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# Experimental evaluation of alternative CO<sub>2</sub>-based blends for transcritical refrigeration systems.

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## ABSTRACT

This work presents two refrigerant CO<sub>2</sub> blends with R32 and R1270 designed with a theoretically non-flammability and a GWP below 150. Both mixtures were tested in a small-capacity vapour compression system with and without IHX, considering the same working conditions of heat rejection temperature and demanding conditions at the evaporator. Taking the pure CO<sub>2</sub> results as a reference in a cycle without IHX, the blend of CO<sub>2</sub>/R32 enhanced the COP up to 18.1% with an optimal pressure reduction of 19.0% and a power consumption minimization of 17.1%. The mixture of CO<sub>2</sub>/R1270 presented a COP enhancement of 8.4% with an optimal pressure reduction of 8.0% and a power consumption minimization of 7.9%. In all cases, the use of the IHX resulted positively with increments compared to the pure CO<sub>2</sub> base cycle of 6.4% for pure CO<sub>2</sub>, 13.3% for CO<sub>2</sub>/ R1270, and 24.7% for CO<sub>2</sub>/ R32.

Keywords: Refrigeration, Carbon Dioxide, COP, Mixture, R1270, R32.

## 1. INTRODUCTION

For the last few years, CO<sub>2</sub> has been established as a reliable solution for high-capacity commercial refrigeration systems to overcome the direct emissions of artificial refrigerants. However, unlike traditional systems, the low critical temperature of CO<sub>2</sub> forces it to work in transcritical conditions where complex configurations need to be implemented to enhance the system's performance above the still active HFC systems. Furthermore, these new configurations based on parallel compressors (Bella and Kaemmer, 2011), ejectors (Haida *et al.*, 2016) or subcooling systems (Catalán-Gil *et al.*, 2020; Aranguren *et al.*, 2021) entail inherent extra-cost and more qualified service technicians with a new perspective of refrigeration systems hardly applied before. Therefore, integrating these configurations in medium or low-capacity systems below 10kW results in a real challenge in cost and performance where more straightforward solutions need to be applied.

Mixing CO<sub>2</sub> with other fluids is the most straightforward technique to solve the main CO<sub>2</sub> issues related to its low critical temperature and high critical pressure (30.98°C, 73.77 bar). It allows for increasing the critical temperature and minimising at the same time critical pressure (Zhang *et al.*, 2013). As a result, the mixture extends the subcritical operation, minimising the compressor work and the throttling loss and allowing a better temperature glide matching between the refrigerant and the secondary fluid (Zhu *et al.*, 2015). During the last twenty years, several authors have discussed using CO<sub>2</sub> mixtures as an alternative to pure CO<sub>2</sub> in vapour compression systems. As reference experimental research, Niu and Zhang (2007) explored CO<sub>2</sub>/R290 (71/29%*m*) in the low-temperature cycle of a cascade to replace R13 with benefits in cooling COP and cooling capacity up to +34.2% and +39.0%, respectively, regarding R13. Kim *et al.* (2008) extend the use of CO<sub>2</sub>/R290 (75/25%*w*) in an air-conditioning system showing an increment of +12.8% in cooling COP at the optimal

charge conditions but a decrease of -22.7% in the cooling capacity. Bouteiller *et al.* (2016) tested the mixtures of CO<sub>2</sub>/R290 (85/15%*m*) and CO<sub>2</sub>/R1234yf (94.5/5.5%*m*) for central heating (CH) and domestic heat pump water heater (DHW) conditions. The results revealed that blends reduce the cycle's performance at CH conditions but increase it at DHW. Tobaly *et al.* (2018) applied different CO<sub>2</sub>/R290 mixtures for air conditioning and refrigerating conditions finding cooling COP improvements of up to 19.7% but with cooling capacity decrements up to 18.0%. Yu *et al.* (2018a, 2018b) introduced different mass fractions of CO<sub>2</sub>/R290 and CO<sub>2</sub>/R41 mixtures in a mobile air conditioning system (MAC) for cooling, finding that cooling COP can be improved from up to 22.1% and 25.7%, respectively, depending on the mass fraction. Jut *et al.* (2018a, 2018b) tested the mixture CO<sub>2</sub>/R290 (88/12%*w*) in a heat pump water heater with increments in heating COP and heating capacity up to 11% and 17.5%, respectively, regarding R22. Sun *et al.* (2019) also performed similar tests for heating and cooling but optimising the mass fraction of a CO<sub>2</sub>/R32 refrigerant blend. The results revealed that the heating and cooling COP increases with the mass fraction of R32, but the heating and cooling capacity diminishes. Vaccaro *et al.* (2022) developed a computational model for different arrangements for CO<sub>2</sub>, including IHX, flash-gas and ejector, using diverse CO<sub>2</sub>-blends with hydrocarbons and HFOs. The results revealed that CO<sub>2</sub>/R1234yf and CO<sub>2</sub>/R290 were the best alternatives, with COP increments up to 12.8% and 7.9%, respectively. Finally, Sánchez *et al.* (2023) evaluated the energy consumption of a vertical beverage cooler using the blends of CO<sub>2</sub>/R32 (78/22%*w*) and CO<sub>2</sub>/R1270 (92.5/7.5%*w*) as drop-ins of pure CO<sub>2</sub>. Using a single-stage cycle with IHX at class III environmental conditions (25°C), the results provided energy savings of 16.5% with CO<sub>2</sub>/R32 and 15.5% with CO<sub>2</sub>/R1270 regarding pure CO<sub>2</sub>.

The results above show that CO<sub>2</sub>-blends result in a COP improvement with a capacity reduction depending on the mixture composition and the operating conditions. However, there are no specifications about the mixture's flammability and GWP, possibly resulting in fluids that cannot be used in commercial systems due to their hazardous or environmental compatibility. Accordingly, this work aims to define two theoretically non-flammable and low-GWP (below 150) mixtures of CO<sub>2</sub> and the refrigerants R32 and R1270 used as drop-ins of pure CO<sub>2</sub>. The resulting blends were tested in a CO<sub>2</sub> transcritical refrigerating plant to determine its optimal operating conditions with and without IHX at Class III environmental conditions (25°C and 60% of RH). The results confirmed that blends of CO<sub>2</sub>/R32 and CO<sub>2</sub>/R1270 are suitable for direct dropping, but further hazard tests are necessary.

## 2. MIXTURE DEFINITION

As the binary mixture of CO<sub>2</sub> aims to be used as a direct drop-in, the resulting mixtures must be non-flammable with a GWP below 150. The fluids selected to define the blend are described in Table 1, including physical properties using RefProp® v.10.0, safety conditions from ASHRAE Standard 34 (2019), flammability levels from Calm (1999) and environmental conditions according to the 5<sup>th</sup> Assessment Report from IPCC (2014).

**Table 1. Properties of the selected fluids**

Fluid	Molar mass (g·mol <sup>-1</sup> )	NBP (°C)	P <sub>crit</sub> (bar)	T <sub>crit</sub> (°C)	Security Group	LFL <sup>1</sup> (%)	UFL <sup>1</sup> (%)	GWP <sub>100</sub>
R-744 (CO <sub>2</sub> )	44.0	-78.4	73.8	31.1	A1	-	-	1
R-32 (CH <sub>2</sub> F <sub>2</sub> )	52.0	-51.7	57.8	78.1	A2L	13.3	29.3	677
R-1270 (CH <sub>2</sub> =CH-CH <sub>3</sub> )	42.1	-47.7	46.7	92.4	A3	2.2	11.0	2

<sup>1</sup> flammable gas volume concentration in the mixture of dry air and flammable gas

Table 1 shows flammable fluids have upper and lower flammability levels that define the explosive range conditions. Therefore, this range could be reduced by adding a non-inert gas such as Carbon Dioxide (CO<sub>2</sub>) until the upper and lower limits are equal (Kondo *et al.*, 2006; Schroeder, 2016). At these conditions, the mixture of dry air, flammable fluid and inert gas becomes theoretically non-flammable and defines the Fuel Inertization Point (FIP). Therefore, FIP expresses the minimum %CO<sub>2</sub> fraction to make a non-flammable substance.

Using the information from Table 1 and the equations from Kondo *et al.* (2006), the FIP of the CO<sub>2</sub> mixtures CO<sub>2</sub>/R1270 and CO<sub>2</sub>/R32 are obtained and gathered in Table 2. For CO<sub>2</sub>/R32 mixture, the FIP does not ensure a GWP below 150, so the %CO<sub>2</sub> fraction was increased to reduce it to the minimum allowed by the current regulation of F-Gas (EU No 517/2014). Table 2 also include the critical point conditions (temperature and pressure), the GWP of the mixture, and the total glide evaluated with the resulting pressure from the evaporating temperature of -10°C and the vapour quality of 50%.

**Table 2. Properties of mixtures (using RefProp® v.10.0)**

Mixture	FIP <sup>2</sup>	%CO <sub>2</sub> mass	%Flammable gas mass	P <sub>crit</sub> (bar)	T <sub>crit</sub> (°C)	Total Glide (K) (-10°C, x=0.5)	GWP <sub>100</sub>
CO <sub>2</sub> + R32	0.602	56.1 %	43.9 %	74.50	54.51	13.40	297.6
CO <sub>2</sub> + R32	0.602	78.0 %	22.0 %	75.81	43.24	6.49	149.7
CO <sub>2</sub> + R1270	0.921	92.4 %	7.6 %	76.17	36.95	3.37	1.1

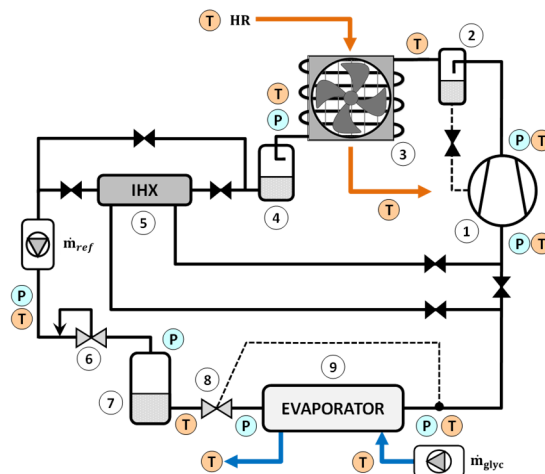
<sup>2</sup> CO<sub>2</sub> molar concentration in the mixture of CO<sub>2</sub> and flammable gas

As Table 2 shows, mixtures with CO<sub>2</sub> provide higher critical temperature and lower critical pressure than CO<sub>2</sub>, which benefits the subcritical operation of the refrigeration cycle with lower pressure operation levels. Moreover, the total glide of the mixture is relatively low (above 10 K), which could contribute positively to the heat exchange due to the temperature match between the refrigerant and secondary fluid.

### 3. EXPERIMENTAL SETUP

#### 3.1. Refrigeration facility

Figure 1 presents the refrigeration facility used to evaluate the CO<sub>2</sub> mixtures defined above. It consists of a small-capacity unit based on a one-stage transcritical vapour compression cycle using air as secondary fluid in the gas-cooler and a mix of water and ethylene glycol (49% in mass) in the evaporator. The setup includes a hermetic compressor (1) with a cubic capacity of 1.75 cm<sup>3</sup> and a nominal rotation speed of 2900 rpm at 50 Hz; a coalescent filter (2) to separate the PAG lubricating oil from the compressor; an air finned-tube gas-cooler (3) with an inner-tube heat transfer area of 0.27 m<sup>2</sup> and an axial fan to reject the heat from the gas-cooler and to cool down the compressor; a small receiver of 200 cm<sup>3</sup> (4) operating as a liquid receiver in subcritical conditions; a suction-to-liquid heat exchanger (IHX) (5) with a by-pass and an inner heat transfer area of 0.022 cm<sup>2</sup>; an electronic back-pressure valve (6) to control the heat rejection pressure; an intermediate liquid receiver of 3700 cm<sup>3</sup> (7) to keep liquid conditions at the inner of the second expansion stage; an electronic thermostatic valve (8) to control the useful superheating at the evaporator; and finally, a brazed-plate evaporator (9) with a heat transfer area of 0.576 m<sup>2</sup>. In addition, the refrigeration facility has a bypass to isolate the back-pressure (6) and the liquid receiver (7) in subcritical conditions. This by-pass is not depicted in Figure 1.



**Figure 1: Schematic diagram of the refrigerating setup**

All pipes and elements of the refrigeration facility are covered with foam with very low thermal conductivity to minimize the effect of heat exchange with the surroundings.

### 3.2. Measurement elements

Figure 1 also includes the measurement elements used to define the pressure and temperature at the inlet and outlet of the components and the mass flow rates of the refrigerant and the secondary fluid used in the evaporator. Temperatures were measured with T-type thermocouples with an accuracy of  $\pm 0.5$  K according to IEC 60584–1. All thermocouple probes were placed inside the fluid for a more accurate measurement. The pressure was registered with pressure gauges from 0-160 bar for high working-side pressure, 0-100 bar for the liquid receiver, and 0-60 bar for the low-pressure part. The accuracy of all of them was  $\pm 0.5\%$  spam. Two Coriolis mass flow meters recorded mass flow rates of CO<sub>2</sub> and the secondary water-ethylene-glycol mixture with an accuracy of  $\pm 0.5\%$  of reading. Air temperature and relative humidity were recorded with a hygrometer with an accuracy of  $\pm 2.0\%$  HR and  $\pm 0.2$  °C. Finally, the compressor's power consumption was obtained with a power meter from 0-600W with an accuracy of  $\pm 0.5\%$  of reading.

All data were acquired by a data acquisition system (DAQ) with a registered time of 5 s for a minimum stationary period of 15 minutes. A personal computer recorded the information, and the thermophysical properties of refrigerants and secondary fluids were calculated with the software RefProp® v.10.0 and SecCool® v1.33, respectively.

### 3.3. Mixture elaboration

The CO<sub>2</sub> blends described in Section 2 were elaborated using a vessel of 13.4 litres to mix the pure fluids at the tested ambient conditions described in Section 3.4. The mass introduced was weighed using a precision scale with an uncertainty of  $\pm 1$  g and a range of 30000 g. As a uniform mixture of the components is essential, the blend was always maintained in phase gas by limiting its mass below the maximum defined by the vessel volume and the density of the mixture at the vapour saturation conditions. Moreover, during tests, a heating resistor was used to warm the vessel, ensuring a phase-gas condition.

### 3.4. Test methodology

To compare the defined CO<sub>2</sub> blends, the refrigeration facility described in Section 3.1 was tested at the environmental conditions of 25°C and 60% of relative humidity (Climatic Class 3 according to UNE-EN ISO 23953–2), resulting in the inlet temperature of the gas-cooler. The heat rejection pressure was varied from a maximum of 95 bar to a minimum defined by the stable conditions of the refrigerating plant. The evaporating conditions were defined by fixing the mass flow rate and the inlet temperature of the water and ethylene glycol mixture to 100 kg/h and 0°C, respectively. Finally, the useful superheating was fixed to 5.5 K in the thermostatic valve controller.

With each refrigerant, the controller was upgraded to the corresponding P-T curves. The test order was pure CO<sub>2</sub>, CO<sub>2</sub>/R1270 and CO<sub>2</sub>/R32. After each refrigerant, the refrigerating cycle was subjected to a vacuum for 30 minutes to remove all the previous fluid. Since CO<sub>2</sub> mixtures have a low critical temperature, a subcritical operation was expected. Therefore, the back-pressure (6) and the liquid receiver (7) were isolated. With this arrangement, the refrigerant mass charge of CO<sub>2</sub> was 1 kg, whilst the mass charge of the CO<sub>2</sub> blends varied depending on the operating pressure.

## 4. EXPERIMENTAL ANALYSIS

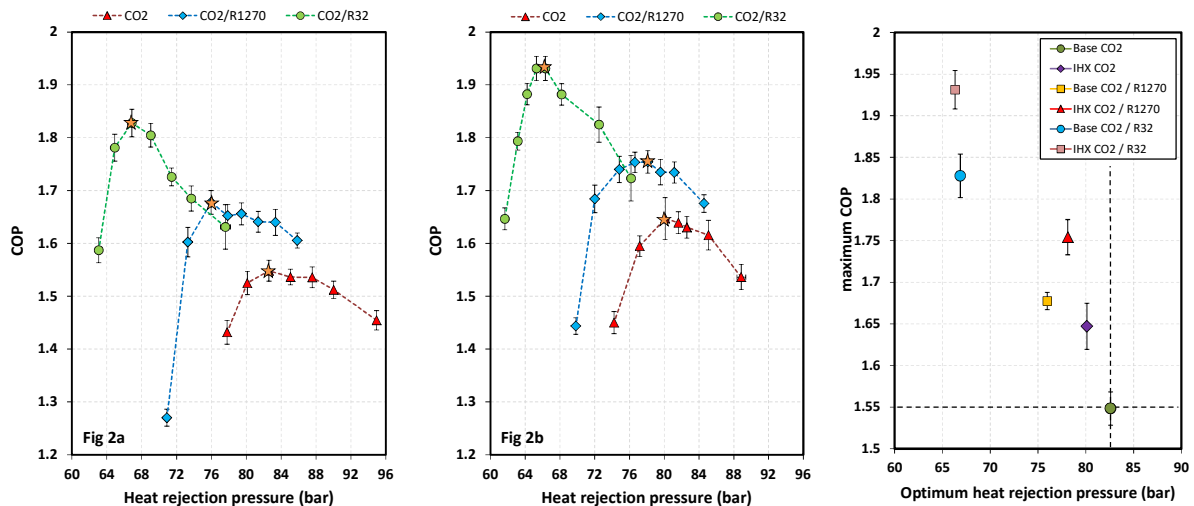
The results from the experimental tests described above are presented and discussed in this section, including working pressures and energetic parameters like cooling capacity, compressor power consumption and COP.

### 4.1. COP and optimum heat rejection pressure

The first parameters analysed correspond to COP and heat rejection pressure since they determine the optimal operating conditions of the refrigerating plant. The COP is defined by Eq. (1) using the cooling capacity ( $\dot{Q}_{ev}$ ) and the electric power consumed by the compressor ( $P_c$ ). Both parameters will be described in the next section.

$$COP = \dot{Q}_{ev}/P_c \quad (\text{Eq. 1})$$

Figure 2 shows how the COP of the refrigerating plant varies with the heat rejection pressure without using the IHX (Fig 2a) and using the IHX (Fig 2b). The optimum values are highlighted with a star-shaped marker in Figures 2a and 2b and presented with the optimum heat rejection pressure in Figure 2c.



**Figure 2: COP vs heat rejection pressure without IHX (Fig 2a) and with IHX (Fig 2b). Maximum COP and optimum heat rejection pressure (Fig 2c)**

The results presented in Figures Fig 2a and Fig 2b evidenced that CO<sub>2</sub> blends enhance the COP of the refrigeration system and reduce the optimum operating pressure regardless of the use of the IHX. Moreover, mixtures have a similar behaviour of CO<sub>2</sub> below the optimal pressure with a significant COP drop, as Cabello *et al.* (2008) reported experimentally operating with a pure CO<sub>2</sub> transcritical cycle.

According to Fig 2c, taking pure CO<sub>2</sub> base-cycle as a reference, CO<sub>2</sub>/R32 provides a COP increment of up to 18.1% without IHX and up to 24.7% with IHX, while the mixture of CO<sub>2</sub>/R1270 provides an increment of up to 8.4% without IHX and up to 13.3% with IHX.

Regarding the heat rejection pressure, the IHX reduces the optimum pressure to 2.5 bar using pure CO<sub>2</sub>, following the results presented by Torrella *et al.* (2011). CO<sub>2</sub>/R1270 blend provides an optimal pressure drop of -6.6 bar without IHX and -4.5 bar with IHX, while the mixture of CO<sub>2</sub>/R32 gives the highest reductions to -15.7 bar without IHX and -16.3 bar with IHX.

## 4.2. Cooling capacity and compressor power consumption

The cooling capacity and the compressor's power consumption were obtained at the experimental optimal heat rejection pressure presented in Fig 2c. The power consumption was measured directly from the power meter installed, and the cooling capacity was calculated using Eq. (2) with the refrigerant mass flow rate ( $\dot{m}_{ref}$ ) measured with the Coriolis mass flow-meter and the specific enthalpies ( $h_{ev out}$  and  $h_{ev in}$ ) calculated with RefProp® using the measurements of temperature and pressure.

$$\dot{Q}_{ev} = \dot{m}_{ref} \cdot (h_{ev out} - h_{ev in}) \quad (\text{Eq. 2})$$

The water-ethylene-glycol mixture used as the secondary fluid in the evaporator was used to validate the cooling capacity obtained from the refrigerant at the optimum operating conditions. Eq (3) was used to determine the cooling capacity in the secondary fluid with a maximum deviation of 6.5%.

$$\dot{Q}_{ev} = \dot{m}_{glyc} \cdot C_{p_{glyc}} \cdot (T_{glyc in} - T_{glyc out}) \quad (\text{Eq. 3})$$

Figure 3 shows the refrigerating plant's power consumption and cooling capacity for the arrangements with and without IHX. From the results obtained under the same operating conditions, it is evident that mixtures reduce the power consumption of the refrigerating plant and introduce a slight reduction in the cooling capacity when the IHX is not used in the refrigerating plant. However, the IHX inclusion enhances the cooling capacity of the facility and makes it similar to the use of pure CO<sub>2</sub> with IHX. The high variability shown in Figure 3 means the standard deviation of measurements due to thermostatic valve regulation.

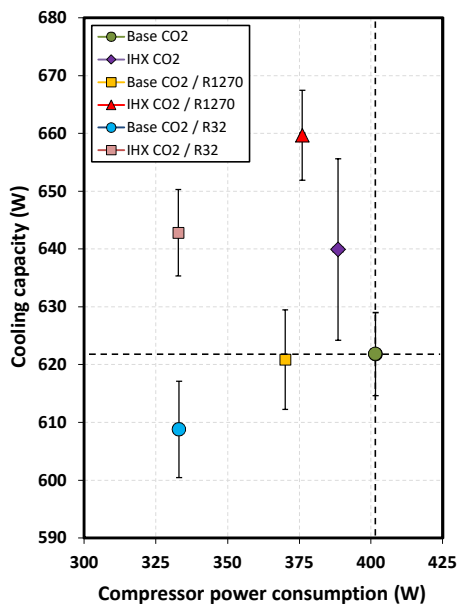


Figure 3: Cooling capacity vs power consumption

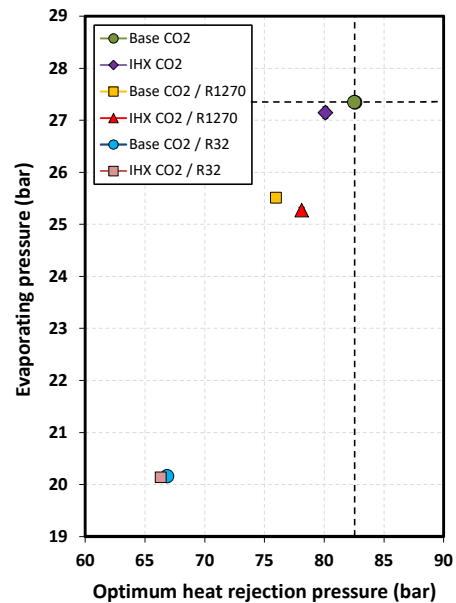


Figure 4: Evaporating and heat rejection pressure

## 4.3. Working pressures

The main effect of mixing CO<sub>2</sub> with R1270 or R32 is incrementing the critical temperature that allows working with lower pressures than pure CO<sub>2</sub>. This effect is reflected in Figure 4, where mixtures minimise the evaporating and heat rejection pressures. The maximum reduction in the heat rejection pressure is 15.7 bar, and the evaporating pressure is 7.2 bar. The use of the IHX reduces the evaporating pressure due to the cooling capacity increment (Figure 3), except with R32. Similarly, using the IHX reduces the heat rejection pressure slightly, except for the mixture of CO<sub>2</sub>/R1270, where the optimal pressure is somewhat higher than the base cycle.

#### 4.4. Evaporating and gas-cooler/condenser exit temperatures

The temperature at the exit of the gas-cooler is a key control parameter in CO<sub>2</sub> transcritical cycles as the evaporating temperature. Therefore, both temperatures have been presented in Figure 5 for all tested alternatives. It is important to highlight that mixture of CO<sub>2</sub>/R32 allows subcritical operation, so in this case, the heat exchanger changes from a gas-cooler to a condenser. The evaporating temperature has been evaluated with the average evaporator pressure, and the vapour quality was assessed in the middle of the evaporating process according to Eq. (4):

$$T_{ev} = f\left(\frac{P_{ev\ in} + P_{ev\ out}}{2}; x_{ev\ in} + \frac{1 - x_{ev\ in}}{2}\right) \quad (\text{Eq. 4})$$

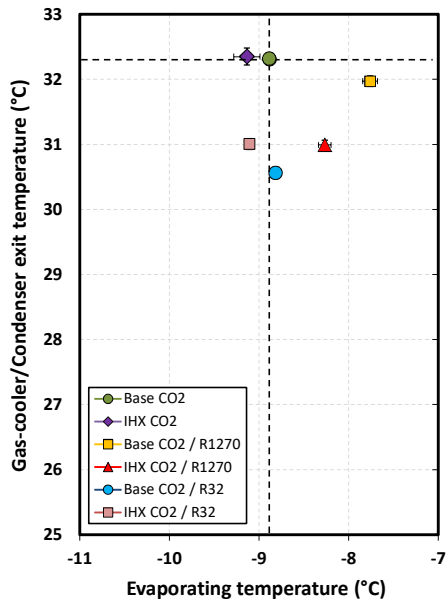


Figure 5: Gas-cooler/condenser exit temperature vs evaporating temperature

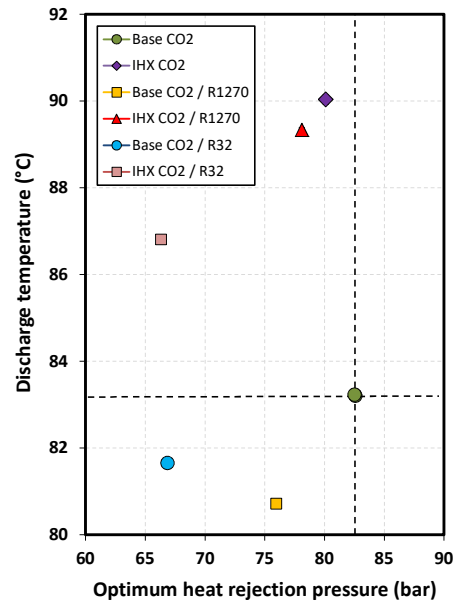


Figure 6: Discharge temperature

As Figure 5 shows, the evaporating temperatures of pure CO<sub>2</sub> and CO<sub>2</sub>/R32 are similar operating without IHX and IHX, so no significant changes are reflected. However, the mixture of CO<sub>2</sub>/R1270 presents an evaporating temperature up to +1.1 K higher than pure carbon dioxide with and without IHX. The increment could be caused by an improvement in the heat transfer process, but further analysis is necessary.

Regarding the gas-cooler/condenser outlet temperature, all CO<sub>2</sub> alternatives perform slightly better than pure CO<sub>2</sub>, which approach temperature to the ambient conditions (25°C) is relatively poor (around 7 K). Therefore, tested mixtures perform better than CO<sub>2</sub>, even the lower gas-cooler efficiency.

#### 4.5. Discharge temperature

Finally, Figure 6 shows the compressor discharge temperature at the optimal operating conditions. This temperature corresponds to the maximum value in a refrigerating plant, so it must be controlled to prevent the deterioration of the lubricating oil. As shown, the use of CO<sub>2</sub> alternatives always reduces the discharge temperature marginally up to 2.5 K working without IHX and up to 3.2 K using the IHX. This last arrangement provides the highest temperature levels with a maximum of 90.0°C for pure CO<sub>2</sub> due to the superheating introduced by the IHX (Torrella *et al.*, 2011).



## 5. CONCLUSIONS

This work presents the experimental results obtained with the binary mixtures CO<sub>2</sub>/R1270 and CO<sub>2</sub>/R32 as direct drop-ins in a CO<sub>2</sub> transcritical refrigerating plant. These blends, developed theoretically as low-GWP and non-flammable, were tested in a small-capacity refrigerating setup maintaining the environmental conditions to 25°C and 60% (climatic class III), and the temperature and mass flow rate of the secondary fluid in the evaporator to 0°C and 100 kg/h, respectively.

Experimental tests demonstrated that the new blends could be used as a direct drop-in in a transcritical refrigerating plant upgrading the expansion valve without changing the compressor or heat exchangers. Furthermore, results revealed a COP enhancement without IHX of up to 18.1% with the mixture of CO<sub>2</sub>/R32 and 8.4% with the blend of CO<sub>2</sub>/R1270. This behaviour is possible thanks to reducing the compressor power consumption with similar values on the cooling capacity. Moreover, these new fluids reduce the optimum heat rejection pressure to 15.7 bar using CO<sub>2</sub>/R32 and 6.6 bar with CO<sub>2</sub>/R1270.

Regarding the evaporating temperature, a slight maximum enhancement of +1.1 K was detected using the CO<sub>2</sub>/R1270, which could be caused by an improvement in the heat transfer process. Still, no significant differences were detected with CO<sub>2</sub>/R32. Similar results were found with the gas-cooler / condenser exit temperature, which is always lower using mixtures.

Finally, non-noticeable differences were found with the discharge temperature at the optimal operating conditions. The use of CO<sub>2</sub> alternatives always reduces the discharge temperature marginally up to 2.5K working without IHX and up to 3.2K using the IHX.

Despite the promising results obtained with the proposed mixtures, a deep analysis is necessary to determine the flammability of the mixtures according to ASHRAE Standard 34 and the compatibility with the lubricant oil. Moreover, a detailed analysis of the heat transfer process in the heat exchangers is necessary to understand the benefits of using zeotropic mixtures in the evaporating process.

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## NOMENCLATURE

<i>COP</i>	Coefficient of Performance	<i>x</i>	Vapour quality
<i>C<sub>p</sub></i>	specific isobaric heat (kJ/kg·°C)	<i>c</i>	compressor
<i>h</i>	specific enthalpy (kJ/kg)	<i>ev</i>	evaporator
<i>ṁ</i>	mass-flow rate (kg/s)	<i>glyc</i>	Mixture of water-ethylene glycol
<i>P</i>	pressure (bar) / power consumption (W)	<i>in</i>	inlet
<i>Q̇</i>	cooling capacity (W)	<i>out</i>	outlet
<i>T</i>	temperature (°C)	<i>ref</i>	refrigerant

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