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Research Paper

Thermodynamic analysis of propane-based zeotropic mixtures in space heating and domestic hot water heat pumps

Gianluca Abrami *, Lorenzo Pistocchini, Jacopo Famiglietti, Tommaso Toppi

Department of Energy, Politecnico di Milano, 20156 Milano, Italy

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ABSTRACT

Propane is considered one of the most promising refrigerants for residential heat pumps due to its favorable thermodynamic properties and negligible climate impact. However, its use remains challenging in high-temperature applications due to reduced capacity and efficiency, as well as high compressor discharge temperatures. A viable strategy to mitigate these issues is the use of zeotropic mixtures, whose properties can be tailored to the specific application, thereby improving cycle efficiency. Building on this approach, the present study investigates the potential of propane-based zeotropic mixtures as working fluids for heat pumps in both space heating and domestic hot water production. A steady-state thermodynamic model of a single-stage vapor compression heat pump was developed to evaluate the performance of six low-global warming potential co-fluids blended with propane. Results show that mixtures can increase the coefficient of performance compared to pure propane, with butane blends achieving the best improvements in space heating (+7%) and CO_2 blends in domestic hot water production (+11%). The use of co-fluids effectively reduced the compressor discharge temperature (up to 14 °C) but penalized the volumetric heating capacity. The analysis highlights the impact of superheating, subcooling, and mixture composition, showing that the highest coefficient of performance was achieved with a temperature match in the evaporator rather than in the other heat exchangers. Overall, propane-based zeotropic mixtures enhance performance while mitigating operational constraints, demonstrating their viability as low-global warming potential refrigerants for residential heat pumps.

1. Introduction

Buildings account for 30% of global final energy consumption and 26% of global operational energy-related emissions (direct and indirect). Within the building's energy demand, almost half is associated with space heating and domestic hot water production [1]. As a highly energy-intensive sector, many countries are working to decarbonize it through policies and related directives, such as the ones of the European Union (EU), that push for the adoption of energy-efficient and low-emission technologies to meet climate-neutrality targets [2].

Heat pumps are regarded as a key technology for this transition, reducing the reliance on fossil fuels in building energy generation devices. Nowadays, the market is still dominated by heat pumps that use hydrofluorocarbons (HFC) as working fluid [3], however, recent regulations, such as the Kigali amendment to the Montreal protocol [4,5] and the European Union F-gas regulation [6], started a phasing-out process for these refrigerants, forcing their replacement by alternatives characterized at the same time by zero Ozone Depletion Potential (ODP) and null or minimum Global Warming Potential (GWP).

However, the transition is not smooth, as, besides environmental constraints, the refrigerant choice should also take into account their thermodynamic properties, which must be suitable for the considered application, their safety, and their compatibility with the materials commonly used for heating appliances. This limits the options for viable refrigerants, as explained by McLinden et al. [7]. Among the different alternatives, propane (R290) is one of the refrigerants that has gained more attention in recent years, resulting in an increasing number of commercial heat pumps adopting it. Propane is characterized by good thermodynamic properties at the conditions required by the typical residential application, making it a suitable drop-in solution to the most common refrigerants [3]. However, as for heat pumps operating with other refrigerants, also the ones working with propane face some challenges at high thermal lifts (i.e., when the temperature difference between the source and sink increases), such as reduced heating capacity and efficiency, and high compressor discharge temperature [8]. The latter is particularly critical, as excessively high discharge temperature can lead to the degradation of the compressor lubricant oil, potentially

* Corresponding author.
E-mail address: gianluca.abrami@polimi.it (G. Abrami).

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Nomenclature

ΔT	Temperature variation (K)
ε	Heat exchanger effectiveness
k	Penalty coefficient
η	Efficiency

Abbreviations

A	Air
BC	Base case
COP	Coefficient of performance
COMP	Compressor
EVA	Evaporator
COND	Condenser
DHW	Domestic Hot Water
DMC	Dimethyl Carbonate
GWP	Global Warming Potential
HFC	hydrofluorocarbons
IHX	Internal Heat Exchanger
ODP	Ozone Depletion Potential
NBP	Normal Boiling Point
PFAS	Per- and polyfluoroalkyl substances
SC	Subcooling (K)
SH	Superheating (K)
SO	Surrogate Optimization
VHC	Volumetric Heating Capacity (MJ/m^3)
W	Water
T	Temperature (°C or K)
p	Pressure (bar)
TEWI	Total Equivalent Warming Impact

Subscripts

a	Air
disch	Discharge
i	Inlet
o	Outlet
tot	Total
obj	Objective
SH	Superheating
SC	Subcooling
HXs	Heat exchangers
w	Water
dew	Dew condition
bubble	Bubble condition
ref	Reference
calc	Calculated
is	Isentropic
crit	Critical

resulting in performance loss or even compressor failure. Although this limit varies with the specific compressor type, a discharge temperature between 115 and 120 °C is commonly considered the upper limit for standard vapor compression heat pumps for residential applications.

Several modifications have been attempted to improve the efficiency of the propane-based heat pump cycle, such as ejector-based systems [9], vapor injection systems [10], multistage compression process [11], by complementing the cycle with an Internal Heat Exchanger (IHX) [12].

One more straightforward method consists of blending propane with other refrigerants (which will be referred to as co-fluid), resulting in a zeotropic mixture. Due to the temperature glide (i.e., the difference between bubble and dew temperatures) shown during phase transition, zeotropic mixtures provide a better thermal matching with the external heat source/sink, especially when they experience a relatively large temperature variation. The cycle with zeotropic mixtures approaches the Lorentz cycle, which has higher efficiencies than the Carnot cycle for variable temperature sources, as demonstrated by Radermacher et al. [13]. Moreover, a properly formulated mixture can be adopted for multiple purposes, such as reducing the compressor discharge temperature/pressure or decreasing the flammability of propane, as demonstrated by Wang et al. [14]. This is particularly relevant because propane is classified as a Class 3 refrigerant with “higher flammability” and requires strict compliance with safety measures when implemented in residential heat pumps [15].

Several authors have demonstrated the advantages of utilizing zeotropic mixtures in heat pump cycles. Zühlsdorf et al. [16] performed many studies highlighting the advantages of a zeotropic mixture. They analyzed various binary mixtures composed of 14 refrigerants, demonstrating that a good glide match can enhance the performance of the cycle. However, while including propane as a component, this study did not focus on typical residential boundary conditions.

Xiao et al. studied the performance of a mixture composed of R290/R600a/R13I1 for a heat pump water heater [17]. They found that the annual average Coefficient of Performance (COP) was approximately 6.2% higher than in the case with R134a, due to lower condensing pressure and compression ratio, as well as higher specific heating capacity. A study with similar boundary conditions was conducted by Jian Liu et al. [18], which evaluated the performance of fifteen different mixtures for typical Domestic Hot Water (DHW) production applications. The study demonstrated higher efficiencies, but lower heating capacities compared to both the high- and low-boiling pure substances of the mixture.

Hakkaki-Fard et al. developed a numerical model for the detailed simulation of an air-source residential heat pump in cold climate regions [19]. They selected 15 pure refrigerants and analyzed the performance of their binary/ternary mixtures compared to R-410A. They found that the mixture R32-CO_2 could increase the heating capacity by 30% compared to R-410A, while mitigating the flammability of R32 and the high operating pressure associated with CO_2. Also, they noted that propane and its mixtures had the highest COP but the lowest heating capacity among the evaluated options.

Kristensen et al. evaluated five different binary mixtures under full and part load conditions [20]. Three cycle layouts were optimized at full load: a standard vapor compression cycle with an internal heat exchanger and a double compression cycle with and without the IHX. The standard cycle with the IHX was also characterized under part-load conditions. In some cases, the COP of the mixtures decreased in the part load condition, while in some other cases it increased. This demonstrated the necessity of evaluating also the part load condition while studying heat pump applications.

Huang et al. demonstrated the advantages of utilizing a zeotropic mixture in a heat pump water heater coupled with a phase change material thermal energy storage [21]. The mixture under analysis was R1234yf/R1234ze(Z), which showed an 18.1% and 6.8% improved COP compared to pure two components, respectively. Heat pump water heaters with low GWP refrigerant mixture were also studied by Kim et al. [22], who simulated the performance of R-32, R-446A, and L-41b in the high- and low-temperature applications of the standard EN 14511–2. Moreover, they optimized the design parameters of the heat exchanger to achieve the maximum COP. Their conclusion was that the alternative refrigerants can improve the performance of the heat pump by up to 6.3% and 4.6%, in the high- and low-temperature scenario, respectively, while decreasing the total equivalent warming impact

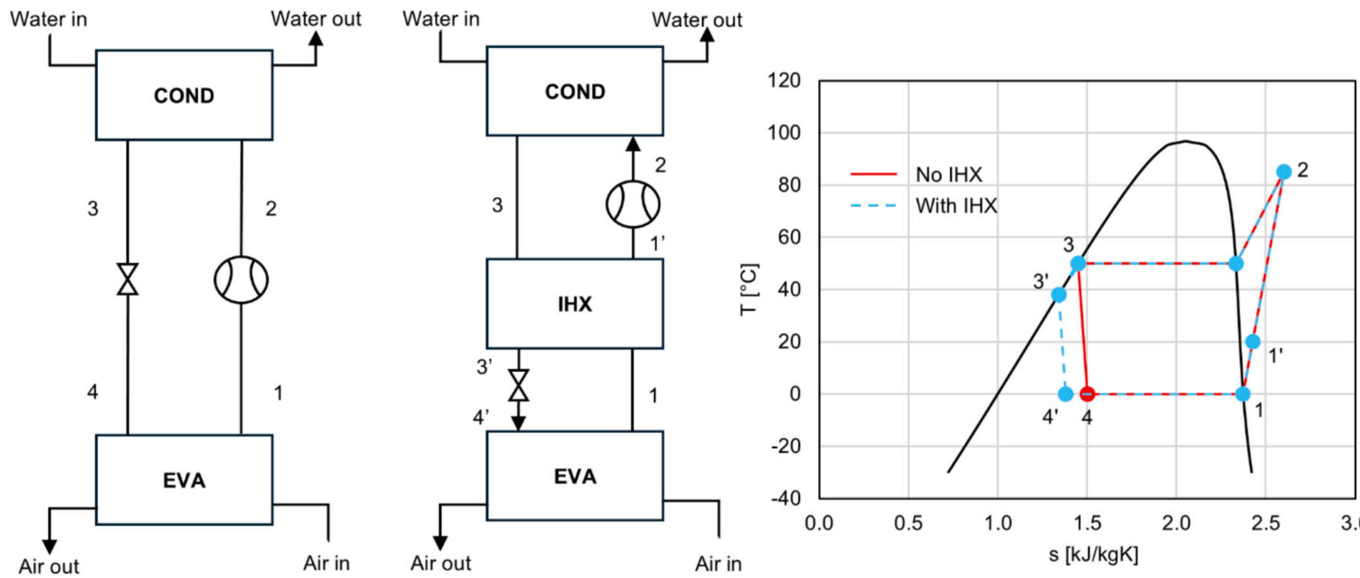

Fig. 1. Heat pump configuration with and without the internal heat exchanger and their T-s diagram.

(TEWI) by 5.9% to 9.9%.

Many studies have focused on CO_2-based mixtures, primarily aiming to address challenges associated with CO_2 low critical temperature and high operating pressure. For example, Zendehboudi et al. [23] performed a techno-economic evaluation of different CO_2-based mixtures, including one with propane, for space heating applications, in accordance with the standard EN 14511–2. The mixtures were found to improve efficiency and lower the optimal discharge pressure. Moreover, the addition of an internal heat exchanger showed a notable effect on the COP.

The reported studies demonstrate the potential of zeotropic mixtures as alternative refrigerants for heat pumps and the interest of the scientific community. However, few works focus on residential applications, and many include mixtures containing high-GWP refrigerants, which will be progressively phased out. Furthermore, there is a lack of systematic investigations on propane-based zeotropic mixtures for residential heat pump applications, despite the growing relevance of propane as a natural, low-GWP refrigerant. This work addresses this research gap by evaluating the performance of six propane-based zeotropic mixtures and comparing them to pure propane under representative space heating boundary conditions, derived from European standards EN 14511–2 [24], and real-world DHW operating scenarios. Unlike most of the previous studies, this work focuses on zero or almost negligible GWP fluids and considers only a single fluorinated refrigerant (R1234ze(Z)), a class of fluids currently under discussion in the European Union in the broader ban of Per- and polyFluoroAlkyl Substances (PFAS) [25]. Additionally, this study includes fluids that have not been addressed in previous studies, according to the authors' knowledge, including blends with significant temperature glide that may offer favorable properties for the targeted applications. Eventually, the analysis incorporates an examination of temperature matching in the heat exchangers and evaluates strategies to limit the compressor discharge temperature, which is of particular relevance for residential heat pumps operating at high temperature lift.

The comparison of the mixtures is performed using a steady-state thermodynamic model of a single-stage vapor compression heat pump (as described in Section 3.1), coupled with an optimization routine that adjusts superheating, subcooling, and mixture composition to identify the operating conditions that maximize the cycle COP. The studied heat pump included an internal heat exchanger, which enables additional subcooling of the high-pressure refrigerant after the condensation, while simultaneously superheating the low-pressure refrigerant before compression [26]. This reduces the throttling irreversibility [27], but the resulting higher compressor inlet temperature increases the compressor discharge temperature.

This study can be of interest to the scientific community working on alternative low-GWP refrigerants, offering insights into the thermodynamic behavior, optimization, and practical limitations of propane-based zeotropic mixtures for residential heat pumps.

2. Method

The refrigerant mixtures were compared by calculating the performance of the heat pump in four conditions, two for space heating applications and two for DHW production. This section begins by presenting the layout of the configuration of the analyzed heat pumps, followed by a description of the investigated mixtures and the boundary conditions under which the analysis was carried out.

2.1. Heat pump layout

Fig. 1 presents the schematic of a single-stage vapor compression heat pump with and without the internal heat exchanger, together with a T-s diagram to illustrate the difference between the two configurations.

The basic cycle without the IHX consists of four main processes:

- State 4 ➔ 1 - The refrigerant evaporates at low pressure, absorbing heat from the external air, leaving the evaporator as a saturated or superheated vapor.
- State 1 ➔ 2 - The refrigerant is compressed to high pressure in the compressor.
- State 2 ➔ 3 - The refrigerant condenses while releasing heat to the sink, leaving the condenser as a saturated or subcooled liquid.
- State 3 ➔ 4 - Eventually, in the expansion valve, the refrigerant is throttled from high to low pressure, closing the cycle.

In the configuration with the internal heat exchanger, the refrigerant does not usually complete the evaporation process in the evaporator, but rather in the IHX (1➔ 1′) by exchanging heat with the high-pressure refrigerant stream, which is subcooled from state 3 to state 3′. When refrigerant mixtures are used, the less volatile component typically evaporates at a slower rate, and the IHX can facilitate this process. This is especially true for refrigerant mixtures exhibiting significant

Table 1
Selected working fluids with their main thermodynamic properties.

Fluid name	ID	ODP	GWP	NBP (°C)	T_{crit} (°C)	p_{crit} (bar)
Propane	R-290	0	3	-42.1	96.7	42.5
CO_2	R-744	0	1	-78.5	31.0	73.8
R1234ze(Z)	-	0 < 1	9.7	150.1	35.3	
Butane	R-600	0	4	-0.5	151.9	38
Pentane	R-601	0	5	36.1	196.6	33.7
Acetone	-	0 < 1	56.1	235.0	46.9	
Dimethyl Carbonate	DMC	*	*	90.1	283.9	49.1

*Depends on the production processes [28].

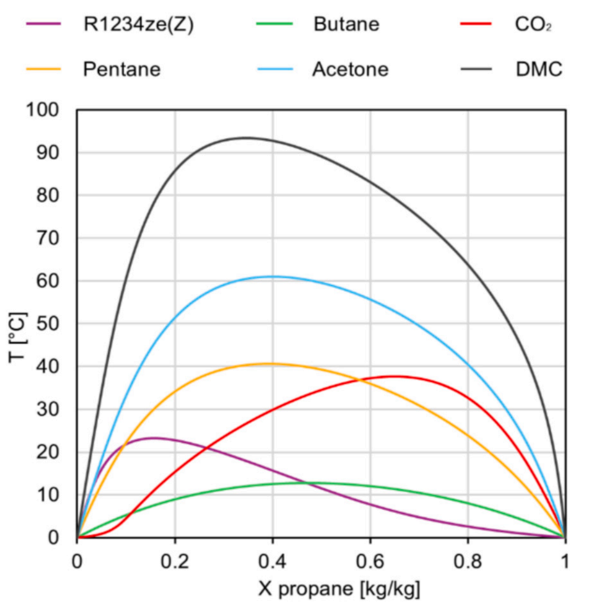

Fig. 2. Glide of the analyzed mixtures as a function of propane mass fraction at a pressure of 8 bar.

differences in the volatility of their constituents. Moreover, by further subcooling the high-pressure refrigerant, the enthalpy at the inlet of the expansion valve is decreased, diminishing the throttling effect and lowering the irreversibility losses associated with the expansion process.

2.2. Mixture selection

Six different propane-based mixtures were analyzed. Propane and the selected co-fluids are listed in Table 1.

The second components of the mixtures were chosen to have low Global Warming Potential (GWP) and Ozone Depletion Potential (ODP), while covering a wide range of normal boiling points. This selection strategy enables the creation of mixtures with varying temperature glides (i.e., the difference between bubble and dew temperature), allowing for the investigation of how the glide affects cycle performances and its adaptation to different boundary conditions. For instance, Fig. 2 shows the glide of the different mixtures at a pressure of 8 bar. However, a similar behavior is observed across the entire operating pressure range of the heat pump at the considered boundary conditions. It must be noted that CO_2 is the only fluid having a lower boiling point than that of propane.

2.3. Selection of the working conditions

The space heating scenario was derived from the rating condition tests of the heat pump according to the European standard. It was decided to adopt the high and medium temperature climatic curve, which implies water inlet and outlet temperatures of $(T_{w,i} = 55\ ^\circ C;\ T_{w,o} = 65\ ^\circ C)$ and $(T_{w,i} = 47\ ^\circ C;\ T_{w,o} = 55\ ^\circ C)$, respectively. In fact, the utilization of a mixture should be particularly favorable in a higher temperature lift scenario, as it can help mitigate excessive compressor discharge temperature. In contrast, under moderate or low lift conditions (corresponding to the intermediate and low temperature climatic curve of the standard), pure propane is sufficient to meet operational requirements.

Table 2
Definition of the selected test conditions for the space heating and domestic hot water scenario (W = water, A = air).

Scenario	Heat sink (in/out)	Heat source (in/out)
Space heating	W55/65 °C	A7/2 °C
	W47/55 °C	
Domestic hot water	W40/60 °C	A7/2 °C
	W15/60 °C	

One of the advantages of utilizing a mixture lies in the glide exhibited during the phase change processes, which could be adapted to the temperature profile of the heat pump sink, increasing the overall efficiency of the cycle. For this reason, two scenarios characterized by a relatively high temperature glide at the sink were evaluated, with temperature levels representative of typical domestic hot water production conditions. The supply temperature was fixed at $T_{w,i} = 60\ ^\circ C$ in line with standardized DHW test procedures. The return temperature, instead, strongly depends on the strategy adopted during the test. Two return temperatures were considered: $T_{w,o} = 15\ ^\circ C$, representing the water heating starting from the water ambient temperature, and $T_{w,o} = 40\ ^\circ C$, representing the partial heating of a DHW buffer tank.

In both space heating and domestic hot water scenarios, the supply and return temperatures of air were set to $T_{a,i} = 7\ ^\circ C$ and $T_{a,o} = 2\ ^\circ C$ respectively. A supply temperature of 7 °C is a typical value used in heat pump testing according to EN 14511–2 and is also frequently reported in the referenced publications. Likewise, a temperature difference of 5 K is representative of typical design and operating conditions for air-source heat pumps under moderate climate scenarios.

Table 2 summarizes the selected test conditions for the space heating and domestic hot water scenarios.

Since the heat source conditions are fixed for all scenarios, the results presented in Section 4 will be identified exclusively based on the heat sink temperature levels as reported in Table 2.

3. Heat pump modeling

In the following section, the numerical model used to characterize the performance of the different refrigerant mixtures in the heat pump, as well as the cycle optimization strategy, will be presented. Furthermore, the calculation of the various performance indicators, which will later be illustrated in the results, will be described.

3.1. Numerical model

The heat pump performance was calculated using a model developed in MATLAB 2024B [29]. The thermodynamic properties of pure propane

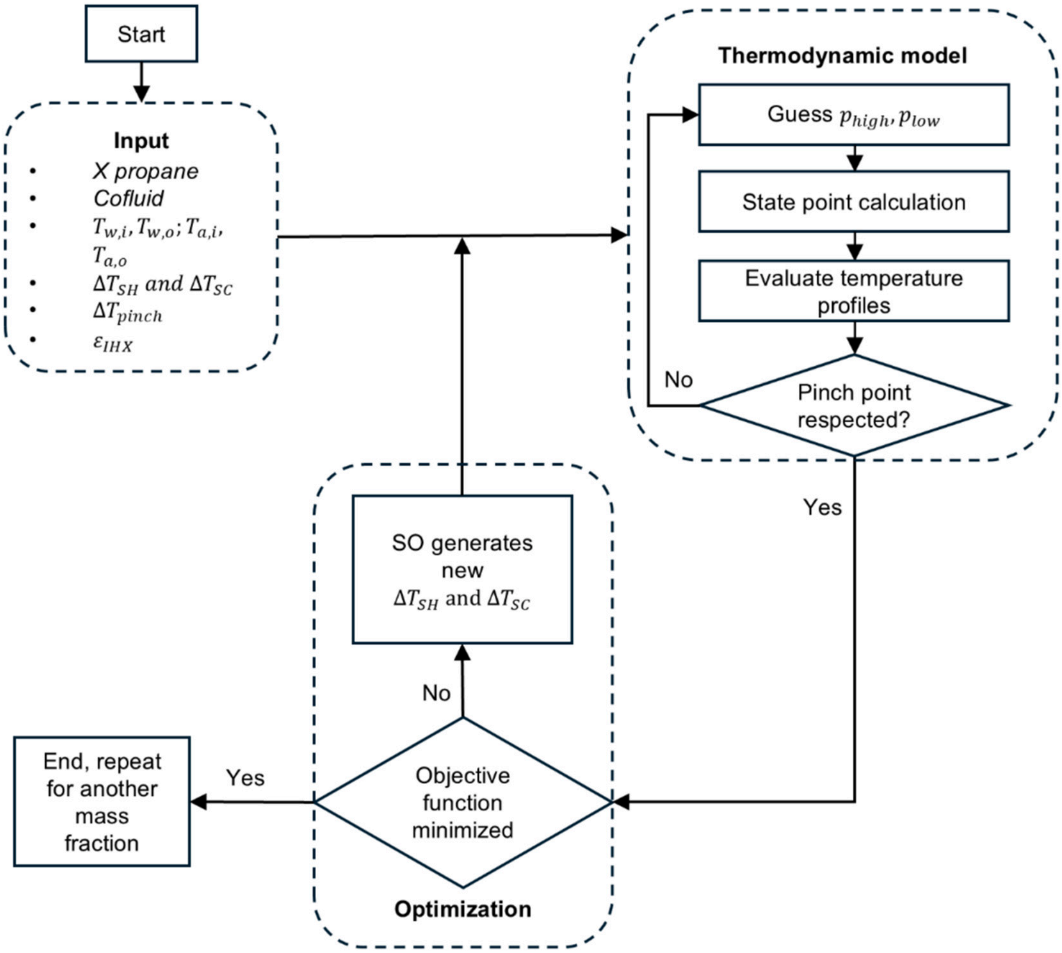

Fig. 3. Schematic view of the optimization procedure implemented.

and its mixtures were calculated using the MATLAB-REFPROP 10.0 [30] interface. The model was built based on the First and Second laws of Thermodynamics to simulate the performance of a vapor compression heat pump with and without the internal heat exchanger operating under steady state conditions. Energy and mass balances were applied to each component, while heat losses and pressure drops were neglected.

The refrigerant mixture composition was provided as an input variable. Based on the external fluid temperatures, initial guesses for the high and low pressures were assumed. The compressor suction state was fixed by a given value of superheating (ΔT_{SH}), expressed as the temperature difference between the temperature at the compressor inlet $(T_{COMP,i})$ and the dew-point temperature at the low pressure $(T_{dew}@(P_{low}))$ (Eq. (1)).

$$\Delta T_{SH} = T_{COMP,i} - T_{dew}@(P_{low}) \tag{1}$$

This choice is justified by the possibility that the evaporator outlet may be in a two-phase state when the IHX is utilized, especially when using a mixture composed of fluids with large volatility differences. Instead, the state at the compressor suction must be superheated to prevent liquid droplets in the component. Likewise, the state at the outlet of the condenser was defined by a given value of subcooling ΔT_{SC}, defined as the temperature difference between the bubble-point temperature at the high pressure $(T_{bubble}@(P_{high}))$ and the condenser outlet temperature $(T_{COND,o})$ (Eq. (2)).

$$\Delta T_{SC} = T_{bubble}@(P_{high}) - T_{COND,o} \tag{2}$$

The minimum values of superheating and subcooling were set to 0.001 K, corresponding to an almost saturated state. The internal heat exchanger was modeled with a fixed effectiveness of $\varepsilon_{IHX} = 0.9$, which allowed the characterization of the states at the evaporator outlet (low pressure) and the expansion valve inlet (high pressure). The compressor isentropic efficiency was estimated from the polynomial expression provided by Da Riva and Del Col [31], which depends on the evaporation and condensation pressures and the temperature at the compressor suction. The evaporator and condenser were modeled as counter-flow devices with a pinch point temperature difference of $\Delta T_{pinch} = 3\,K$. The model solves the thermodynamic cycle iteratively by adjusting the high and low pressures to satisfy the pinch-point. Since the relationship between temperature and enthalpy is not linear during the heat exchange processes, both heat exchangers were discretized into 40 elements to build the temperature profiles. At each step, the local temperature difference (ΔT_{step}) was calculated and the pinch point was identified as the minimum ΔT_{step} value. The expansion process was considered isenthalpic.

To characterize and compare the temperature difference across the heat exchangers, the total temperature difference was determined as the sum of the temperature difference at each discretized step, as expressed in Eq. (3). This was calculated for each heat exchanger: evaporator, condenser, and internal heat exchanger.

$$\Delta T_{tot} = \sum_{i=1}^{40} \Delta T_{step,i} \tag{3}$$

The Coefficient of Performance (COP) of the cycle was defined as the ratio between the enthalpy difference at the condenser and the compressor, as shown in Eq. (4).

$$COP = \frac{\Delta h_{COND}}{\Delta h_{COMP}} \tag{4}$$

The volumetric heating capacity was calculated as the product of the density at compressor suction and the condenser enthalpy variation, Eq. (5).

$$VHC = \rho_{COMP,i} \times \Delta h_{COND} \tag{5}$$

It was found that superheating, subcooling, and mixture composition strongly influenced the cycle performance; therefore, these parameters were subjected to an optimization procedure, which is described in the following section.

3.2. Optimization procedure

The Surrogate Optimization (SO) routine from MATLAB's Global Optimization Toolbox was employed to determine the values of superheating and subcooling that maximized the COP of the cycle. The SO algorithm works by treating the heat pump model as a black box. At each iteration, the superheating and subcooling values are varied, the thermodynamic cycle is solved as described in Section 3.1, and the objective function is evaluated. The latter is defined as the negative of the COP, as the algorithm works as a minimization process.

The optimization proceeds until no significant improvement in the objective function is detected, or the maximum number of function evaluations (set to 80) is reached. Under each specified boundary condition and mixture composition, the cycle is closed in accordance with thermodynamic constraints, and the optimal performance is determined.

Once the concentration providing the maximum COP was identified, the performance of the mixture was reported over a concentration interval of ±0.05 around this optimum with a step size of 0.01. The entire procedure was repeated at each step.

Fig. 3 provides a schematic view of the utilized approach.

In case the compressor discharge temperature was higher than 115 °C, two different alternatives were evaluated:

1. Evaluate a vapor compression cycle without the internal heat exchanger. This solution drastically reduces the compressor's discharge temperature but penalizes the COP of the cycle.
2. Limit the compressor discharge temperature of the cycle with the internal heat exchanger by constraining superheating and subcooling values. Since the surrogate optimization does not explicitly handle constraints on the system's variables, this limitation was implemented through a penalty function, as described in [32]. The objective function (f_{obj}) in the constrained optimization problem is given in Eq. (6):

$$f_{obj} = -COP + k \times [\max(0, T_{disch} - 115)]^2 \tag{6}$$

The penalty is null for discharge temperatures below 115 °C, while it increases quadratically when this threshold is exceeded. This approach allows the model to vary the optimization parameters ($\Delta T_{SH}, \Delta T_{SC}$) in search of an optimum, while discouraging solutions associated with higher compressor discharge temperature. A penalty coefficient of $k = 0.04$ was found to provide a smooth variation of the objective function, avoiding a sudden reduction when the discharge temperature exceeded the threshold value.

3.3. Model verification

To ensure the model's reliability, its predictions were compared with results reported by Zühlsdorf et al. in [16,33], two of the most authoritative and frequently cited studies on zeotropic mixtures for heat pump applications, both based on detailed thermodynamic cycle models. The comparison was carried out based on COP, VHC, and the high and low cycle pressures. Two reference cases from both studies were considered.

Table 3 summarizes the design choices adopted by Zühlsdorf et al. for both reference cases, including the utilized refrigerant, the inlet and outlet temperature of the source and of the sink, whether the internal heat exchanger was adopted, the compressor isentropic efficiency (η_{is}), and the pinch point in the heat exchangers ($\Delta T_{pinch,HXs}$). These assumptions were implemented in the present model to enable a consistent and meaningful comparison.

The discrepancies between the present model and that of Zühlsdorf et al. were found to be very small across all analyzed cases, as shown in Table 4, confirming the robustness and reliability of the proposed modeling approach.

It is worth noting that the compressor isentropic efficiency predicted using the Da Riva and Del Col [31] correlation was lower than the fixed efficiency assumed by Zühlsdorf et al., with values around 0.6–0.7 under the same operating conditions. This difference can be attributed to the fact that Zühlsdorf's study focuses on industrial applications, where compressor efficiencies are typically higher than in the residential systems examined in the present work. This observation highlights the importance of adopting a compressor efficiency model rather than relying on fixed values.

Table 3
Design choices and boundary conditions adopted by Zühlsdorf et al. in [16,33] in four analyzed cases.

Case	Refrigerant	Heat source $T_{source,i} \rightarrow T_{source,o}$	Heat sink $T_{sink,i} \rightarrow T_{sink,o}$	IHX	η_{is}	$\Delta T_{pinch,HXs}$
1	Propane	40 °C→35 °C	40 °C→80 °C	No	0.8	5 °C
2	10% Ethane – 90% Propane	40 °C→30 °C	40 °C→80 °C	No	0.8	5 °C
3	50% Butane – 50% Propane	20 °C→10 °C	45 °C→75 °C	Yes	0.8	3 °C
4	70% Propane – 30% Isopentane	35 °C→10 °C	45 °C→75 °C	Yes	0.8	3 °C

Table 4
Comparison of COP, VHC, and high and low pressure of the cycle between the reference model of Zühlsdorf et al. (subscript "ref") and the present model (subscript "calc.") adopting the design choices reported in Table 3.

Case	COP_{ref}	COP_{calc}	VHC_{ref}, kJ/m^3	VHC_{calc}, kJ/m^3	$(p_h; p_l)_{ref}$, bar	$(p_h; p_l)_{calc}$, bar
1	5.82	5.84 (+0.3%)	8093	8088 (−0.1%)	(10.80; 31.10)	(10.79; 30.96) (−0.1%; −0.5%)
2	5.60	5.61 (+0.2%)	8761	8754 (−0.1%)	(12.30; 35.90)	(12.25; 34.68) (−0.4%; −3.4%)
3	4.5	4.76 (+5.8%)	924	936 (+1.3%)	(0.80; 5.00)	(0.85; 5.01) (+6.3%; +0.2%)
4	4.96	5.23 (+5.4%)	3583	3581(−0.1%)	(4.40; 15.00)	(4.49; 14.91) (+2.1%; −0.6%)

4. Results

The results of the comparison among the different mixtures are presented in this section. These are reported only for the cycle with the IHX, which will be referred to as the Base Case (BC), as a preliminary analysis of the mixtures under the identified boundary conditions demonstrated its higher efficiency compared to the cycle without the IHX.

At first, the variation of the COP with the mass fraction of propane is reported for the four working conditions. Once the compositions that return the highest COP were identified, the corresponding values of subcooling at the condenser outlet and superheating at the compressor inlet were analyzed. The impact of the mixture glide on cycle performance will also be discussed in that section.

Then, the impact of the mixture composition on the volumetric heating capacity is examined, followed by an analysis of the compressor discharge temperature. As it will be shown, in some scenarios the temperature exceeded the 115 °C threshold; only in such cases, the constrained configuration with the IHX and the configuration without the IHX were analyzed and compared to the reference case.

4.1. Impact of the composition on the coefficient of performance

The analysis of the impact of the composition was done by calculating the Coefficient of Performance (COP) of the heat pump for the optimized values ΔT_{SH} and ΔT_{SC} in a range of mass fractions. The results are shown in Fig. 4, which reports for each refrigerant mixture the variation of the COP with the composition for the four operating conditions. The composition is expressed as the mass fraction of propane in the mixture.

The maximum achievable COP decreases as water inlet temperature increases, due to the higher temperature lift required by the heat pump.

For space heating applications, the butane blend demonstrated the highest performance, achieving a 7% increase in COP compared to pure propane in both the W55/65 °C and W47/55 °C cases. The performances of the other mixtures were relatively similar, with acetone showing the lowest improvement of around 5%.

For domestic hot water applications, CO_2 blends achieved the highest COP, with a 9% increase for the W40/60 °C case and an 11% increase for the W15/60 °C case compared to pure propane, followed by Dimethyl Carbonate (DMC), which settled around a 7–5% improvement for the two cases, respectively. The worst-performing mixture was the one with R1234ze(Z).

The location of the optimal concentration, i.e., the one yielding the highest COP, depends on the selected blend. For fluids with a greater difference in volatility, such as those with DMC and acetone, the max COP tends to occur at a higher propane concentration. This is because these mixtures have a higher temperature glide for the same propane concentration, as reflected by the steeper glide-concentration curve shown in Fig. 2. The curves of such mixtures also show a more pronounced curvature with a sharp drop off around the maximum. See, for example, the DMC curve compared to that of butane. R1234ze(Z), which has the lowest glide among the chosen mixtures, appears on the left side of the chart, i.e., lower concentrations of propane.

Additionally, the location of the maximum is slightly influenced by the water temperatures: in all cases, higher water temperatures shift the maximum COP toward lower propane concentrations. This suggests that mixtures with higher co-fluid concentration are more advantageous in scenarios where the system operates under more demanding conditions. This is true except for the CO_2 blend, which exhibits the lowest propane

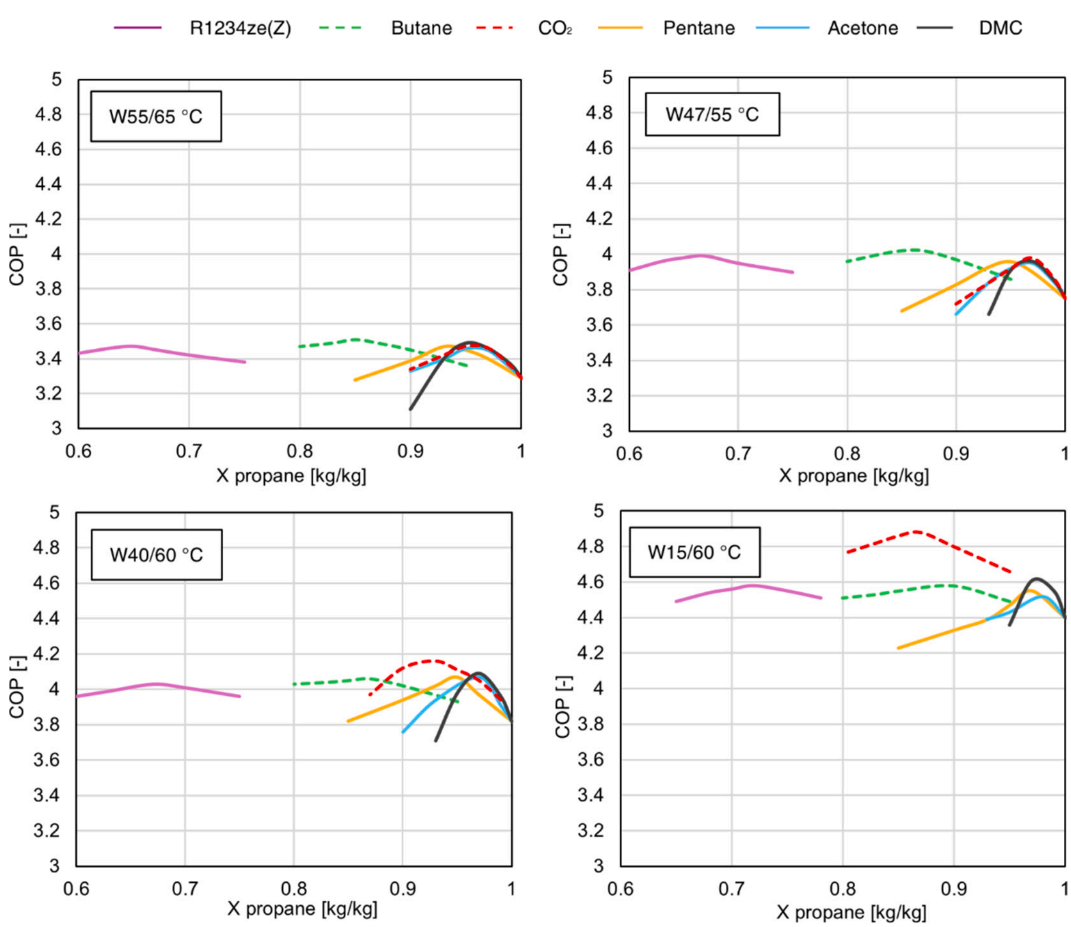

Fig. 4. Optimized COP variation as a function of propane mass fraction for the different mixtures in the analyzed scenarios.

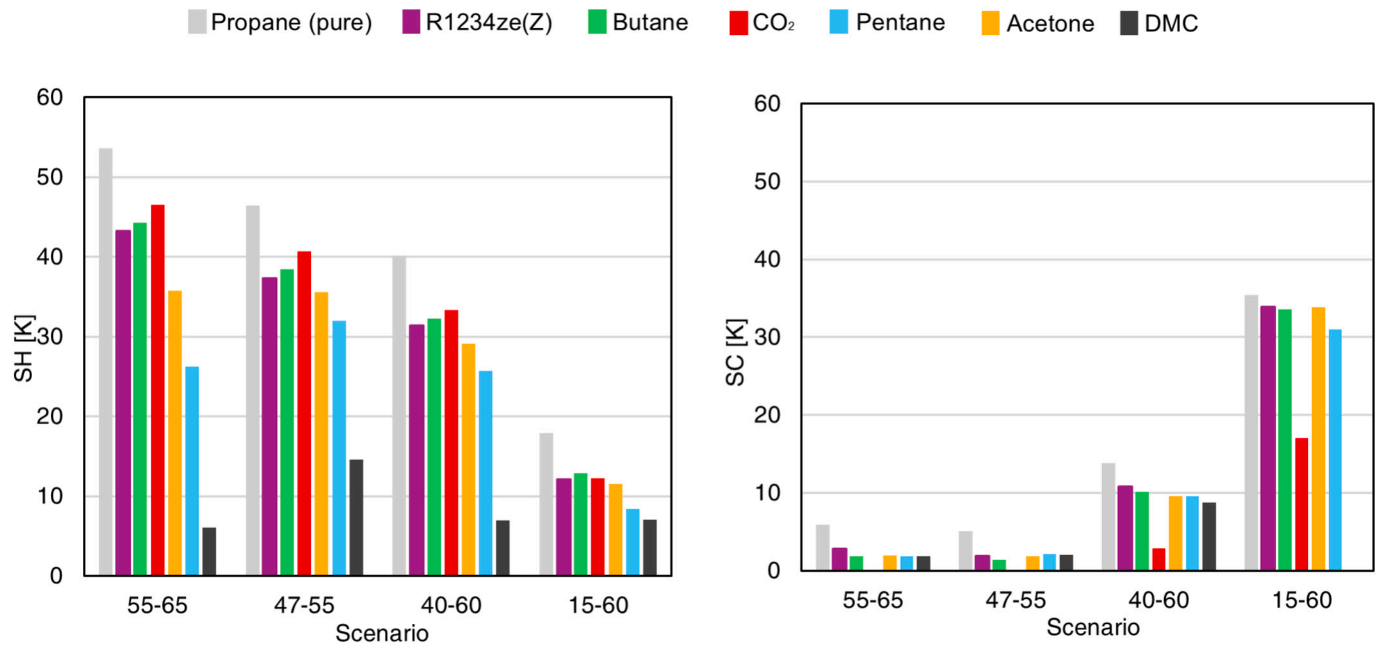

Fig. 5. Superheating and subcooling values for the different mixtures and scenarios for mass fraction, providing maximum COP.

concentration in the W15/60 °C case, although it has a considerable glide.

4.2. Analysis of the degree of superheating and subcooling

The results in Fig. 4 derive from an optimization process that determines for each working condition the value of subcooling at the condenser outlet and superheating at the compressor inlet, which maximizes the COP. The values of ΔT_{SH} and ΔT_{SC} depend on both the mixture and the operating conditions. Fig. 5 shows the values of ΔT_{SH} and ΔT_{SC} for the mass fraction corresponding to the highest COP.

The superheating and subcooling values reported in the figure may appear relatively high. The superheating level is mainly affected by its definition, which is referenced to the compressor inlet state (see Section 3.1 and Eq. (1)). Higher superheating values are observed in scenarios characterized by high sink temperatures and low condenser glide. Conversely, subcooling increases in low sink temperature scenarios with higher condenser glide. The large subcooling values observed are a direct outcome of the optimization procedure and correspond to the thermodynamic optimum of the cycle. Similar behavior has also been observed experimentally, where optimal subcooling values were found to be significantly higher than typical design values [34].

For all the mixtures, except the one containing CO_2, both superheating and subcooling were observed to be lower for larger glide mixtures and lower propane concentration.

This behavior can be attributed to the fact that a larger glide enables the refrigerant blend to better match the temperature profiles of the external fluid during heat exchange. The CO_2 blend, on the other hand, despite exhibiting a glide comparable to the acetone and pentane mixtures, showed superheating values similar to those of the R1234ze(Z) mixture, while its subcooling values were the lowest among all tested blends. This deviation may be due to a more irregular relationship between temperature variation and exchanged heat. To further elaborate on this aspect, Fig. 6 shows the temperature profiles at the condenser and evaporator for the different mixtures in the W55/65 °C and W15/60 °C operating conditions at optimal concentration. It is evident that the CO_2-propane mixture shows a more pronounced path compared to the mixtures with a similar glide, whose profiles are more linear and closer to that of pure propane.

In both cases, at the evaporator, the temperature profile of the mixtures aligns more closely with the external fluid profile, compared to the pure propane. In fact, the entire process occurs within the phase transition region, where the glide is effectively utilized. In this case, with the external air glide being only 5 °C, mixtures with larger glides are penalized, as they exhibit a higher temperature difference with the air.

In contrast, at the condenser, the improved temperature matching of the mixtures is less pronounced. This is because de-superheating and subcooling play a significant role in the overall heat exchange process. By controlling subcooling, even pure propane can achieve a good temperature match with water, thereby reducing the potential advantages of adopting zeotropic mixtures.

The temperature matching was also analyzed numerically by calculating the total temperature difference (Eq. (3)) in the three heat exchangers to identify in which case an optimal match was achieved (i.e., minimum temperature difference between refrigerant and external fluid).

For each mixture and scenario, six different compositions were examined, and an optimal concentration providing the maximum COP was identified, as described in Section 4.1. The corresponding ΔT_{tot} was then compared with the ΔT_{tot} values obtained for the remaining five concentrations. In this way, it was possible to assess whether the ΔT_{tot} was minimized for a given operating condition and mixture.

The analysis revealed that, in most cases, the optimization process resulted in a minimum temperature difference at the evaporator rather than at the condenser or the IHX. Table 5 highlights, with green cells, the cases where the maximum COP coincided with a minimum temperature difference in the heat exchangers. Out of the possible 24 cases for each heat exchanger (i.e., six mixture x four scenario), this occurred in 88% of the cases at the evaporator, 21% at the condenser, and 13% at the IHX.

This is an interesting result as, although the temperature glide of the

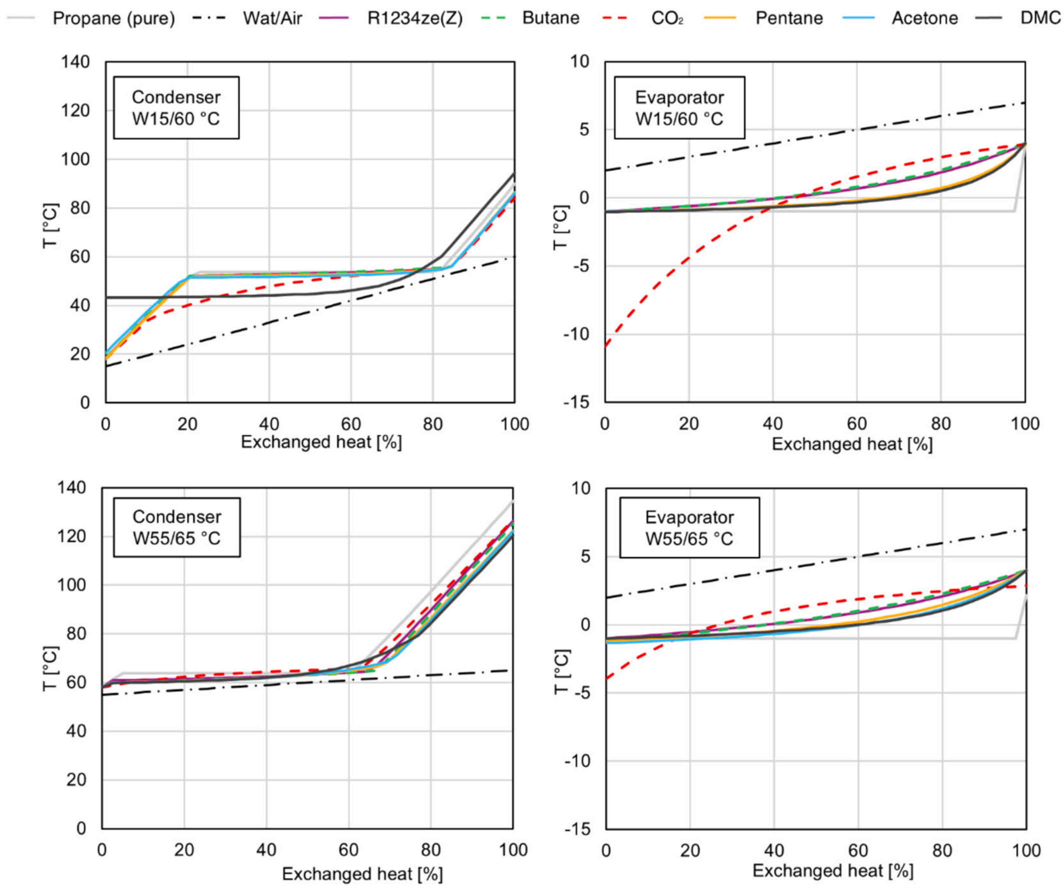

Fig. 6. Temperature profile in the condenser and evaporator for the different mixtures at optimal concentration in the W15/60 °C and W55/65 °C scenarios.

Table 5
Green cells highlight instances where a minimum temperature difference in the corresponding heat exchanger was achieved at the optimal concentration.

Refrigerant	W55/65 °C			W47/55 °C			W40/60 °C			W15/60 °C		
	EVA	CON	RHX	EVA	CON	RHX	EVA	CON	RHX	EVA	CON	RHX
R1234ze(Z)	✓			✓			✓			✓		✓
Butane	✓			✓	✓		✓			✓		
CO_2	✓	✓		✓	✓							✓
Pentane	✓			✓			✓			✓		
Acetone	✓						✓		✓	✓		
DMC	✓	✓		✓			✓	✓		✓		

air is lower compared to that of the water, the optimum is found for an optimal match of the evaporator rather than the condenser.

4.3. Impact of the composition on the volumetric heating capacity

Another important parameter to consider when evaluating refrigerant mixtures is the Volumetric Heat Capacity (VHC), which directly affects compressor sizing. Refrigerants with higher VHC require lower volumetric flow rates, leading to smaller displacement volumes and thus more compact components. The VHC is reported in Fig. 7 for all mixtures and cases, as a function of propane concentration. The propane concentration values used to represent the VHC are the same as those used for the COP curves in Fig. 4. A dot is placed on each curve to indicate the concentration at which the COP is maximized, showing that the value of propane mass fraction that maximizes the COP does not correspond to the maximum of the VHC.

As expected, the VHC decreases with higher water temperatures. As for the impact of the mass fraction, an increasing trend with the propane mass fraction is found for all the mixtures except for the one with CO_2. As this substance is more volatile than propane, the operating pressures of the mixture increase with a lower propane concentration, which is directly linked to a higher VHC. In the case corresponding to maximum COP, the CO_2 – propane blend exhibits VHC values that are 9 to 12% higher than pure propane for the space heating cases. These values increase to 16 and 23% for the two DHW cases. The other mixtures, instead, show a VHC that is between 1% to 18% lower compared to the pure fluid.

Generally, the larger the glide of the mixtures, the higher the VHC in the optimal configuration. DMC shows the highest VHC values, except for the W15/60 °C case, where a sudden drop in the curve results in the lowest VHC among the mixtures at optimal concentration. It should be noted that increasing the propane concentration by just 0.01 would increase the VHC by approximately 0.3 MJ/m^3, making it comparable to the other fluids without significantly affecting the COP. The butane blend, which was among the best-performing ones in terms of COP, has the lowest VHC, alongside R1234ze(Z).

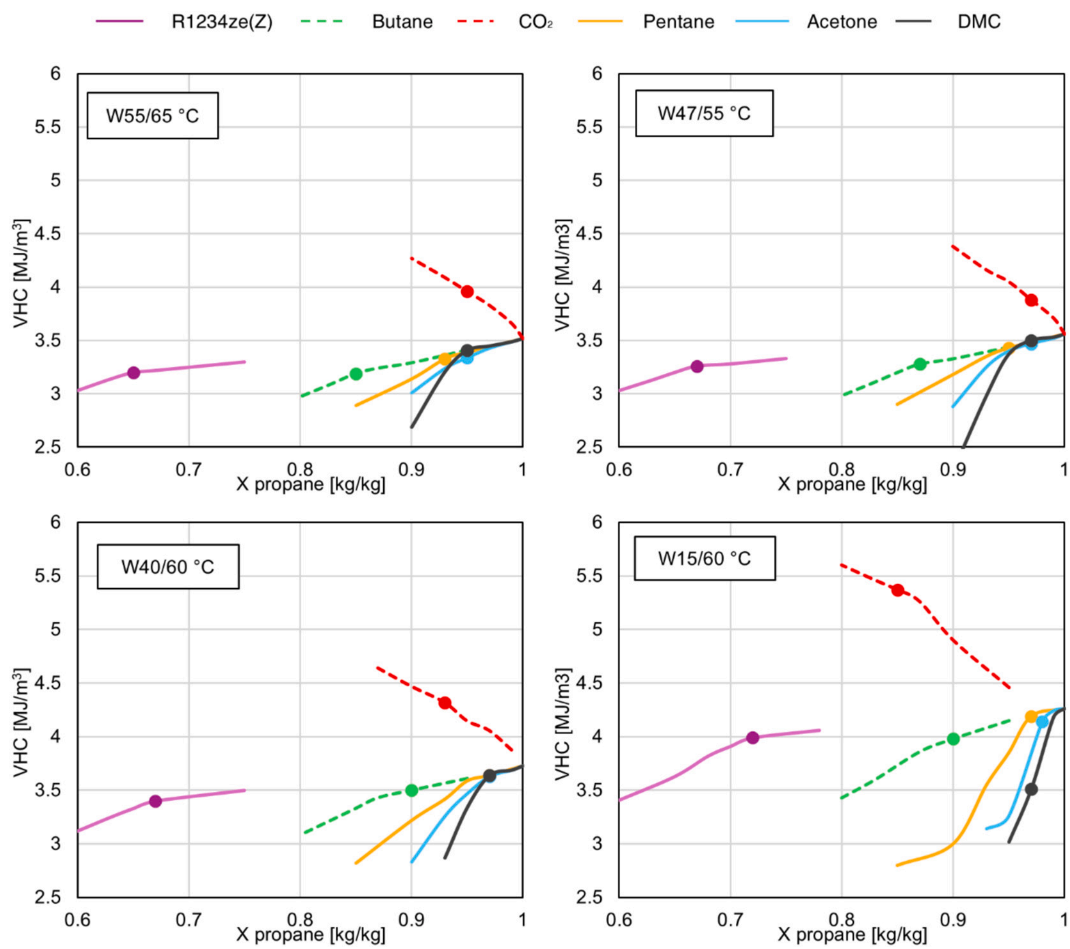

Fig. 7. Optimized VHC variation as a function of propane mass fraction for the different mixtures in the analyzed scenarios. A dot corresponds to the concentration providing maximum COP.

4.4. Compressor outlet temperature

The compressor discharge temperature is a critical parameter to ensure the reliable operation of a heat pump. As mentioned above, higher discharge temperature may determine the shortening of the lifetime of the compressor due to the lubricant oil degradation. A threshold of 115 °C was adopted as a limit to avoid this phenomenon and ensure safe operation. Fig. 8 shows the discharge temperature for the optimal case across the different scenarios and refrigerant blends.

Using a mixture helps to decrease the discharge temperature compared to the pure fluid case. For the W47/55 °C and W40/60 °C cases, all mixtures have very similar discharge temperature values, settling around 4 to 7 °C less than pure propane. In the W15/60 °C case,

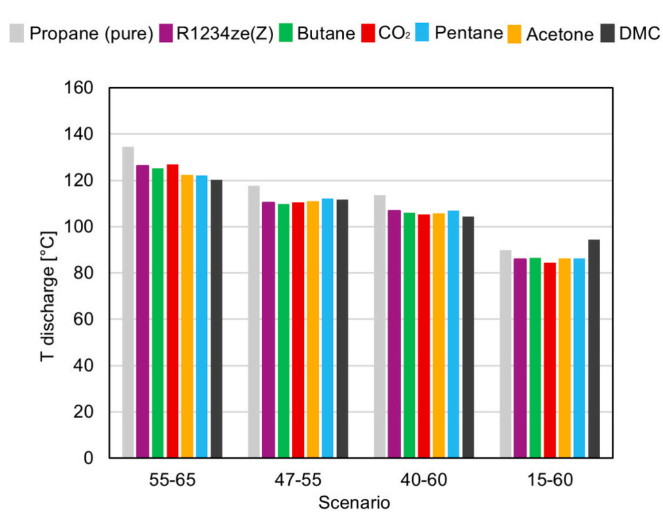

Fig. 8. Compressor discharge temperature for the optimal case across different scenarios and refrigerant blends.

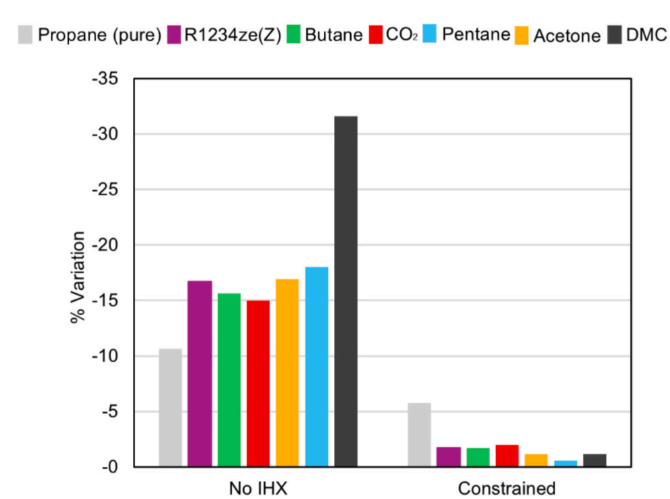

Fig. 9. COP percentage decrease in the "no IHX" and "Constrained" cases compared to the base case.

Table 6
Comparison of the constrained and "no IHX" case with the base case in the W55/65 °C scenario.

Refrigerant	Concentration (%)			Superheating [°C]			Subcooling [°C]		
	BC	Constrained	No IHX	BC	Constrained	No IHX	BC	Constrained	No IHX
Propane (PURE)	100	100	100	53.7	31.8	5.0	5.9	6.7	7.7
Butane	85	82	83	44.3	33.3	0.0	1.9	1.7	3.1
Pentane	93	92	97	35.7	27.2	0.0	2.0	1.6	5.5
Acetone	95	94	99	26.3	17.2	0.7	1.9	1.8	6.3
DMC	95	95	99	6.1	0.0	0.0	1.9	1.7	4.6
R1234ze(Z)	65	61	69	43.2	30.4	0.2	2.8	2.6	4.9
CO_2	95	96	96	46.5	34.9	2.9	0.0	0.4	3.2

which is the least challenging for the heat pump, the discharge temperature of pure propane is almost identical to that of the blends.

The W55/65 °C case shows the greatest impact of using a mixture compared to pure fluid. The blends result in discharge temperatures that are 8 to 14 °C lower than pure propane, with Dimethyl Carbonate (DMC) being the best choice in this regard. However, using a mixture alone is not sufficient to meet the target of keeping the discharge temperature below 115 °C in the optimized case with the highest COP. Thus, two alternatives are explored:

- Eliminate the IHX, referred to as "No IHX" case.
- Constraining the optimization process to prevent solutions with compressor discharge temperature above 115 °C. This is done by penalizing the objective function (COP) as explained in Section 3.2. This case will be referred to as "Constrained."

Fig. 9 presents the COP percentage decrease of the two alternatives with respect to the base case (i.e., the one with the IHX). The data are reported only for the concentration at which the COP is maximum.

Not using the IHX highly penalizes the COP, as shown in Fig. 9, especially for the mixtures, which have a COP that is between 10 and 32% lower compared to the base case. This is because using a mixture with a less volatile component forces a reduction in low pressure to ensure the refrigerant is fully evaporated before the compressor inlet. This effect is mitigated when the IHX is used because the evaporation of the less volatile fraction of the mixture takes place in the heat exchanger at a higher temperature than the cold source temperature. Among the mixtures, the ones with DMC and acetone are the most penalized due to their lower volatility compared to the other substances. In this case, the compressor discharge temperature was between 89 °C and 94 °C. Moreover, the optimal concentration in this configuration was significantly higher than in the BC since a higher propane concentration facilitates evaporation when the process takes place without the aid of the IHX.

In the constrained case (Constrained), the optimization process maximizes the COP by changing propane mass fraction and the superheating and subcooling degrees, while avoiding compressor discharge temperature above 115 °C. The variation of the COP is below 3% for the refrigerant blends and about 6% for propane. Looking at the outcome of the optimization process (see Table 6), compared with the non-constrained case, the maximum COP is obtained with lower superheating at the evaporator outlet and with minor variations in the composition. Instead, the subcooling values were almost unchanged with respect to the base case.

5. Conclusions

This study assessed the potential of propane-based zeotropic mixtures as low-GWP alternatives to pure propane for residential heat pumps, addressing the limited availability of systematic analyses in the existing literature. The work examined several refrigerants that have not been previously investigated in mixtures for residential heat pump applications, thereby expanding the set of candidate fluids considered in earlier studies. A steady-state thermodynamic model of a single-stage vapor compression heat pump with an internal heat exchanger was combined with an optimization procedure to identify the mixture composition, superheating, and subcooling that maximized system performance under typical space heating and domestic hot water production conditions.

The results show that the use of a mixture improves the coefficient of performance of the heat pump compared to pure propane, with butane blends performing best for space heating (+ 7%) and CO_2 -based mixtures for domestic hot water production (+11%). In contrast, the volumetric heating capacity generally decreases with increasing co-fluids concentration, except for the CO_2, which demonstrated the opposite trend. For each scenario, an optimal mixture composition was identified, strongly dependent on water temperature level, with higher sink temperatures requiring lower propane concentration. Superheating and subcooling were found to have a major influence on the heat pump performance: mixtures characterized by larger glides required lower levels of both parameters for optimal performance. The configuration yielding the highest coefficient of performance was also associated with the minimum temperature difference at the evaporator, indicating that optimal temperature matching is particularly relevant at this heat exchanger. Finally, compared to pure propane the use of mixtures reduced the compressor discharge temperature, especially in the higher temperature sink scenario (W55/65 °C), although the reduction was insufficient to meet the target limit of 115 °C. Two mitigation strategies were therefore investigated: constraining the optimization procedure to limit the discharge temperature, resulting in a moderate performance penalty (up to 5%), and removing the internal heat exchanger, which significantly reduced the discharge temperature but led to a substantial decrease in performance.

Overall, the results indicate that adding a co-fluid to propane can enhance heat pump performance under the investigated conditions, and that the internal heat exchanger and appropriate cycle control play a key role in achieving high efficiency. These outcomes form the basis for the next step of this work, in which this approach will be implemented and verified. The practical implications will be addressed, particularly in terms of control strategies for achieving optimized conditions and determining the required amount of refrigerant mixture for various working conditions.

Declaration of generative AI in scientific writing

During the preparation of this work the authors used Grammarly software in order to check the spelling and grammar during the article's writing process. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

CRediT authorship contribution statement

Gianluca Abrami: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Data curation, Conceptualization. **Lorenzo Pistocchini:** Methodology, Investigation, Data curation, Conceptualization. **Jacopo Famiglietti:** Writing – review & editing, Visualization, Supervision, Data curation. **Tommaso Toppi:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Investigation, Conceptualization.

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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Data availability

Data will be made available on request.

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