Evaluating the use of CO_2-Hydrocarbon blends as working fluids in high temperature heat pumps

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ABSTRACT

Using natural substances in mixtures aims to develop an eco-friendly refrigerant that meets current greenhouse gas regulations and overcomes the in thermodynamic and safety drawbacks of individual refrigerants. A CO_2/HC_s mixture has the advantages of lowering operating pressures and increasing the critical temperature compared to pure CO_2. The ability of the zeotropic mixture to increase performance through glide and reduce heat exchanger irreversibility is investigated. In addition, the resulting mixture is non-toxic, has low global warming potential (GWP), avoids the impact of per- and polyfluoroalkyl substances (PFAs) and is low cost, making it a solution to the environmental damage caused by synthetic refrigerants. The aim of this work is to identify promising mixtures suitable for high temperature heat pump applications and to evaluate them under several operating conditions, with the ultimate goal of initiating experimental evaluations. A theoretical model, with CO_2/R-290, CO_2/R-600a, and CO_2/R-600 mixture properties simulated in REFPROP v10.0, is presented, and preliminary results are reported in this study.

Keywords: Heat Pump, Carbon Dioxide, Zeotropic mixtures, COP, Hydrocarbons, Energy Efficiency.

1 INTRODUCTION

High-temperature air-water heat pumps play a significant role in the panorama of sustainable energy technologies, as operating a vapor-compression refrigeration cycle, they provide an eco-friendly alternative to gas boilers for space heating and domestic hot water (DHW) production. Nevertheless, high temperature applications are still challenging and technical solutions should be implemented in order to enhance performance.

Of the various refrigerants used, carbon dioxide (CO_2) stands out as an environmentally friendly and energy-efficient choice, in line with greenhouse gas emission reduction targets. In addition, CO_2 has excellent thermodynamic properties, is non-toxic and non-flammable, and its wide availability and relatively low cost make it a sustainable refrigerant option. These systems work in trans-critical conditions, with the cycle that usually shows high efficiency for hot water production due to the high volumetric heating capacity and temperature match during the heat transfer process (Yokoyama et al., 2007). The challenges associated with the trans-critical cycle are mainly the high initial costs and safety risks due to the high operating pressure of low-boiling point refrigerants (Zhang et al., 2013) and the large exergy loss during the expansion process (Hakkaki-Fard et al., 2013; Llopis et al., 2016). Therefore, various high-boiling point refrigerants are added to the low-boiling point refrigerants to reduce the operating pressure and improve the efficiency of the heat pump. In addition, the zeotropic mixtures show a glide temperature to meet the thermal matching during the heat transfer process and improve the heat pump performance. For this reason, several studies have focused on the application of large glide temperature zeotropic mixtures on heat pumps.

In refrigeration, Kim et al. (2008) carried out measurements showing that blends of CO_2 with propane enhanced the performance of an air-conditioning system by aligning the glide in the heat exchangers. Their results showed that the CO_2/R-290 mixture [85/15%] yielded an 8% higher coefficient of performance (COP) compared to pure CO_2. Moreover, they found that adding small amounts of other fluids to CO_2 reduced the optimal working pressures, even if at the expense of reduced plant capacity and introducing a significant

glide during phase change. Zhao et al. (2023) evaluated the use of butane, isobutane and two pure HFOs as CO_2 doping agents in single-stage and two-stage cycles with IHX for LT applications. All the combinations offered COP improvements with respect to CO_2 and they selected the ternary mixture R744/R1234ze(E)/R1234ze(Z) as best mixture. Martínez-Ángeles et al. (2023) evaluated a performance improvement of 6.9% theoretically and of 7.3% experimentally (Sicco et al., 2024) with a mixture CO_2/R-152a [90/10%] compared to the pure CO_2 cycle.
Sarkar and Bhattacharyya (2009) have developed a thermodynamic model of the high-temperature heat pump and assessed the possibility of zeotropic mixtures R744/R-600a and R744/R600 to replace pure R114 for medium and high temperature heat pumps. In comparison to pure refrigerants, the blends notably enhanced the heat pump performance by matching temperature glides, resulting in the highest coefficient of performance (COP) observed with a mass fraction of R744 at approximately 0.3. Additionally, the operating pressures were reduced to 3.4 MPa. Luo et al. (2022) experimented with zeotropic mixture R744/R600a in a single-stage compression cycle air source heat pump. They achieved a heating COP of 1.834 at -30 °C, producing water at 75 °C. Ju et al. (2018) investigated the potential of zeotropic mixture R744/R290 for heat pump water heaters. The optimal ratio (12%/88% mass fraction) displayed promising performance, with a maximum COP of 4.731, an improvement of 11.00% over pure R22. Dai et al. (2014) evaluated CO_2-based mixtures in heat pump cycles using energetic and exergetic models, covering hot water production and drying. The results showed improved thermodynamic performance, including COP and exergy efficiency, with zeotropic mixtures. High boiling point fluids reduced operating pressure.

Given the growing interest in these mixtures, the aim is to theoretically select the most promising mixtures for experimental testing. With that objective, this work aims to present a model attempting to predict heat pump behaviour by evaluating aspects of superheating, heat transfer coefficients and compressor modelling with non-azeotropic mixtures. The model has been characterized with the design data of the plant in preliminary testing. The mixtures considered in this work are CO_2/R-290, CO_2/R-600a and CO_2/R-600 with heat pump behaviour only analysed in transcritical conditions. The maximum hydrocarbon percentage is set at 10%.

2 MIXTURE PROPERTIES

The advantages of using CO_2 as a refrigerant are contrasted by its low critical temperature, which limits its performance at temperature above 25°C, and its high pressure, which increases design complexity. By introducing small amounts of other fluids into CO_2, its thermodynamic properties can be adjusted. REFPROP (Lemmon et al., 2018) is commonly used to assess thermophysical properties. However, it is important to recognise that the properties of the mixture are determined by mixing rules that are based on four adjustable Helmholtz energy parameters and a binary-specific multiplier (Bell et al., 2021). These parameters are calibrated using published data (from experimental or molecular simulation results) through an automatic fitting process (Bell and Lemmon, 2016). Three mixtures are proposed in this work, and they are all with natural, low-GWP refrigerants. Figure 1 shows the trends in critical pressure and critical temperature with the addition of the hydrocarbons studied in this paper. The solid line shows the critical temperature (always increasing with respect to CO_2) while the dashed line shows the critical pressure, with an increase for the addition of R-600a and R-600 up to about 40 %, while the addition of R-290 results in a decrease of the critical pressure at all additional mass percentages.

3 THE SYSTEM

A simplified scheme of the heat pump is proposed in Figure 2. It's a typical transcritical one stage CO_2 cycle with a variable speed compressor, gas-cooler, an internal heat exchanger (IHX), back pressure valve (BPV) that allows the pressure control in the gas-cooler, the liquid receiver, an expansion valve that allows superheating to be fixed. The water circuit is controlled by a pump (WP) with the aim of achieving a specific water temperature at the outlet of the gas cooler. The gas-cooler is a brazed plate heat exchanger with area of 1.15 m^2 and the IHX is simulated with a fixed efficiency at this stage. The volumetric displacement of the semi-hermetic compressor (D3-1.9TK, Frascold) is 1.9 m^3/s at 50 Hz.

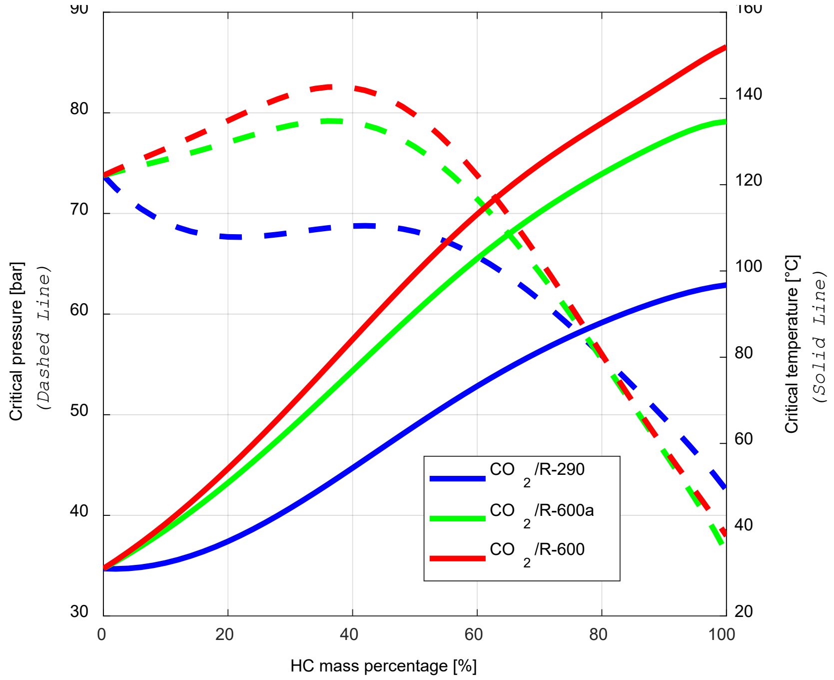

Figure 1: Critical pressure and critical temperature trends with the addition of hydrocarbons to CO_2

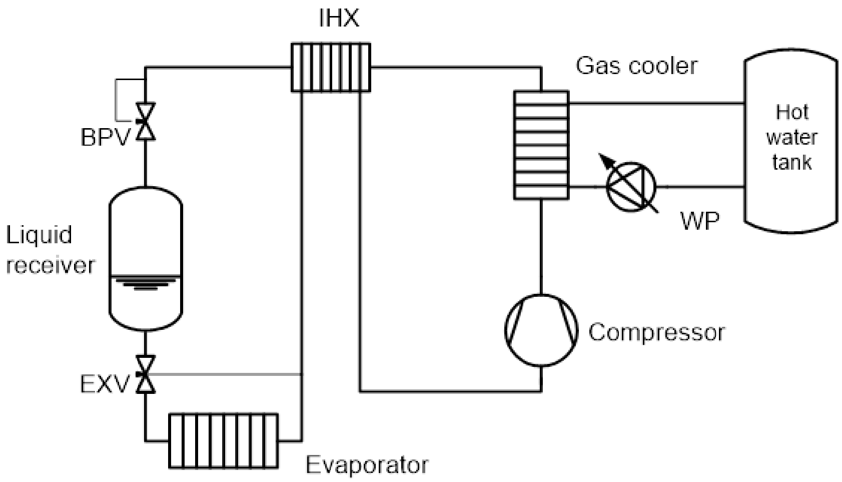

Figure 2: Simplified scheme of the Heat pump water heater

4 NUMERICAL MODEL

The numerical model for the heat pump behavior has been developed in MATLAB (The MathWorks Inc., 2022), linked to the software REFPROP 10 (Lemmon et al., 2018) to estimate the thermodynamic properties of the fluids. The model inputs are presented in Table 1. The gas cooler water outlet temperature $T_{w,set}$ is also called set point temperature in this work.

Table 1: Model input parameters and values

Parameter		Value
Superheating	SH	5 K
IHX efficiency	ε	0.5
Water inlet temperature	$T_{w,in}$	10 °C
Water outlet temperature	$T_{w,set}$	50 - 90 °C
Evaporation temperature	T_{ev}	-5 °C

For a given evaporating temperature ($T_{ev,}$), the evaporation pressure (p_{ev}) is computed considering the mean enthalpy in the evaporator to count for the glide effects of the blends, as in Eq. (1).

$$p_{ev} = \mathrm{f}\left(T_{ev,} \frac{h_{ev,in+}\, h_{ev,out}}{2}\right) \quad \text{Eq. (1)}$$

In order to simulate the compressor using the polynomials provided by the manufacturer, the coefficients were readjusted to take into account the evaporation pressure rather than the temperature, which is arbitrarily defined. The form of the equations used is the same as for manufacturer polynomials (Eq. (2)) with p_{gc} pressure in the gas cooler. The new coefficients are listed in Table 2 for the mass flow rate in kg/s and the electrical power in W. The coefficients are calculated using a nonlinear regression tool, with a mean squared error (MSE) of $2.1 \cdot 10^{-2}$ for power and $7.6873 \cdot 10^{-9}$ for mass flow. In Eq. (2) X has the meaning of mass flow and power consumption according to the coefficients used.

$$X = C1 + C2 \cdot p_{ev} + C3 \cdot p_{gc} + C4 \cdot {p_{ev}}^2 + C5 \cdot p_{ev} \cdot p_{gc} + C6 \cdot {p_{gc}}^2 + C7 \cdot {p_{ev}}^3 + C8 \cdot p_{gc} \cdot {p_{ev}}^2 + C9 \cdot p_{ev} \cdot {p_{gc}}^2 + C10 \cdot {p_{gc}}^3 \quad \text{Eq. (2)}$$

Table 2: Calculated coefficients for compressor equations (Eq.2)

	C1	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*	*C10*
$\dot{m}$	$4.120 \cdot 10^{-3}$	$2.281 \cdot 10^{-3}$	$-8.091 \cdot 10^{-4}$	$-3.776 \cdot 10^{-5}$	$6.017 \cdot 10^{-6}$	$8.398 \cdot 10^{-6}$	$9.816 \cdot 10^{-7}$	$-5.907 \cdot 10^{-7}$	$1.480 \cdot 10^{-7}$	$-4.899 \cdot 10^{-8}$
W	$1.056 \cdot 10^{3}$	-3.783	1.862	-1.249	$8.713 \cdot 10^{-1}$	$5.719 \cdot 10^{-3}$	$7.709 \cdot 10^{-3}$	$3.168 \cdot 10^{-3}$	$6.570 \cdot 10^{-4}$	$-5.445 \cdot 10^{-4}$

To adapt the polynomials provided by the manufacturer for pure CO_2 to a mixture, a simplified method is presented in Eq. (3).

$$\frac{\dot{m}_{mixture}}{\dot{m}_{CO_2}} = \frac{\rho_{mixture}}{\rho_{CO_2}} \quad \text{Eq. (3)}$$

Where $\rho_{mixture}$ and ρ_{CO_2} are the suction densities of the fluids at the compressor suction under the conditions provided by the manufacturer (SH =10°C). As mentioned above, at this stage the maximum hydrocarbon additions are set at 10 per cent, so it is likely that the coefficients will not change that much and therefore this single correction could meet the accuracy required by the blend selection model. Nevertheless, verification requires an experimental test and consequently a more accurate model that predicts the compressor's behaviour independently of the manufacturer's coefficients polynomials.
In order to take into account the flow rate and the power absorbed by the heat pump with different superheating, Eq. (4) and Eq. (5) are proposed for calculation.

$$\frac{\dot{m}_{new}}{\dot{m}_{data}} = 1 + F\left(\frac{\rho_{suc,new}}{\rho_{suc,data}} - 1\right) \quad \text{Eq. (4)}$$

$$\frac{W_{new}}{W_{data}} = \frac{\dot{m}_{new}}{\dot{m}_{data}} \frac{\Delta \mathrm{h}_{is,new}}{\Delta \mathrm{h}_{is,data}} \quad \text{Eq. (5)}$$

where the correction factor F is assumed to be 0.75, ρ is density, new represents the adjusted superheat state (the value that needs to be calculated), $data$ is the state from the manufacturer data, and $\Delta \mathrm{h}_{is}$ denotes the enthalpy difference in an isentropic process (Illán-Gómez et al., 2021).

For the calculation of the gas-cooler, the heat exchanger is discretized in *n* parts where the temperature difference is assumed to be constant. The procedure presented by Otón-Martínez et al. (2022) and then validated in (Toffoletti et al., 2023) is used. The inlet conditions (mass flow, pressure, enthalpy) of both fluids are known and the hot fluid outlet temperature is estimated like in Eq. (6) at the first iteration.

$$T_{hot,out} = \frac{T_{high} + T_{low}}{2} \quad \text{Eq. (6)}$$

where

$$T_{high} = T_{hot,in} \quad \text{Eq. (7)}$$

$$T_{low} = T_{cold,in} \quad \text{Eq. (8)}$$

Then, the outlet high enthalpy is calculated as well as the overall heat exchanged; applying the energy conservation equation to each control volume, the thermodynamic variables of all nodes of the cold stream are calculated. The experimental correlation (Gnielinski, 1976) is used for the calculation of the local heat transfer coefficient at the average thermophysical properties in each refrigerant cell and thus the exchange area of each control volume. Finally, an overall exchange area is calculated (A_{calc}) and compared with the experimental area (A_o) to re-calculate $T_{hot,out}$ as shown in Eq. (9) and Eq. (10).

If	$A_o < A_{calc}$	Then	$T_{high} = T_{hot,out}$	Eq. (9)
If	$A_o > A_{calc}$	Then	$T_{low} = T_{hot,out}$	Eq. (10)

The convergence criterion is $T_{high} = T_{hot,out} = T_{low}$ (Otón-Martínez et al., 2022; Toffoletti et al., 2023). Finally, the expansion is isenthalpic and the efficiency of the internal heat exchanger (IHX) is maintained constant. The heating capacity and COP are therefore defined as:

$$\dot{Q}_h = \dot{m}_{ref}(h_{dis} - h_{gc,out}) \quad \text{Eq. (11)}$$

$$COP = \frac{\dot{Q}_h}{W} \quad \text{Eq. (12)}$$

Where h_{dis} and $h_{gc,out}$ are the enthalpy at the compressor discharge and gas cooler outlet respectively. $\dot{m}_{ref}$ is the refrigerant mass flow taken into account the different mixture from CO_2 (Eq.(3)) and the different superheating due to the IHX (Eq.(4)).

The process is performed iteratively ensuring the input evaporation temperature defined as in Eq. (1) and various pressures at the gas-cooler are calculated to identify the conditions that maximise COP; the gas cooler pressure that achieves this goal is called "optimum gas cooler pressure" in this work. At this stage, all analyses are done at a fixed evaporation temperature; this has been shown to have no significant impact on the analysis of the amount of charge added or the conditions that maximise COP (Martínez-Ángeles et al., 2023). However, it is a parameter that must be taken into account in a more complete discussion of heat pump behaviour.

The REFPROP calls have the major impact on the computational time; in order to allow larger investigations of different blends, short computational time is required. To address this, the properties of the required mixtures are fitted from pre-calculated databases, without significantly affecting accuracy.

5 RESULTS

Following the assumptions of the previous chapter, the optimum COP is calculated as a function of the percentage of added hydrocarbon. The results shown in Figure 3 are relative to a set point temperature (water temperature at the gas cooler outlet) of 60 °C (typical for DHW purposes) and parameters values summarised in Table 1. All points presented are considered under "optimum conditions", i.e. after a choice of pressure at the gas cooler that maximises COP.

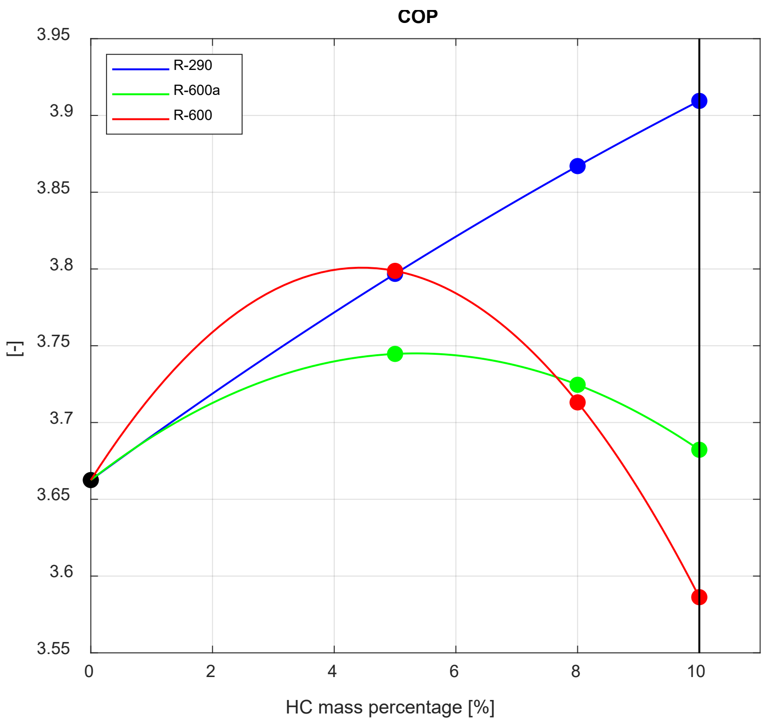

Figure 3: Heat pump COP trend with the addition of HCs at T_{ev}=-5 °C $T_{w,in}$=10 °C $T_{w,set}$=60 °C

It is possible to identify the mass percentage of R-600 and of R-600a that maximise the COP in this condition, whereas for propane (R-290) the higher the percentage, the better the COP. As mentioned above, the limit is set at 10% and therefore all work involves transcritical operation only. The lines are the result of an interpolation of the results calculated at the added hydrocarbon percentages of 5, 8 and 10%.

With the aim of selecting a mixture to test experimentally, it was decided to proceed by analysing six mixtures, with an addition of 5% or 10% of the three hydrocarbons R-290, R-600a and R-600. The trend of the COP, the optimum gas cooler pressure, the compressor discharge temperature and the heating capacity for $T_{w,set}$ varying from 50 to 90 °C, in 5K steps and under optimum conditions, is shown in Figure 4, Figure 5 and Figure 6 respectively. As also predicted by the Figure 3, the mixture that improves COP the most respect to pure CO_2 (black solid line) is CO_2/R-290 [90/10%] with an average improvement of 6.75 %. Mixtures with a 5% addition improve the COP for all water gas cooler outlet temperatures. Furthermore, the increase in COP is approximately independent with $T_{w,set}$, in particular for 5% HC percentage. On the other hand, for the CO_2/R-600a [90/10%] mixture, there is a temperature threshold value ($T_{w,se}$) of around 58 °C. Beyond this temperature, it becomes more efficient to use, with better performance as the outlet water temperature increases. The mixture CO_2/R-600[90/10%] shows a lower COP than the pure CO_2 for $T_{w,set}$ below approximatively 78 °C.

Figure 5 (left) shows an advantage of using these non-azeotropic mixtures: all mixtures used, whether at 5% or 10%, reduce the pressure at the gas cooler. In particular, for a $T_{w,set}$ at 60 °C, there is evidence of maximum pressure reduction with the mixture CO_2/R-600 [90/10%] respect to pure CO_2, from 98.86 bar to 80.82 bar (-18.2%). CO_2/R-290 [90/10%] and CO_2/R-600a [90/10%] allow a reduction compared to pure CO_2 of 12.4% and 15% respectively. As was to be expected, the higher the added hydrocarbon component, the lower the pressure that maximises COP compared to pure CO_2. Figure 5 (right) shows the compressor discharge temperature trend as $T_{w,set}$ changes. With the sole exception of propane, the other mixtures show an increasingly higher discharge temperature compared to pure CO_2; Of this effect, account must be taken of the glide at the evaporator which increases the compressor suction temperature, and the pressure at the gas cooler which is lower than pure CO_2. As a result, the propane blends remain about constant with CO_2 having a lower evaporator temperature glide than the other hydrocarbons, while the other blends (in particular CO_2/R-600[90/10%]) show a significant increase. It is important to note that this is a parameter that must be considered, trying to limit this temperature while avoiding oil degradation (Toffoletti et al., 2023), so further analyses must be carried out at an experimental stage.

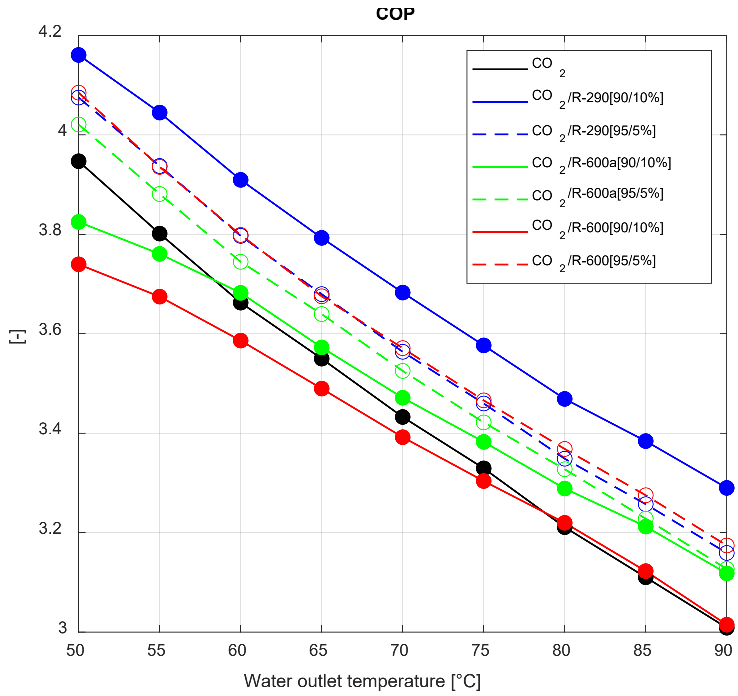

Figure 4: COP trend with $T_{w,set}$ at T_{ev}=-5 °C, $T_{w,in}$=10 °C

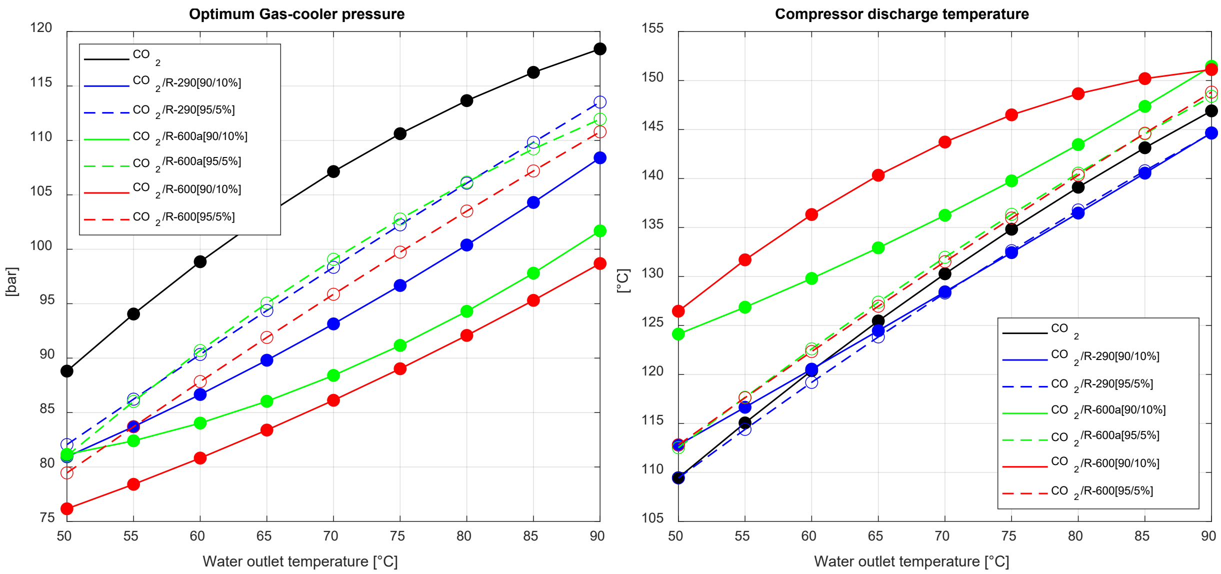

Figure 5 (left): Optimum gas cooler pressure trend with $T_{w,set}$ at T_{ev}=-5 °C, $T_{w,in}$=10 °C
Figure 5 (right): Compressor discharge temperature trend with $T_{w,set}$ at T_{ev}=-5 °C, $T_{w,in}$=10 °C

Finally, Figure 6 shows the heating capacity trend for the different refrigerants under the same conditions as before. The heating capacity trend is the same for all mixtures due to the control method chosen for this heat pump; the lower the set point temperature ($T_{w,set}$), the higher the heating capacity due to a higher value of mass flow rate that must be elaborated. The mixture that increases heating capacity the most respect to pure CO_2 (black solid line) is CO_2/R-600[90/10%] showing an increase of around 3% of with a set point temperature of 60 degrees. In general, the model predicts a heating capacity similar to that of CO_2 (within 3%). Unlike the condensation cases, here the effect of the temperature glide with respect to the pure fluid (CO_2) is minimal, operating under transcritical conditions. Therefore, the reduction in heating capacity that could occur by using zeotropic mixture is small under the assumptions of transcritical operation.

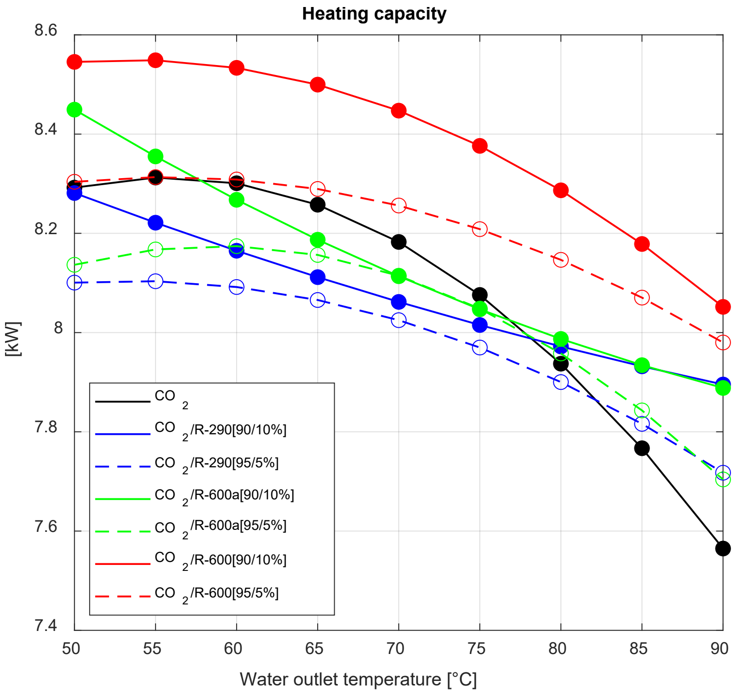

Figure 6: Heating capacity trend with $T_{w,set}$ at T_{ev}=-5 °C, $T_{w,in}$=10 °C

6 CONCLUSIONS AND FUTURE WORK

In this study, we theoretically analysed six non-azeotropic mixtures of CO_2 and hydrocarbons (R-600, R-600a and R-290) and compared performance and operative conditions with pure CO_2 in a single stage high-temperature heat pump system. These mixtures effectively reduced the operating pressure of the gas cooler. In particular there is a maximum pressure reduction with the CO_2/R-600 mixture [90/10%] compared to pure CO_2 of 18.2% for a supply water temperature $T_{w,set}$ at 60 °C. The maximum improvement in COP is evidenced with the CO_2/R-290[90/10%] mixture, with a 6.75 % improvement compared to the pure fluid with a set temperature of 60 °C; this mixture in fact, due to the compressor inlet conditions, the pressure reduction at the gas cooler, and the approximately constant heating capacity, realizes the best COP improvement over pure CO_2. Variations in heating capacity cannot be appreciated between mixtures under transcritical operating conditions for this heat pump. In addition to these results, it is worth emphasising the potential for further investigation in two key areas. First, a comprehensive analysis of compressor dynamics is essential to optimise system performance. The development of a model independent of manufacturer-supplied compressor polynomial data, tested for pure CO_2 only, could provide insights into system behaviour and efficiency. Secondly, the exploration of higher HC mass percentage that could allow subcritical operation deserves attention Subcritical operation not only simplifies control strategies, but also offers opportunities for system simplification and cost reduction provided that no flammability issues arise in the mixture. This aspect deserves in-depth examination in future research efforts. Finally, as previously mentioned, the subsequent work involves experimental testing with its attendant challenges. The main challenges include avoiding fractionation and the need to measure blend components during use, not just during the preparation of the mixture.

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NOMENCLATURE

BPV	Back pressure valve	A	Area (m^2)
COP	Coefficient of performance	h	Specific enthalpy ($kJ \cdot kg^{-1}$)
HPWH	Heat pump water heater	$\dot{m}$	Mass flow ($kg \cdot s^{-1}$)
GWP	Global warming potential	p	Pressure (bar)
IHX	Internal heat exchanger	T	Temperature (°C)
MSE	Mean squared error	W	Compressor electrical power (kW)
SH	Super heating	ε	Efficiency (-)
WP	Water pump	ρ	Density ($kg \cdot m^{-3}$)

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