable according to our criteria.

Another factor that should be considered is the compatibility of the fluids with the materials of the installation. In the available data [33,34], all the refrigerants have compatibility with Carbon Steel (CS), except for R-601, which has compatibility with stainless steel (SS). Moreover, there are still some fluids that its compatibility is not known.

As shown, no significant hazards are predicted. Moreover, before testing a mixture on the installation, this mixture should be tested in the laboratory. The U.S. National Fire Protection Agency (NFPA 704 [35]) standards can be visited for more details about refrigerants compatibility and hazards, and the work of Frate et al. [36] for suitable ranges for the different fluids employed.

Final candidates as a components

Attending to the discussion followed in the present section, the main thermodynamic properties of refrigerants that will be mixed are shown in Table 1, together with other main characteristics.

Estimation of blend parameters

The ideal blend must fulfill several conditions, and it is impossible to optimize all simultaneously. In this way, the main parameters to consider in the optimization are COP, GWP, flammability, and proper zeotropic behavior. A trade-off solution has to be searched because all these characteristics cannot be reached once by a mixture. In the following, the methodology for calculating all of them is presented, summarized in Fig. 3.

Global warming potential

The global warming potential (GWP) indicates how much energy the emissions of 1 ton of a gas will absorb during a certain period. With this, the direct environmental impact of the refrigerants is compared with that of carbon dioxide.

In blends, the GWP can be estimated depending on the amount of each component and their GWP values, Eq.(1).

$$\mathrm{GWP}_{\mathrm{mix}} = \sum_{k}^{n} \mathrm{w}_{\mathrm{k}} \mathrm{GWP}_{\mathrm{k}} \tag{1}$$

Flammability limits

Flammability is one of the main parameters to control for reducing the hazards of the installation. The method for estimating this parameter is explained by Linteris et al. [37]. This empirical model uses the ratio of hydrogens/fluorides of the blend and the adiabatic flame temperature. The adiabatic flame temperature can be calculated with Cantera 2.5.1 [38], a program for performing detailed chemical thermo-kinetics and transport models that can be connected to MATLAB R2018b.

This method proposes a parameter for estimating the flammability of the refrigerants quantitatively with an index Π, Eq. (2). And it is normalized with Eq. (3)

$$\Pi = \arctan2\left(\frac{\mathrm{T}_{\mathrm{ad}} - 1600}{2500 - 1600}, \frac{\mathrm{F}}{\mathrm{F}+\mathrm{H}}\right)\frac{180}{\pi} \tag{2}$$

$$\Pi_{\mathrm{norm}} = \frac{\Pi - \Pi_{1,2\mathrm{L}}}{90 - \Pi_{1,2\mathrm{L}}} \tag{3}$$

$\Pi_{norm} = 0$ represents the 1/2L boundary and $\Pi_{norm} = 100$ estimates high flammability. The boundary between 3/2L has more uncertainties and is taken as$\Pi_{norm} = 40$ as a conservative approach. Negative values correspond to an estimated nonflammable mixture.

Table 1
Candidates as components of the mixtures and their main characteristics.

ASHRAE designation R-	Chemical formula	GWP[a]	T_{cri} (°C)	p_{cri} (bar)	NBP (°C)	C.S. compatibility[b]	Safety class[c]
601	CH3-3(CH2)–CH3	5	196.55	33.67	36.06	No (S.S.)	A3
1336mzz(Z)	CF3CH = CHCF3(cis)	2	171.35	29.03	33.45	N/A	A1
1233zd(E)	CF3CH = CHCl	1	166.45	36.23	18.26	Yes	A1
1224yd(Z)	CF3CF = CHCl (cis)	1	155.54	33.37	14.62	Yes	A1
245fa	CF3-CH2-CHF2	1030	153.86	36.51	15.05	N/A	B1
600	CH_3-2(CH2)–CH3	4	151.97	37.96	−0.49	Yes	A3
1234ze(Z)	CHF = CHCF3 (cis)	1	150.12	35.30	9.73	N/A	A2L
600a	CH(CH3)3	3	134.66	36.29	−8.75	Yes	A3
717	NH3	0	132.41	113.63	−33.32	Yes	B2L
152a	CHF2-CH3	124	113.26	45.16	−24.02	N/A	A2
1234ze(E)	CHF = CHCF3	6	109.36	36.34	−18.97	N/A	A2L
161	C2H5F	86	102.05	50.45	−37.54	N/A	N/A
134a	CF3-CH2F	1430	101.06	50,46	−26.07	N/A	A1

a. Values taken from REFPROP v10.0 [29].
b. Values taken from Frate et al. [36].
c. Values taken from ASHRAE Std 34 [31].

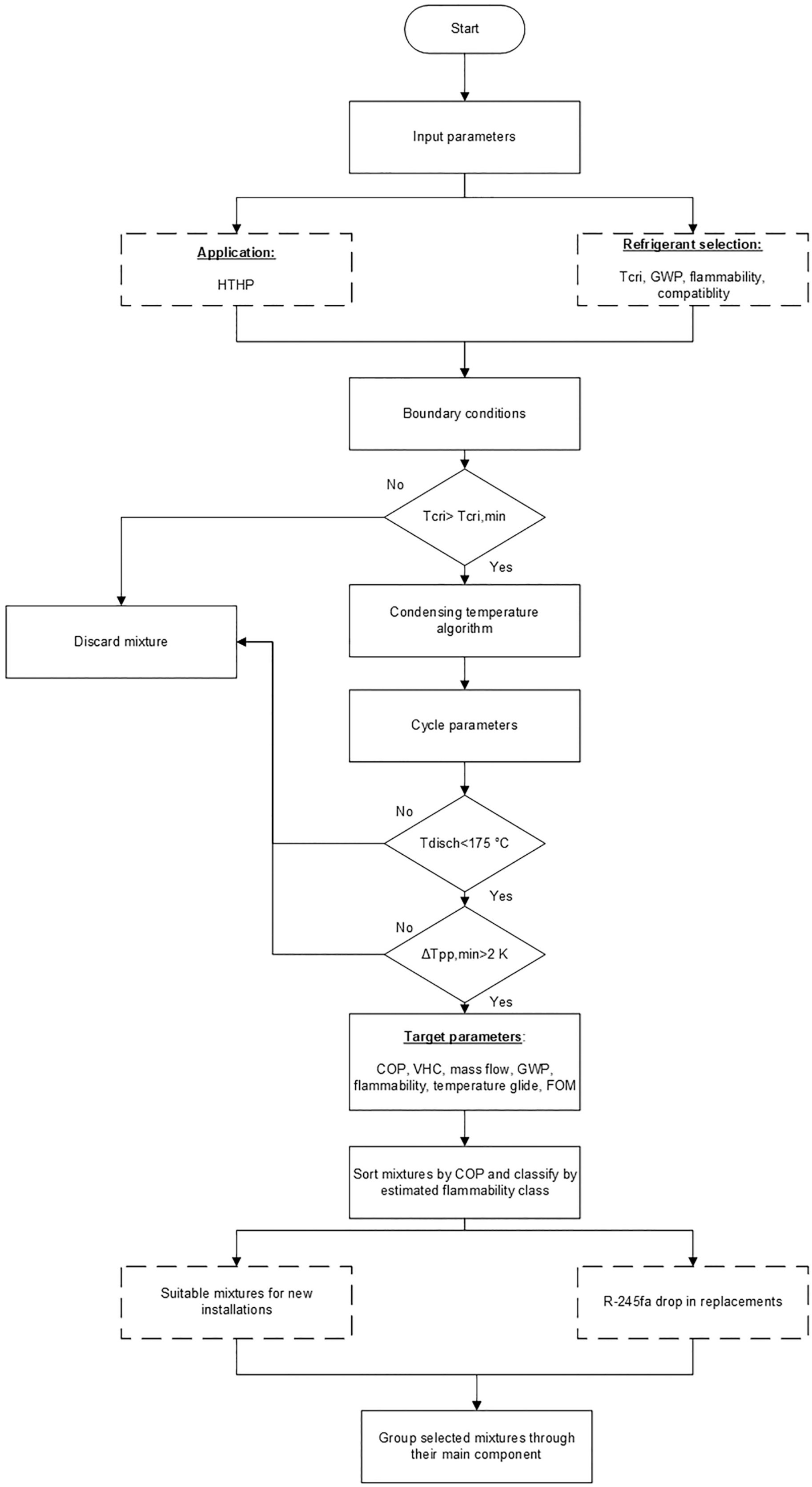

Fig. 3. Flow chart of the followed methodology. Except for the pecularities of the HTHP model, the same method can be used in other applications.

Simplified cycle

The configuration proposed for the model is a single-stage with an internal heat exchanger (IHX). It is simple robust and commonly seen in HTHPs with a moderate temperature difference between evaporation and condensation [11,17,38]. The IHX is necessary for blends as it is difficult to predict if the compression will be dry with traditional superheating degrees (below 10 K). Moreover, in HTHPs, the increase of the discharge temperature due to the effect of the IHX is beneficial for heat production [10]. All the input parameters of the cycle are shown in Table 2.

The main boundary parameters are the approach temperatures, as they serve to control the necessary area of the heat exchanger. This approach appears on the evaporator's inlet and the condenser saturated vapor section for azeotropic fluids and is set to be 4 K and 7 K, respectively. The higher these values are, the higher the temperature lift. Therefore, the performance decreases. On the other hand, less heat exchange area is needed when approach temperatures increase.

In zeotropic mixtures, a minimum approach has to be set in any part of the heat exchanger. In this case, we selected 2 K. Note that if this limit is higher than the difference between the superheating degree and the approach temperature in the evaporator, the available temperature glide of the refrigerant would be below the HTF temperature glide, which is not optimum for the glide matching (discussed in following sections).

This cycle requires an iterative method where the condensing temperature is a function of an undetermined intermediate temperature of the HTF. This temperature sets the condensing pressure, as shown in Eq. (4), and is calculated from the energy balance for the desuperheating zone in Eq.(5).

$$p_k = f(x_v = 1, T_k = T_i + \Delta T_{pp,k}) \tag{4}$$

$$\dot{Q}_{DSH} = \dot{m}_{HTF} c_{p,HTF} \left(T_{sink,out} - T_i\right) = \dot{m}_r \left(h_{k,in} - h_i(f(p_k))\right) \tag{5}$$

This method estimates the saturated states in the evaporator's inlet and in the condenser's saturated vapor temperature, which McLinden and Radermarcher [39] show as an option that favors zeotropic mixtures. This means that when using condenser's and evaporator's size as an input of the cycle (expressed by the minimum approach temperature), the temperature glide benefits zeotropic mixtures as it reduces the temperature lift, improving the efficiency of the cycle.

Regarding the output parameters, the COP measures the amount of heat produced over the work done by the compressor and is one of the main parameters for evaluating the performance of the cycle, Eq.(6).

$$COP = \frac{h_{k,in} - h_{k,out}}{h_{disch,is} - h_{suc}} \eta_{em} \eta_{is} \tag{6}$$

The volumetric heating capacity (VHC) indicates the size of the required compressor and can be calculated with Eq.(7), taking volumetric efficiency as 100%. Then, the mass flow rate is calculated with Eq.(8).

$$VHC = \left(h_{k,in} - h_{k,out}\right) \eta_{vol} \rho_{suc} \tag{7}$$

$$\dot{m}_r = \frac{\dot{Q}_o}{\left(h_{o,out} - h_{o,in}\right)} \tag{8}$$

Table 2
Working conditions for the HTHP cycle.

Parameter	Value
Heating production temperature, $T_{sink,out}$ (°C)	140
Waste heat temperature, $T_{source,in}$ (°C)	70
Heat sink temperature glide, ΔT_{sink} (K)	10
Heat source temperature glide, ΔT_{source} (K)	10
Condenser temperature approach, $\Delta T_{pp,k}$ (K)	4
Evaporator temperature approach, $\Delta T_{pp,o}$ (K)	7
Minimum temperature approach, $\Delta T_{pp,min}$ (K)	2
Superheating degree, SH (°C)	5
Subcooling degree, SC (°C)	2
Cooling capacity, $\dot{Q}_o$ (kW)	8
IHX effectiveness, ε_{IHX}	40%
Electromechanical compressor efficiency, η_{em}	80%
Isoentropic compressor efficiency, η_{is}	80%

Perfect glide matching

Zeotropic mixtures have temperature variations during phase change (temperature glide), affecting the system's overall performance and producing pinch points. This happens because when phase change occurs, the different boiling point values of the components create differences in liquid and vapor phases [40]. Achieving a perfect glide matching (PGM) can significantly reduce the entropy generated in the exchange process, which is represented by Lorentz's Cycle, known as the ideal cycle for zeotropic mixtures [41]. This effect has been widely studied in ORC systems [42–45]. For estimating and quantifying this effect, several methods have been proposed in the literature. This paper uses the variance method [46], and the same assumptions were made.

The PGM occurs when setting a counterflow configuration on the evaporator and condenser [47]. This glide matching depends on one main parameter, which is the $\frac{\delta T}{\delta h}$ of the refrigerant. Constant values of this partial derivative along the phase change will traduce on a better approach to PGM as the temperature function of the heat transfer fluid (HTF) is linear.

Different sections along the condenser must be considered, as shown in Eq. (9). The average temperature difference in the k-th section is expressed in Eq. (10). To evaluate the approach to this perfect glide matching, the variance can be used to express how a random variable (in our case, the temperature differences of refrigerant and HTF) is close to the desired constant temperature difference. The variance is calculated in Eq. (11) as a discrete variable of 15 points along the condenser with the expected value expressed in Eq. (12).

$$\Delta T_{htf-r,k} = T_{r,k} - T_{HTF,k} = \text{constant} \ \mathit{for} \ k = 1, 2, 3 \cdots n \tag{9}$$

$$\overline{\Delta T_{htf-r,k}} = \frac{T_{HTF-r,k+1} - T_{htf-r,k}}{2} \tag{10}$$

$$DX = \sum_{k=1}^{14} \left(\Delta T_{HTF-r,k} - EX\right)^2 prob_k \tag{11}$$

$$EX = \sum\nolimits_{k=1}^{15} \Delta T_{HTF-r,k} prob_k \tag{12}$$

$T_{r,k}$ is the temperature of the refrigerant, and it is a function of enthalpy. $T_{f,k}$ is the HTF (water) temperature, it variates linearly and is an input of the cycle. This HTF temperature may vary beyond the different applications. The aim is to check if the temperature differences between the two fluids are constant. The difference in the inlet and outlet temperature of HTF is set as 10 K. The key for obtaining this PGM is to have an equilibrate composition of two fluids with different boiling points, as this difference in boiling point increases the temperature glides. It is also remarkable that at low glides, this non-linear behavior is negligible.

Finally, $prob_k$ can be obtained from Eq. (13), representing the probability of having the temperature differences of the k-th section along the exchanger, where h_k denotes the enthalpy of the mixture on the k-th section.

$$prob_k = \frac{h_{k+1} - h_k}{h_{15} - h_1} \mathit{for} k = 1, 2, 3 \cdots 14 \tag{13}$$

With this, the proximity of the temperature glide to the condenser to the PGM is estimated based on its approach to the Lorentz cycle. It is also helpful for predicting pinch points as significant values for variances are traduced on pinch points inside the exchanger, and a PGM avoids the apparition pinch points [46,50].

Figures of merit

Another interesting approach for selecting the optimal mixtures is an analysis based on their thermodynamic and transport properties. With this, the different correlations of pressure drops and heat transfer can be compared for estimating the heat exchanger sizes for different fluids under the same conditions. This is known as figures of merit (FOM) and has been used by some other researchers such as Mateu-Royo et al. [10] and Palm et al. [48]. It is on the last one where the details for arriving at the final equation are shown.

The first FOM employed is for quantifying pressure drops, Eq. (14) which shows that lower FOM values indicate lower pressure drops in the installation. This FOM works for a single-phase turbulent flow, liquid or vapor but may be used for a two-phase state. Eq. (14) shows that pressure drops do not depend only on viscosity but also on the latent heat of vaporization.

$$\mathrm{FOM}_{\Delta p} = \frac{\mu^{1/4}}{\rho {h_{fg}}^{7/4}} \tag{14}$$

Then, Eq. (15) expresses the heat transfer process in boiling and condensation states, which is more critical in vapor compression cycles. This FOM uses Cooper's pool boiling correlation and is used with a surface roughness of 1 μm. The higher this value is, the better the heat transfer process will be.

$$\mathrm{FOM}_{pb} = {p_r}^{0.12}(-\log_{10} p_r)^{-0.55} M^{0.5} \tag{15}$$

Screening of mixtures

The model presented above was programmed in MATLAB R2018b for performing the mixture calculations. First, the COP of all the possible ternary mixtures of the selected fluids was done with a mole fraction variation of 5%. Then, the ternary mixtures with higher COP were taken for a finer optimization with a 1% mole fraction variation. The main restriction was that blends with critical temperatures below 150 °C were instantly discarded. Then, the other requirements were a maximum discharge temperature of 175 °C and a minimum pinch point temperature of 2 K.

In Fig. 4, the COP of the mixtures is screened versus the VHC, also showing the selected pure fluids. As it can be seen, the single fluid that gives higher performance is R-601, which corresponds to the fluid with higher critical temperature. Then, R-1233zd(E) is shown as the second fluid with higher COP, which follows the trend of some studies [10,13]. Then, it appears R-245fa, which is the most commonly used refrigerant on HTHPs. It is also appreciated that there is a slight increase of COP in relation to the single fluids, which shows the potential of some mixtures that will be discussed later. The fluids that do not appear are because they do not fulfill the criteria.

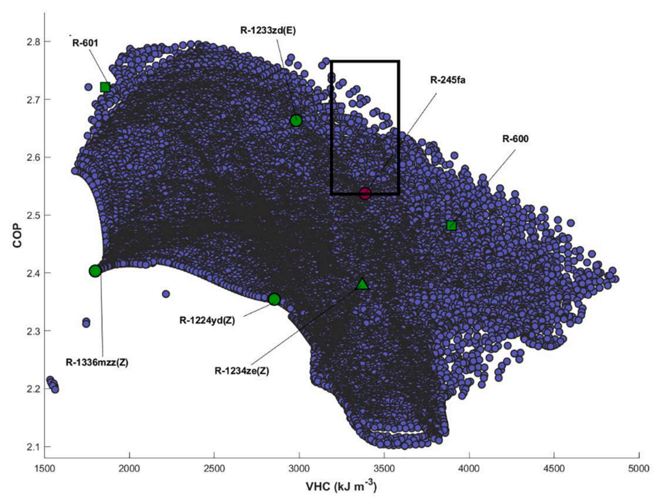

Fig. 4. Screening of all the calculated mixtures for a simplified HTHP cycle. Blue points are mixtures, and the others are pure fluids. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

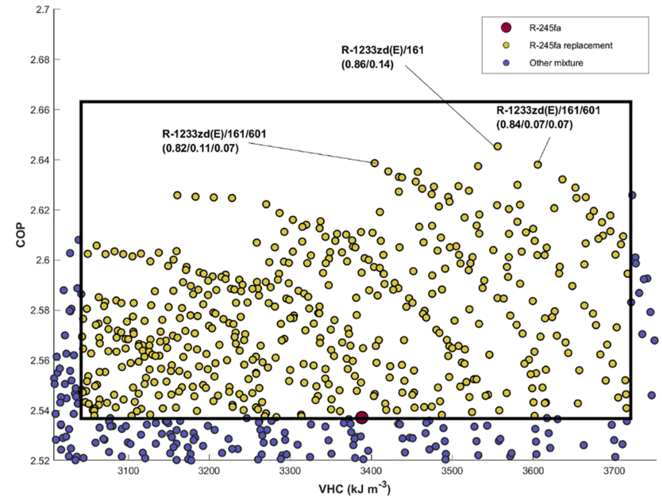

Fig. 5. Screening of R-245fa drop-in replacements. The yellow dots have a flammability class of 1 and are in the range of ±10% of R-245fa VHC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

However, a good selection of mixtures must consider different ranges of flammability and GWP as this restricts the desired application. Fig. 6 splits all the mixtures into 6 subplots depending on the flammability class and the GWP. This division has to be consequent with the selected fluids. The GWP was divided into two classes, GWP lower than 150 and higher than this value, which is the threshold in most applications.

Fig. 6 provides an insight into how two of the main parameters, flammability, and GWP, affect the rest of them, COP and VHC. The low GWP and flammable subplot in the upper left have more mixtures. This is seen as a consequence of the finer calculation process, which prioritized mixtures with estimated flammability class 3 which had the highest COP. Then, the amount of mixtures in the mildly flammable range is higher than in the nonflammable.

Regarding the COP, the low GWP and flammable subplot is the one that has higher COPs. There is a trade-off between flammability and COP that makes the probable 1 and 2L mixtures worse in relation to efficiency. Some estimated 2L mixtures have a slightly higher COP but not so big as when passing from the 2L class to 3.

In addition, GWP does not seem to be a critical parameter for optimization. Higher COPs are obtained for lower GWPs. This can be explained through the fact that the single fluids that had higher efficiencies were also the ones with lower GWP.

Mixture selection

Optimal mixtures for new installations

For selecting the best mixtures, several parameters must be taken into account. The results section shows that not all the parameters can be the best simultaneously, so some of them must be prioritized. In this case, the most optimal mixture is searched for a new installation made exclusively for the selected refrigerant.

As one of the critical parameters is flammability, mixtures are

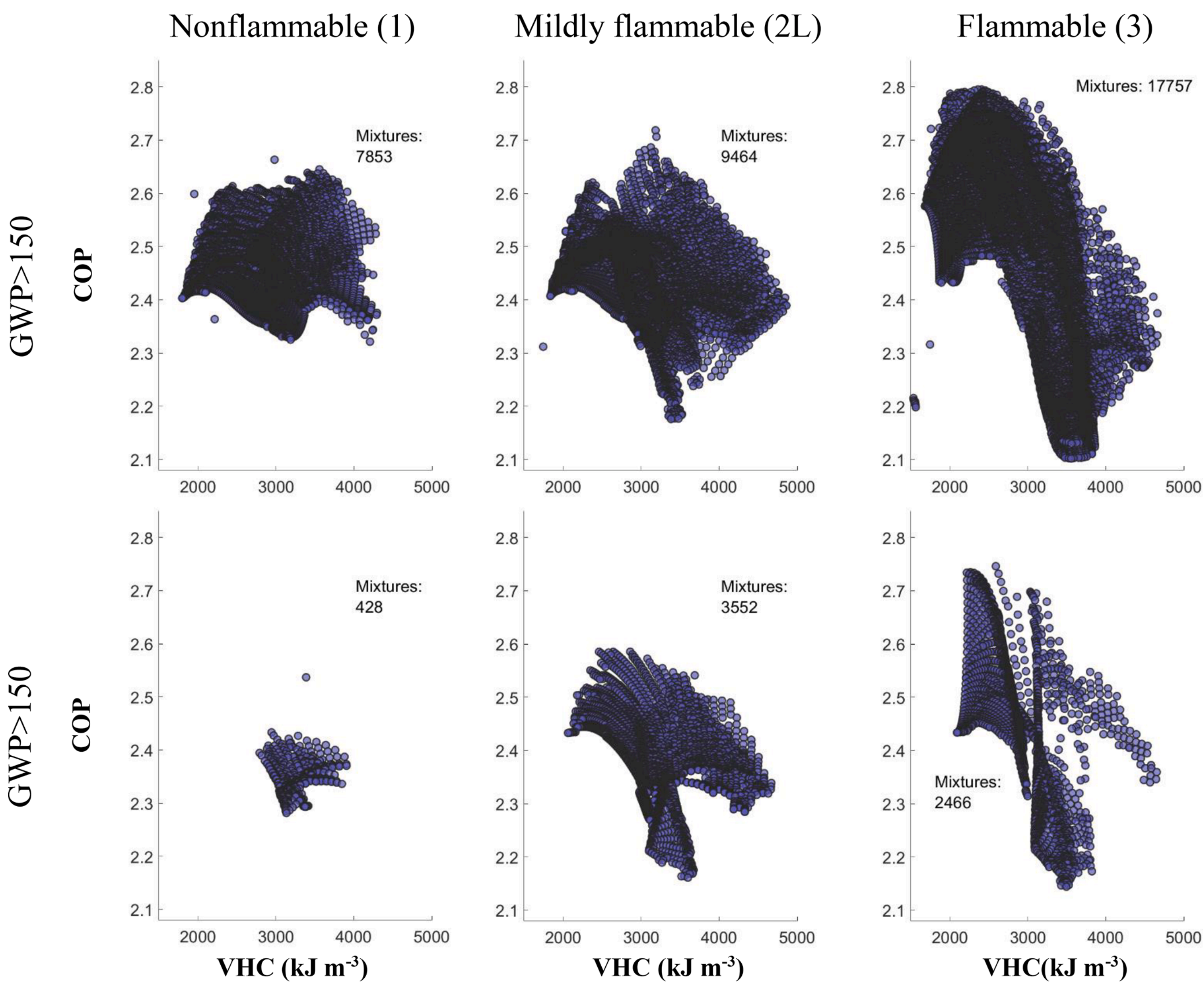

Fig. 6. Performance screening of calculated mixtures. The upper left subplots belong to the nonflammable mixtures with low GWP and the lower right to the flammable mixtures with high GWP. This screening method is the one performed by Bell et al. [25].

Table 3
Selected mixtures ordered by COP and classified by estimated flammability class.

Designation	Mixture	Composition (mole fraction)	COP	VHC (kJ m^{-3})	$\dot{m}$(kg s^{-1})	T_{cri} (°C)	GWP	Temperature glide (K)
Flammable (estimated)								
1	R-601 /1234ze(Z)	0.74/0.26	2.80	2406	0.05	180.8	5.6	8.3
2	R-601/1234ze(Z)	0.75/0.25	2.80	2361	0.05	182.0	5.7	8.3
3	R-601/600a/1234ze(Z)	0.7/0.22/0.08	2.79	2422	0.04	182.2	4.3	8.6
4	R-601/1234ze(Z)/161	0.84/0.13/0.03	2.79	2189	0.04	185.8	4.4	8.3
5	R-601	1	2.72	1958	0.04	196.5	6.0	0
Mildly flammable (estimated)								
6	R-1233zd(E)/601/152a	0.65/0.25/0.1	2.72	3184	0.07	165.5	14.4	6.7
7	R-1233zd(E)/601/152a	0.66/0.24/0.1	2.71	3195	0.07	165.1	14.3	6.4
8	R-1224yd(Z)/601/152a	0.67/0.21/0.12	2.63	3170	0.08	160.4	15.1	6.8
9	R-1336mzz(Z)/601/152a	0.7/0.16/0.14	2.61	2417	0.08	167.1	18.9	8.0
10	R-1233zd(E)/152a/1336mzz(Z)	0.67/0.2/0.13	2.61	3526	0.08	157.1	25.6	7.0
Nonflammable (estimated)								
11	R-1233zd(E)	1	2.66	2981	0.07	166.5	1.0	0
12	R-1233zd(E)/152a/161	0.86/0.04/0.1	2.64	3531	0.08	160.1	14.4	6.7
13	R-1336mzz(Z) /152a/601	0.79/0.16/0.05	2.61	2444	0.09	165.9	20.9	8.0
14	R-1336mzz(Z) /152a/601	0.8/0.16/0.04	2.61	2429	0.09	166.0	20.8	7.9
15	R-1233zd(E)/161	0.88/0.12	2.64	3457	0.08	161.1	11.2	6.5
16	R-1336mzz(Z)	1	2.40	1798	0.1	171.3	16.8	0

classified according to this parameter. This is a suitable classification as the chosen refrigerant depends on the level of hazards assumed in the installation.

Table 3 presents mixtures with higher COPs. As seen, a COP of 2.8 can be achieved at most for a binary mixture of R-601 with R-1234ze(Z). The dominance of R-601 in all the best mixtures is explained by its high critical temperature, moving away from the working pressures from the upper saturation curves where the latent heat is lower. This analysis matches with other previous investigations [8,51,52]. In addition, these mixtures show a high temperature glide, presenting a dominant zeotropic behavior as expected in the selection of the saturated states due to the reduction of temperature lift. If the hazards of using a flammable can be assumed, M1, R-601/R-1234ze(E) (0.74/0.26) is a good option as it has low GWP and gives additional COP in relation to the pure R-601.

It is also remarkable that, as shown by Bell et al. [49], only 3 mixtures with R-601 are on the ASHRAE Std 34 (mixed with R-600, R-125, or R-134a), which means that this kind of mixtures has not been studied in-depth yet so there is room of improvement.

Things get more interesting when looking at the mildly flammable mixtures. The COPs are lower, and three different ternary mixtures (M6, M8, and M9) dominate. Those mixtures are the R-1233zd(E), R-1336mzz(Z), and R-1224yd(Z) based, being the first considerably better in relation with COP. They have one main characteristic in common; their second component most present is R-601. As the higher COPs are achieved with R-601, mixtures with high mole fractions of these fluids also do. Then, the presence of R-601 in the mixture should be higher as the flammability restriction allows it.

In-depth, R-1233zd(E), R-1336mzz(Z) and R-1224yd(Z) have also low GWP. This makes those three mixtures appropriate for A2L solutions. One point that should be added is that R-1233zd(E) mixtures do not improve efficiency considerably. In fact, for the estimated A1 class, the single fluid is the one with higher performance. Otherwise, on the estimated 2L classification, it can be slightly improved. There is also a highlighted improved performance when mixing with R-601 and R-152a (M9) in the case of R-1336mzz(Z). M6, M7, M8, M9, and M10 are proposed as the best with the mild flammability restriction.

Like in the mildly flammable class, the most optimal mixtures are R-1233zd(E) and R-1336mzz(Z) mixtures on the nonflammable restriction. The decrease in COP for the nonflammable class is reduced compared to the previous. M12, M13, M14, M15, and R-1233zd(E) are shown as the best for these restrictions. In addition, R-1224yd(Z) based mixtures do not appear in the estimated flammability class 1.

Another interesting things are that all of them are zeotropic, for the reasons presented previously. Then, they have all low GWP as no trade-off was seen between the GWP and the COP. Moreover, the higher the presence of R-601 is, the lower the mass flow rate is, as its density is reduced compared to the others. This is also a drawback of the estimated 2L and 1 mixtures because their higher mass flow rates would produce higher pressure drops, decreasing the performance.

R-245fa drop-in replacements

R-245fa is the most widely used refrigerant for HTHP and Organic Rankine Cycles as it has a high critical temperature and good performance. However, its main drawback is high GWP and high toxicity, so different studies were carried out looking for immediate replacements that could work on operating installations [5,10,11].

The main conditions that a drop-in replacement must fulfill are similar P-T relation, similar VHC, as this parameter defines the size of the compressors, the same flammability class, and compatibility with lubricant and materials. In addition, a zeotropic mixture replacing a single fluid should not have high temperature glides.

In Fig. 5, drop-in replacement candidates are shown in yellow dots, removing the ones with different estimated flammability classes. It can be seen that there is room for improvement for this kind of cycle. Table 4 includes the most suitable replacements of R-245fa. All of them show a higher predicted COP and considerably reduce the GWP. There are 2 groups of mixtures, the ones with high temperature glides (M17, M18, M19, and M20), and the rest (M21 and M22). However, the second group does not provide a significant increment of energy performance.

The main component of the selected mixtures is R-1233zd(E), which Dawo et al. found [53] as the most suitable R-245fa replacement, taking into account the interaction with the lubricant. In this case, it is mixed with additional components such as R-161, R-601, or R.152a, which is traduced on a closer VHC to the desired for a drop-in replacement.

Regarding the compatibility topic, Eyerer et al. [54] concluded that R-1224yd(Z) had similar material compatibility with R-245fa for ethylene propylene diene rubber and chlorobutadiene rubber. However, it is necessary to perform individual compatibility investigations to determine which one is the most suitable, attending to the compatibility criterion. This suggests experimental studies evaluating the real performance and compatibility of the selected drop-in replacement as low-GWP alternatives.

Zeotropic behavior

Zeotropic mixtures allow the alignment of refrigerant and HTF temperature profiles, which affects the temperature differences during phase change. This alignment decreases the irreversibilities during the phase change process but has a drawback that sometimes is ignored. The reduction of the temperature difference affects the required heat exchange area by the degradation of the heat transfer process. This sometimes leads to optimistic results in relation to zeotropic mixtures. Then, when using this kind of mixture, a trade-off decision has to be made.

A more in-depth study of the selected mixtures must take into account the effect of temperature glide. In this study, the method for evaluating this behavior is presented by Jin and Zhang [46], based on statistical variance. Fig. 7 shows the best mixtures temperature glide (green bars) and variance of the temperature difference between HTF and variance (purple bars). PGM, which corresponds to a variance of nearly 0, is not achieved in these higher performance mixtures. However, when looking at mixtures with lower performances, mixtures 2 and 3 are an example of good glide matching. Due to its glide approach to the HTF temperature difference and its linear enthalpy-temperature relation on phase change presents a low variance.

Fig. 8 shows the relation between composition, glide, COP, and glide matching of mixture 2. As seen, the temperature glides in the edges are

Table 4
R-245fa drop-in replacements candidates.

Designation	Mixture	Composition (mole fraction)	COP	VHC (kJ m^{-3})	$\dot{m}$(kg s^{-1})	T_{cri} (°C)	GWP	Temperature glide (K)
R-245fa replacements								
17	R-1233zd(E)/152a	0.86/0.14	2.65	3556	0.08	160.1	13.6	7.0
18	R-1233zd(E)/161/601	0.82/0.11/0.07	2.64	3404	0.07	161.4	11.4	6.7
19	R-1233zd(E)/152a/161	0.84/0.07/0.07	2.64	3605	0.08	159.1	17.6	6.8
20	R-1336mzz(Z)/1234ze(Z)/152a	0.48/0.36/0.16	2.59	3132	0.08	156.2	20.6	6.9
21	R-1233zd(E)/1234ze(Z)/161	0.86/0.12/0.02	2.56	3117	0.08	162.5	2.7	1.5
22	R-1233zd(E)/1224yd(Z)/152a	0.84/0.12/0.04	2.56	3102	0.08	162.4	6.0	1.7
23	R245fa	1	2.54	3388	0.08	153.9	726.0	0.0

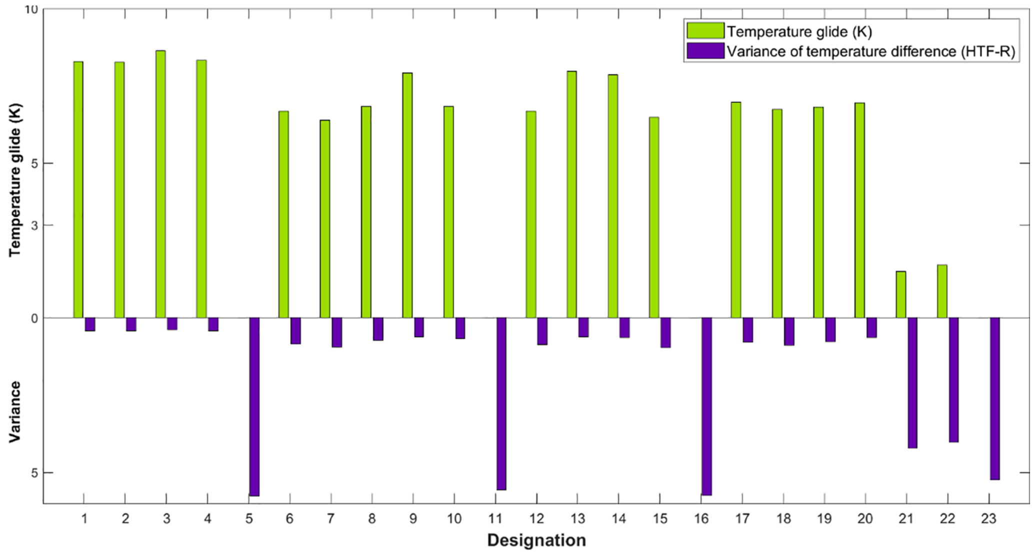

Fig. 7. Screening of temperature glide and variance of the temperature difference between heat HTF and refrigerant of the selected mixtures.

near to 0 due to the dominance of the boiling point of one fluid. The highest temperature glides are given for the binary mixture R-601/R-1234ze(Z) due to its difference in boiling points of 26.3 K. On the other hand, R-1234ze(Z)/R-1233zd(E) shows relatively low temperature glide due to the difference in boiling points of 8.5 K. Through this, it can be deduced that if it is desired to work with low temperature glides, the mixing components should have similar boiling points. Then, if it is preferred to get a PGM, the difference in the boiling points should be higher enough to give the mixture a similar temperature glide to the HTF temperature difference.

The most proper glide matching is achieved with a temperature glide of 6.2 K due to its approach to the glide of the HTF during the condensation and its enthalpy/temperature linear relation, providing to this composition the minimum variance and therefore being the composition with a more closely PGM. It is noted that the surrounding area of this point, all the blue zones in Fig. 8 (a), also gives low variances, but the better is just set at one composition. It also can be seen how the temperature profiles are for good glide matching on a condenser. Looking at Fig. 8 (b), in relation to the two others can be seen that there is not a trade-off between achieving good glide matching and COP. Then, another advantage of designing the cycle through the inlet approach temperatures is that it tends to favor mixtures with proper glide matching.

FOM analysis

Table 5 expresses the estimation of the FOM's of the selected mixtures. The first and second are for pressure drops, and the third for the heat transfer process during boiling and condensation.

Regarding the pressure drops, it is noted that the estimated flammability class would have fewer pressure drops. The main reason for this is that R-601, the main component in these mixtures, has a higher heat of vaporization, which directly affects pressure drops. Then, R-1233zd(E) has a lower density but higher heat of vaporization than R-1336mzz(Z) which contributes directly to its mixtures, being those based on R-1233zd(E) the ones with lower expected pressure drops.

The third column of Table 4 shows that R-245fa has the highest value, corresponding to a better heat transfer coefficient. By contrast, M5, R-601, has a lower value. Then, it is seen that R-1233zd(E) mixtures tend to have higher values of this FOM than R-1336mzz(Z).

This analysis concludes that R-601 based mixtures tend to have lower pressures drops than the others, and R-1336mzz(Z) mixtures are higher. On the other hand, the heat transfer coefficient would be higher for those R-1233zd(E) mixtures and lower for R-601 mixtures.

Environmental concernings

R-1233zd(E) is commonly known as zero ODP refrigerant, but it has an ODP of 0.00034. It can be classified as low ODP refrigerant and even mixed the ODP of the mixture should be even lower. Through this, the ODP for these mixtures could be taken as negligible, but it depends on the development of the new regulations. As an example, the German Federal Environment Agency (UBA) is pushing for a ban on R-1233zd(E) [55]. If this new regulation must be fulfilled, R-1336mzz(Z) mixtures are shown as appropriate alternatives.

Other countries are pushing to ban a wide range of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), in which HFOs are included [56]. By contrast, other studies claim that the impact of R-1234yf in recent years on the TFA emission has been insignificant [57]. Unfortunately, if this restriction goes ahead, the number of low GWP, nonflammable candidates for HTHP dramatically decreases. One of the most suitable alternatives would be using HCs with a small charge, which would reduce the potential of HTHP to limited applications.

Model uncertainties

During the calculations of all the mentioned parameters, certain assumptions have been made that may affect the reliability of the final results. For preventing this, all the estimations made have to be commented.

One of the parameters that have not been considered on this cycle and directly affect the global efficiency is pressure drops and heat transfer parameters [15]. For taking this into account, FOMs of the best mixtures are analyzed, which provides a more accurate description of their response. Nevertheless, the FOM analysis is made through REFPROP v10.0 estimation of transport properties, which has limitations due to the uncertainties. The uncertainties given by REFPROP v10.0 for viscosity for the calculated fluids are between 3% and 6%, depending on if it is vapor (higher uncertainties) or liquid phase. This is the main uncertainties for the FOM calculation, which makes possible a qualitative comparison between different mixtures. Other FOMs, such as the convective heat transfer from the Dittus-Boelter equation, have not been computed due to the uncertainties in estimating thermal conductivity.

Another thing that must be considered is the estimation of thermodynamical properties for fluids and mixtures. For pure fluids, REFPROP

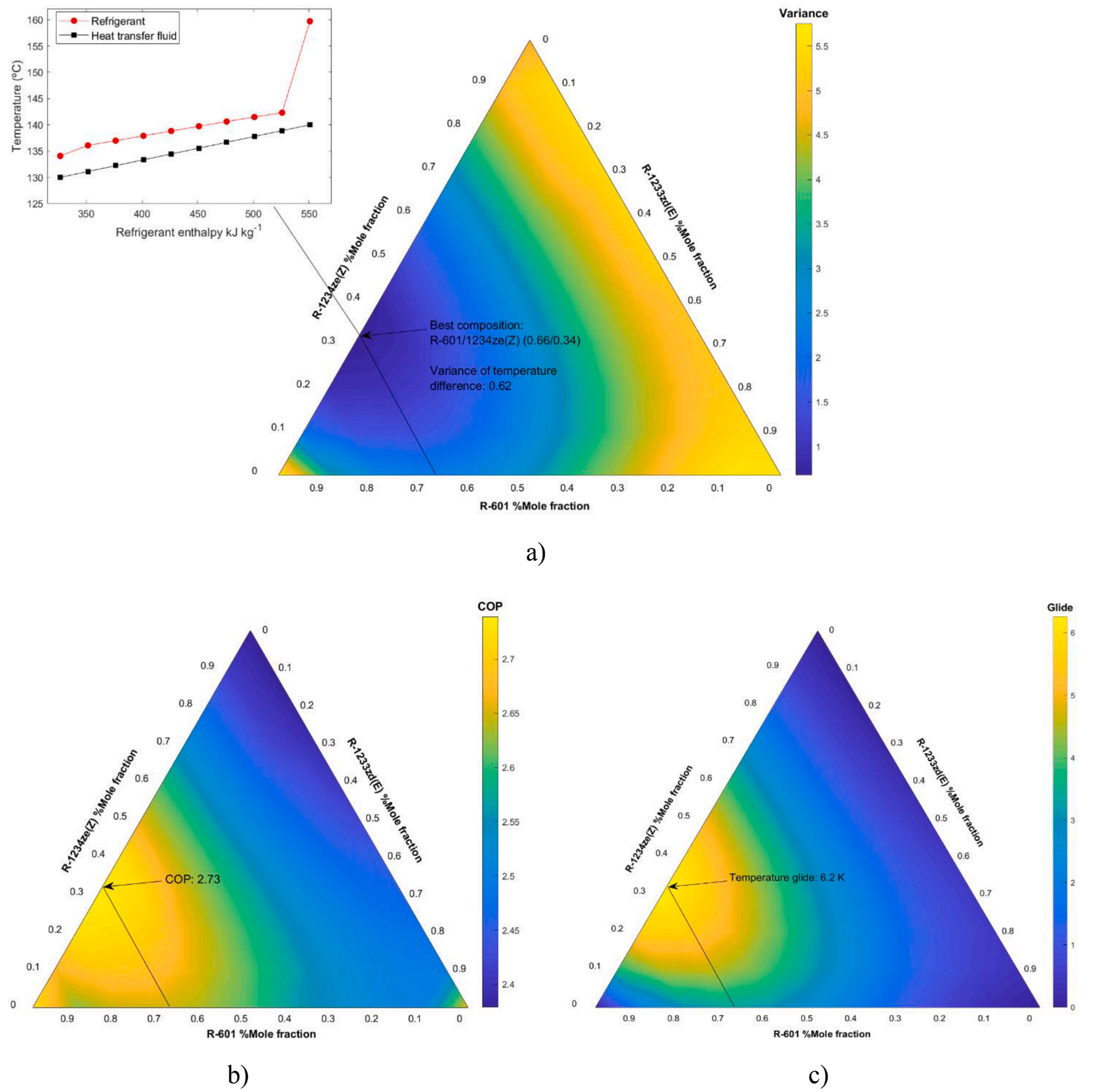

Fig. 8. Screening of temperature difference between HTF and refrigerant, COP, and glide temperature for an R-601/1233zd(E) mixture.

v10 gives high-accuracy predictions for all fluids presented in this work (a maximum of 2% uncertainty for heat capacity in case of R-600a is found on the NIST REFPROP database) when not working near critical. Regarding the effect of mixing fluids, the mentioned software uses the combination of the equations of state for the different pure fluids of the mixture, making in most of the cases estimations for the interaction parameters [58,59]. Bell et al. [25] took 0.05 as the global mean estimated uncertainty of the main interaction parameter between mixtures containing HFCs, HFOs, and natural refrigerants. This is found as one of the limitations of this work, and generally, all the theoretical models that estimate mixtures with no available data. However, the theoretical model is a widely used method for the initial estimation of potential new refrigerants before starting experimental studies. The results presented in this paper serve as a first approach for zeotropic mixtures in the HTHP breakthrough technology.

Conclusions

We have done a screening of the mixture for high-temperature heat pumps. The main restrictions for the refrigerants were to have a critical temperature above 150 °C, a minimum pinch point temperature difference of 2 K, and a discharge temperature below 175 °C. The presented mixtures maximize COP in relation to the GWP and flammability restrictions. There is also performed a glide matching approach for estimating the zeotropic behavior of mixtures. In addition, a FOM analysis is performed for having a qualitative estimation of pressure drops and heat transfer coefficients. No mixture was found that maximizes all these parameters, so the different trade-off approaches are discussed.

GWP is not a critical parameter for this temperature range, as mixtures with similar performances were obtained for different GWPs. The parameter which becomes more critical is flammability. The highest COP for mixtures also shows high flammability, being necessary to mix

Table 5
Figures of merit of the best mixtures.

Designation	$FOM_{\Delta p,l}(x10^6)$	$FOM_{\Delta p,v}(x10^6)$	FOM_{pb}
Flammable			
1	0.60	3.41	0.19
2	0.58	3.39	0.18
3	0.55	3.13	0.20
4	0.54	3.36	0.18
5	0.43	3.11	0.17
Mildly flammable			
6	1.04	4.13	0.21
7	1.06	4.16	0.21
8	1.33	4.79	0.22
9	1.19	5.25	0.18
10	1.51	4.77	0.18
Nonflammable			
11	1.13	4.41	0.20
12	1.31	4.43	0.23
13	1.26	5.45	0.22
14	1.27	5.50	0.22
15	1.27	4.41	0.17
16	1.19	5.85	0.16
R-245fa replacements			
17	1.31	4.43	0.22
18	1.24	4.37	0.23
19	1.35	4.45	0.22
20	1.61	5.30	0.23
21	1.24	4.44	0.22
22	1.28	4.57	0.22
23	1.67	4.69	0.28

the flammable refrigerants with other nonflammable refrigerants, reducing the COP.

R-601/1234ze(Z) (0.74/0.26) is the mixture that probably provides the highest COP. It is a low GWP, flammable, and zeotropic mixture. It is also estimated that lower pressure drops are expected due to its low viscosity and high heat of vaporization. R-1233zd(E)/601/152a (0.69/0.2/0.11) and R-1233zd(E)/R-601/161 (0.68/0.22/0.1) are the ones that provide higher performances when complying with the predicted A2L safety class. Then, R-1233zd(E) shows the highest predicted COP when achieving the A1 safety class. Then, R-1336mzz(Z)/152a (0.79/0.16/0.05) is the zero-ODP mixture estimated as A1 safety class that gives higher performance.

Regarding R-245fa direct replacements, R-1233zd(E)/161/601 (0.86/0.14) is found as the most probable appropriate drop-in replacement when moderate temperature glides are permitted. If temperature glides should be lower, R-1233zd(E)/1234ze(Z)/161 (0.86/0.12/0.02) has a temperature glide of 1.5 K in the condenser but presents a lower COP.

We noted that the glide matching provides interesting results with high COP mixtures. Therefore, zeotropic mixtures for HTHP are initially found as good candidates for future experimental studies. Future studies will have to consider the trade-off between reduction of irreversibilities and heat transfer coefficient degradation more in-depth.

Finally, this study has its own limitations that must be completed with future investigations. Experimental verification, in-depth compatibility/miscibility study with lubricants and materials, heat transfer evaluation, and other boundary conditions are topics that must be covered in future researches for assuring the real applicability of mixtures to the high-temperature heat pump technology.

CRediT authorship contribution statement

Adrián Fernández-Moreno: Conceptualization, Methodology, Software, Writing – original draft, Writing – review & editing. **Adrián Mota-Babiloni:** Conceptualization, Methodology, Writing – review & editing. **Pau Giménez-Prades:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Joaquín Navarro-Esbrí:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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