International Journal of Refrigeration 148 (2023) 108–116

Contents lists available at ScienceDirect

International Journal of Refrigeration

journal homepage: www.elsevier.com/locate/ijrefrig

# Ternary refrigerant blends for ultra-low temperature refrigeration☆

## *Mélanges ternaires de réfrigérants pour la réfrigération à ultra-basse température*

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ARTICLE INFO

*Keywords:*
Mixtures
Ultra-low temperature (ULT) refrigeration
Coefficient of performance (COP)
Flammability
Global warming potential (GWP)
Carbon dioxide ($CO_2$)

*Mots clés:*
Réfrigération à ultra-basse température (ULT)
Coefficient of performance (COP)
Inflammabilité
Potentiel de réchauffement global
Dioxyde de carbone ($CO_2$)

ABSTRACT

The absence of GWP limitation for refrigerants operating in vapour compression systems with a target temperature below –50 °C has caused slower market development. Therefore, while typical refrigeration applications have several mixtures offering different characteristics, a few mixtures already exist for –80 °C refrigeration (R-469A, R-472A, and R-473A). This paper explores the combination of pure fluids with varied characteristics as three-component mixtures for ultra-low temperature refrigeration. Different parameters have been considered in the theoretical screening, such as volumetric cooling capacity, coefficient of performance, global warming potential, and flammability at constant operating conditions. R-32, R-41, R-125, R-134a, R-152a, R-170, R-227ea, R-290, R-744, R-1132a, R-1150, R-1234ze(E) and RE-170 have been combined at steps of 5%. Mixtures with the lowest global warming potential and highest coefficient of performance result in high flammability, particularly at −80 °C. Environmental and energy aspects would require a lower priority in trade-off selections to reduce the flammability classification.

## 1. Introduction

Ultra-low temperature (ULT) refrigeration refers to the preservation of products at temperatures between −50 °C and −80 °C (ASHRAE, 2018). In the last years, this application was not included in the regulations that aimed to phase-down greenhouse gas working fluids in refrigeration, heat pump, and air conditioning systems. Most of these regulations controlled refrigerants to −50 °C applications (Mota-Babiloni et al., 2020a). Different reasons can be listed not to cover ULT applications, f.i. a relatively low number of systems in operation and a lack of ready-to-use low global warming potential (GWP) alternatives. Moreover, a higher pressure ratio implies low energy performance and can produce problems with lubricating oil.

Wang et al. (2020) studied the pull-down performance of *a* −80 °C ULT freezer. When the startup temperature was −20 °C instead of 24 °C, the maximum discharge temperature of the low-temperature stage (LTS) compressor was 11.6 °C lower. The superheating degree was the main factor influencing the rapid cooling phase, while the evaporation and condensation pressures decreased in the stable cooling phase. Besides, the volumetric efficiency of the high-temperature stage (HTS) compressor deteriorated during the pull-down and had a higher potential for performance improvement than the LTS compressor. Faugeroux (2016) validated three ULT freezers vendors. All had similar performance levels and consumed less than 10 kWh per day. Still, the Stirling freezer absorbed less electricity and offered a larger storage capacity. The Thermo freezer remained closest to the temperature setpoint and showed the best internal temperature uniformity. Song et al. (2021) experimentally proposed the pair R-404A/R-508A with pentane as the oil carrier in the LTS. The highest discharge temperature appeared in the first half of the cooling process. Additionally, the operational stability and security would be highly strengthened by decreasing the charging amount, increasing the zeotropic component fraction, and declining the heat collector opening.

*Abbreviations:* ACR, auto-cascade refrigeration; HC, hydrocarbon; HFC, hydrofluorocarbon; HTS, high-temperature stage; LHR, Linde-Hampson refrigeration; LTS, low-temperature stage; ULT, ultra-low temperature.

☆ This work extends and updates Manuscript ID 1105 presented at the 7th IIR International Conference on Sustainability and the Cold Chain (ICCC2022), 11th to 13th April 2022

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https://doi.org/10.1016/j.ijrefrig.2023.01.006
Received 25 July 2022; Received in revised form 1 December 2022; Accepted 7 January 2023
Available online 10 January 2023

**Nomenclature**

| | |
|---|---|
| *COP* | coefficient of performance (-) |
| GWP | global warming potential ($CO_2$e) |
| h | enthalpy (kJ $kg^{-1}$) |
| $\dot{m}_r$ | mass flow rate (kg $s^{-1}$) |
| NBP | normal boiling point ( °C) |
| p | pressure (kPa) |
| $\dot{Q}$ | heat transfer (W) |
| T | temperature (K) |
| VCC | volumetric cooling capacity (kJ $kg^{-3}$) |
| $x_v$ | vapour quality (-) |
| $\dot{W}_c$ | compressor power consumption (kW) |
| *Subscripts* | |
| is | isentropic |
| in | inlet |
| k | condenser |
| out | outlet |
| o | evaporator |
| vol | volumetric |
| *Greek* | |
| $\eta$ | compressor efficiency |
| $\rho_{suc}$ | suction density |

The offer of ULT freezers was based on the hydrofluorocarbon (HFC) R-23 and R-508B, with a GWP value of around 14000 (having a direct contribution to the greenhouse effect of 14,000 times higher than the same amount of carbon dioxide). Like other applications, 4th generation refrigerants in natural or synthetic alternatives are available to replace these HFCs. Therefore, in the coming years, ultra-low normal boiling point (NBP) ethane (R-170), ethylene (R-1150), carbon dioxide ($CO_2$ or R-744), R-41 or R-1132a can be considered (Mota-Babiloni et al., 2020b). In this way, Rodríguez-Criado et al. (2021) proposed an R-170 indirect cascade system, retrofitting a standard R-290 packaged unit. The results showed successful behaviour, exhibiting a coefficient of performance (COP) from 0.6 to 1.6 for cold room temperatures between −80 °C and −65 °C, respectively. Thus, most of the research is focused on the LTS of ULT two-stage cascade refrigeration systems (CRS). Udroiu et al. (2022) proposed 42 combinations of advanced configurations based on R-170 and R-290 (LTS and HTS, respectively) for two-stage cascade systems, with up to a 43.5% increase in COP compared to basic cycles.

Logesh et al. (2019) analysed R-134a/R-23, R-410A/R-23 and R-404A/R-170 pairs. R-134a/R-170 has a greater COP and lower mass flow rate, whereas the opposite is observed with R-404A/R-508B. Aktemur et al. (2021) used R-41 in the LTS, whereas R-1243zf, R-423A, R-601, R-601A, R-1233zd(E) and RE170 are used for the HTS. For ULT applications, R-41/R-423A exhibits the lowest COP and exergy efficiency (1.1 and 33.9%, respectively), whereas R-41/RE170 presents the highest COP and exergy efficiency (1.21 and 37.2%). Dashtebayaz et al. (2021) presented an energy-exergoeconomic-environmental model, including R-41/R-161, R-41/R-1234yf, R-41/R-1234ze, R-744/R-161, R-744/R-1234yf, R-744/R-1234ze(E). The maximum COP and exergy efficiency of 2.1 and 35.3% are obtained at condenser and evaporator temperatures of 40 °C and −30 °C. R-41/R-161 and R-41/R-1234ze(E) are optimal refrigerant pairs with the highest COP/exergy efficiency and the lowest total cost rate.

Sun et al. (2016) compared R-41/R-404A and R-23/R-404A pairs. The input power of R-41/R-404A is lower and optimal COP, and maximum exergy efficiency is higher than that of R-23/R-404A. Sun et al. (2019b) extended the analysis to R-23, R-41 and R-170 in the LTS and R-32, R-1234yf, R-1234ze(E), R-161, R-1270, R-290 and R-717 in the HTS. R-41/R-161 is superior to other refrigerants, improving COP and thermodynamic performance when the evaporation temperature exceeds −60 °C. Then, Sun et al. (2019a) studied a three-stage CRS. R-1150 can replace R-14 in the LTS, R-41 and R-170 can replace R-23 in the medium-temperature cycle, and in the HTS, R-717, R-152a and R-161 are recommended. Walid Faruque et al. (2002) evaluated four hydrocarbon refrigerants: 1-Butene/Heptane/m-Xylene, 1-Butene/-Trans-2-Butene/m-Xylene, 1-Butene/Toluene/m-Xylene and 1-Butene/-Cis-2-Butene/m-Xylene for the temperature range −90 °C to −120 °C.

R-744 cannot be used for applications below −50 °C due to its triple point at −56 °C. R-744 mixtures are commonly investigated for the LTS of CRS. Di Nicola (2005) proved that R-744 blends with R-125, R-41, R-32, and R-23 are viable in a cascade cycle for −70 °C refrigeration using ammonia (R-717) as the high-temperature-circuit refrigerant. They developed software based on the Carnahan–Starling–De Santis equation of state using binary interaction parameters derived from experimental data. Massuchetto et al. (2019) evaluated R-744 mixtures with R-1270, R-717 and RE170 in a cascade cycle. After optimisation, COP increased from 18% to 32% compared to pure refrigerants. R-744/RE170 mixture showed the best results with a COP of 2.34, increasing exergetic efficiency to 30%. A novel wet sublimation cascade refrigeration system was developed by Sobieraj (2021) using mixtures of R-744 with hydrocarbons (HC) and hydrofluorocarbons (HFCs). With R-290 and R-32 serving as solvents for solid R-744, temperatures as low as −72 °C were obtained with mixtures containing 67% $CO_2$ by mass. Heat transfer rates up to 3465 W $m^{-2}$ $K^{-1}$ were obtained in the sublimator/evaporator section. Sobieraj and Rosinski (2019) investigated the effects of carbon dioxide crystallisation, the heat flux, and the vapour quality of R-744/600a mixtures in a 10 mm inner diameter horizontal copper tube. The crystallisation and formation of a solid fraction greatly influence the heat transfer characteristics, which are approximately ten times higher for wet R-744 sublimation than for a single phase. Kauffeld et al. (2020) proposed mixtures of $N_2O$ (R-744A) and R-744 and different lubricants in two low-temperature systems at evaporation temperatures down to −80 °C. The units achieved similar energy efficiency as the standard HFC equipment for freeze-drying. They listed measures to suppress the possible decomposition of R-744A.

Apart from those mainly based on R-744, other refrigerants have been proposed for ULT refrigeration. Bai et al. (2021) used R-170/290 mixture in a Joule-Thomson cycle for −60 °C refrigeration. The lowest freezing temperature, fastest cool-down rate, and minimum daily energy consumption were obtained at 35% R-170 concentration. However, excessive concentration of R-170 could significantly increase the discharge pressure and temperature. Additionally, the compressor worked with a high compression ratio, ranging from 21.8 to 26.8. Qin et al. (2021b) theoretically analysed a single-stage LHR using R-1234yf mixtures with R-170, R-23, R-41 and R-1132a to replace R-23 down to −60 °C. The R-1234yf/41 mixture performed better than the rest.

These fluids can also be found in mixtures proposed in auto cascade refrigeration (ACR) systems, another type of cycle proposed in ULT applications. An R-600a/1150 mixture was evaluated by Rodríguez-Jara et al. (2022) in an ACR which included an ejector as an expansion device at the outlet of the phase-separator or as a pre-compression stage. The results showed a 12% potential COP improvement for the case of the ejector as an expansion device, with an 0.45 optimal R-1150 mass fraction. Bai et al. (2022) simulated an ejector-enhanced R-1150/600a ACR system for −80 °C freezers. An internal heat exchanger at the evaporator outlet is more energy-efficient than the condenser outlet. The average COP and exergy efficiency improvements reached 55.2%, and the compressor displacement and system initial capital cost were reduced by 52.9% and 17.5%, respectively. Sivakumar et al. (2014) studied a three-stage ACR system using R-290/23/14 and R-1270/170/14 zeotropic mixtures. The mixture R-290/23/14 (0.218/0.346/0.436 in mass percentage) performed better at −97 °C with a COP of 0.25 and 58.5% exergetic efficiency. Qin et al.

(2021a) developed a mathematical model based on the energy and exergy methods for a modified vapour compression refrigeration cycle coupled with a Linde-Hampson refrigeration (LHR) system and a three-stage ACR using low-GWP mixtures. The LHR-ACR system has a better thermodynamic performance with exergy efficiency of 15.2% and COP of 0.14 at −150 °C when the R-1234yf/32 composition, R-170/14/50 composition and vapour quality are 0.54/0.46, 0.52/0.22/0.26 and 0.45, respectively. Qin et al. (2022) experimentally coupled R-1234yf, R-32 and R-170 with the same system. The cooling capacity, COP and relative Carnot efficiency were 182.9 W, 0.12 and 16%.

Up to this day, three mixtures have been registered for the LTS of ULT freezers, R-469A, R-472A and R-473A. R-469A has a bubble point at −78.5 °C and a dew point at −61.5 °C, GWP value of 1357. R-472A bubble and dew points are −84.3 °C and −61.5 °C, respectively, presenting the lowest GWP with 353. Finally, R-473A is a refrigerant blend with a mean molar mass of 52.6 g $mol^{-1}$ and a critical temperature of 33 °C. R-473A bubble and dew point are at −75 °C, and its GWP of 1830. ASHRAE safety classification of the three mixtures is A1. Table 1 summarises the composition of these mixtures.

As is shown, the number of refrigerants for ULT applications is limited. Therefore, and given the need to find suitable environmentally friendly alternatives to commonly used refrigerants, this work focuses on searching for new potential mixtures for ULT refrigeration.

This paper proposes three-component mixtures for ULT refrigeration. Several ULT and other temperature refrigerants have been considered as potential components. A multi-parameter evaluation is performed, including energy parameters such as the coefficient of performance and volumetric cooling capacity, environmental assessment through the global warming potential, and safety concerns (flammability of the mixture).

## 2. Methodology

### 2.1. Refrigerants used for the mixtures

Refrigerants used in LTS of ULT refrigeration systems must have a significantly lower normal boiling point (NBP) than other refrigerants typically used in more common vapour compression system applications. In these refrigeration and heat pump systems, most refrigerants present an NBP between −20 °C and −50 °C. However, ultra-low temperature refrigeration requires an NBP between −50 °C and −90 °C.

A limited number of common refrigerants have such a low NBP; therefore, the list of potential refrigerants is notably shortened. Mota-Babiloni et al. (2020b) proved that a few refrigerants met this standard: natural refrigerants R-170, R-1150 (or R-744), and synthetic fluids R-41 and R-1132a. The list of alternatives considering only pure refrigerants is restricted; none is "perfect", and a few negative characteristics must be accepted. As it is happening for standard refrigeration and air conditioning applications, mixing refrigerants can mitigate these drawbacks.

When mixing refrigerants, amongst other characteristics, the NBP is also tunned (Albà et al., 2020; Calleja-Anta et al., 2022; Halon et al., 2022; Ramírez-Hernández et al., 2022). Therefore, this can extend the list of candidate refrigerants as components for the mixtures to other refrigerants with higher NBP than those pure refrigerants in ULT refrigeration.

**Table 1**
Registered mixtures for LTS of ULT freezers.

| Refrigerant | $GWP_{100yr}$ [$CO_2$e] | Composition | |
|---|---|---|---|
| R-469A | 1357 | 35% | Carbon dioxide (R-744) |
| | | 32.5% | Difluoromethane (R-32) |
| | | 32.5% | Pentafluoroethane (R-125) |
| R-472A | 353 | 69% | Carbon dioxide (R-744) |
| | | 19% | 1,1,1,2-Tetrafluoroethane (R-134a) |
| | | 12% | Difluoromethane (R-32) |
| R-473A | 1830 | 60% | Carbon dioxide (R-744) |
| | | 20% | 1,1-Difluoroethylene (R-1132a) |
| | | 10% | Trifluoromethane (R-23) |
| | | 10% | Pentafluoroethane (R-125) |

Table 2 shows the substances considered in this work as candidate components for the ternary mixtures. A few interesting properties have been included, such as the NBP, which has been previously stated, GWP (constantly referring to a 100-year basis), and ANSI/ASHRAE Standard 34 Classification of Refrigerants (ASHRAE, 2019).

This list includes various refrigerants, from natural to synthetic, with no flame propagation to highly flammable, ultra-low GWP to high GWP fluids restricted in many refrigeration applications and with NBP from −20 °C to −100 °C. The wide variety of characteristics and thermodynamic and transport properties ensures the proposal of mixtures with concrete features close to what is needed in each application.

### 2.2. Composition of the mixtures

A MATLAB R2019a (The MathWorks Inc, 2019) code was written for the calculations. All the thermodynamical properties are extracted from REFPROP v10.0 (Lemmon et al., 2018), and the flammability of the mixture has been estimated with the method proposed by (Linteris et al., 2019). The NBP of all the possible binary and ternary mixtures are calculated raw with a mole variation. The nonsense values are eliminated. Only those mixtures with an NBP lower than the evaporation temperature were considered for preventing vacuum operation.

### 2.3. Simulation strategy

Refrigeration at temperatures between −50 and −80 °C is typically performed using two-stage cascades. Single-stage compression at high-temperature lifts (or pressure ratio) ends with excessive discharge temperature, low compressor efficiency, and high-power consumption. The significant temperature lift makes single-stage cycles not practical in this application.

Two-stage cascades divide the compression into low and high-temperature circuits (LTS and HTS). In the first step, only the LTS is simulated, and the HTS will not interact with or influence the system's operation and performance. Then, once the optimal mixtures in terms of performance are obtained, a complete cascade system (LTS and HTS) is simulated with obtained mixtures in LTS and commonly used refrigerants in HTS. The overall cascade system performance is then analysed.

The LTS evaporation and condensation temperatures vary from −80 to −50 °C and from −30 to 0 °C, keeping a temperature lift of 50 °C. The aim is to observe if the NBP can limit the composition of the ideal mixture. Then, for HTS, the condensation temperature is fixed at 35 °C, and the evaporation temperature is 5 K lower than the LTS condensation temperature.

Selecting the saturation states is critical when making cycles with zeotropic mixtures (McLinden and Radermacher, 1987). In this case, the saturation states are expressed in Eq. (1) and (2), taking the outlet saturated condenser temperature for the condensing pressure and the outlet evaporator temperature for the evaporation pressure. Consequently, evaporation and condensation pressures are defined from dew and bubble points, respectively. This conservative method maximises irreversibilities and favours mixtures with low glide and pure refrigerants (Bell et al., 2019).

$$P_k = f(x_v = 0,\ T_k) \tag{1}$$

$$P_o = f(x_v = 1,\ T_o) \tag{2}$$

Then, the performance parameters used for this work are volumetric cooling capacity (VCC) and COP, representing the required size of the compressor and the system's energy performance, respectively. Eq. (3) to (5) can be used to obtain these parameters.

**Table 2**
Refrigerants considered for the mixtures.

| ASHRAE Designation | Substance | Chemical formula | NBP ( °C) | $GWP_{100\text{-}yr}$ | ASHRAE classification |
|---|---|---|---|---|---|
| R-32 | Difluoromethane | CH2F2 | −52 | 675 | A2L |
| R-41 | Fluoromethane | CH3F | −79 | 107 | N/A |
| R-125 | Pentafluoroethane | CHF2CF3 | −48 | 3500 | A1 |
| R-134a | 1,1,1,2-Tetrafluoroethane | CF3CH2F | −26 | 1430 | A1 |
| R-152a | 1,1-Difluoroethane | CHF2CH3 | −24 | 124 | A2 |
| R-170 | Ethane | CH3CH3 | −89 | 5.5 | A3 |
| R-227ea | 1,1,1,2,3,3,3-Heptafluoropropane | CF3CHFCF3 | −17 | 3.3 | A1 |
| R-290 | Propane | CH3CH2CH3 | −42 | 1 | A3 |
| R-744 | Carbon Dioxide | CO2 | −88 | 1 | A1 |
| R-1132a | 1,1-Difluoroethylene | CH2=CF2 | −84 | 1 | N/A |
| R-1150 | Ethene | CH2=CH2 | −103.7 | 3.7 | A3 |
| R-1234ze(E) | trans-1,3,3,3-Tetrafluoropropene | CHF=CHCF3 | −19 | 6 | A2L |
| RE-170 | Methoxymethane | (CH3)2O | −25 | 1 | A3 |

$$VCC = \left(h_{o,in} - h_{o,out}\right) \eta_{vol}\, \rho_{suc} \tag{3}$$

$$\dot{W}_c = \frac{(h_{is} - h_{suc})}{\eta_{is}} \dot{m}_r \tag{4}$$

$$COP = \frac{\dot{Q}_o}{\dot{W}_c} \tag{5}$$

Additional parameters, such as superheating and subcooling degrees, are defined for these calculations and compressor efficiencies. All used parameters are summarised in Table 3.

## 3. Results and discussion

Understanding the limitations of the mixtures with a trade-off analysis is essential. A few properties of different types must be prioritised for selecting the best mixtures. The main parameters optimised are GWP, flammability, COP and VCC.

Fig. 1 shows the COP values against the VCC for the four temperature ranges (according to different colours), where each point represents an obtained refrigerant blend. The curves above and to the right of each subplot visually indicate the number of mixtures obtained for the values of VCC and COP, respectively. The figure is divided into nine subplots for every GWP (below 150, between 150 and 750, and above 750) and flammability condition (A1, A2L or A3). The upper left subplot is the most desired condition, with GWP under 150 and no flame propagation (A1), and the lower right is the contrary condition (high GWP and high flammability).

The lowest number of potential mixtures is obtained with an evaporation temperature of −80 °C. Most possible combinations do not have an NBP lower than −80 °C because many pure components present an NBP above these values. Therefore, only these combinations that include a high percentage of R-744, R-170, R-41 and R-1150 are valid.

**Table 3**
Working conditions for the ULT refrigeration cycle.

| Parameter | Value |
|---|---|
| Superheating degree (K) | 7 |
| Subcooling degree (K) | 2 |
| Volumetric compressor efficiency (Granryd et al., 2011) | $\eta_{vol} = 1 - 0.06\left(\left(\frac{P_k}{P_o}\right)^{\frac{1}{1.1}} - 1\right)$ |
| Isentropic compressor efficiency (Granryd et al., 2011) | $\eta_{is} = 1 - 0.06\left(\left(\frac{P_k}{P_o}\right)^{\frac{1}{1.1}} - 1\right)$ |
| $T_{k,LTS}$ ( °C) | [−30; 0] |
| $T_{o,LTS}$ ( °C) | [−80; −50] |
| $T_{k,HTS}$ ( °C) | 35 |
| $T_{o,HTS}$ ( °C) | $T_{k,LTS}$−5 |

The NBP results are a condition limiting the opportunity to mix different refrigerants. However, the number of mixtures is significantly higher in the flammable (A3) condition. This is because of the selection of the fluids employed, as most were highly flammable and had lower NBPs (highlighting hydrocarbons R-170, R-1170 and RE-170, followed by R-41 and R-1132a). It also can be appreciated that the number of available mixtures for the mildly and non-flammable rows is significantly higher for a GWP higher than 750 (only R-32, R-125 and R-134a have a GWP that can be considered remarkable).

COP results only regard the LTS of the two-stage cascade. Higher values are obtained for higher evaporation temperatures derived from the Carnot cycle. The most significant trade-off is between the highly and mildly flammable classes. To operate with the highest energy performance, the charge of the system should be lower, as A3 installations have more restrictions. The trade-off with GWP is not as crucial as with flammability. For the −50 °C evaporation temperature, the highest COP is obtained for higher GWPs, but there are also good options with low GWP in the other conditions. About the VCC, the flammable condition also ends with higher values. On the other hand, their VCC is significantly lower for the higher GWP mixtures than in other cases. Refrigeration at lower temperatures would require a compressor with a higher displacement.

Fig. 2 gives an idea of each subplot's dominant component to understanding the analysis derived from Fig. 1. A higher radial value in Fig. 2 means refrigerants have more presence in that subplot (names of the most prevailing refrigerants in each subplot have been added for better understanding). This is made with a sum of all the mole percentages for every subplot of every refrigerant and then normalising the results.

The main component of the low GWP non-flammable subplots is R-744, which is also the main component of registered mixtures, as shown in Table 1. Therefore, the results confirm that the low NBP of R-744 (low GWP and A1) is ideal for ULT. R-744 also has a high prevalence in the A2L low GWP and the A1 medium GWP mixtures, reducing the GWP and flammability of other components included. On the other hand, for the higher GWP values, R-125 is predominant (as in high GWP mixtures for other refrigeration applications), especially for the evaporation temperature of −50 °C, as its NBP is slightly higher than this temperature. For the A3 estimated class, the predominance is R-41 for the low GWP class and R-1132a for the medium and high GWP classes.

Fig. 3 summarises potential mixtures for every temperature range and flammability class. The COP and VCC values are also displayed. It is shown how, for the −50 °C condition, the A1 and A2L best mixture is an R-125-based mixture combined with R-290 or R-32. It also can be appreciated that R-170 is the main component of the flammable class, combined with R-41 or R-32. Then, in the cases of evaporation temperature lower than −60 °C and low flammability class, R-744 dominates.

The blend results in higher energy performances (COP) if mixed with

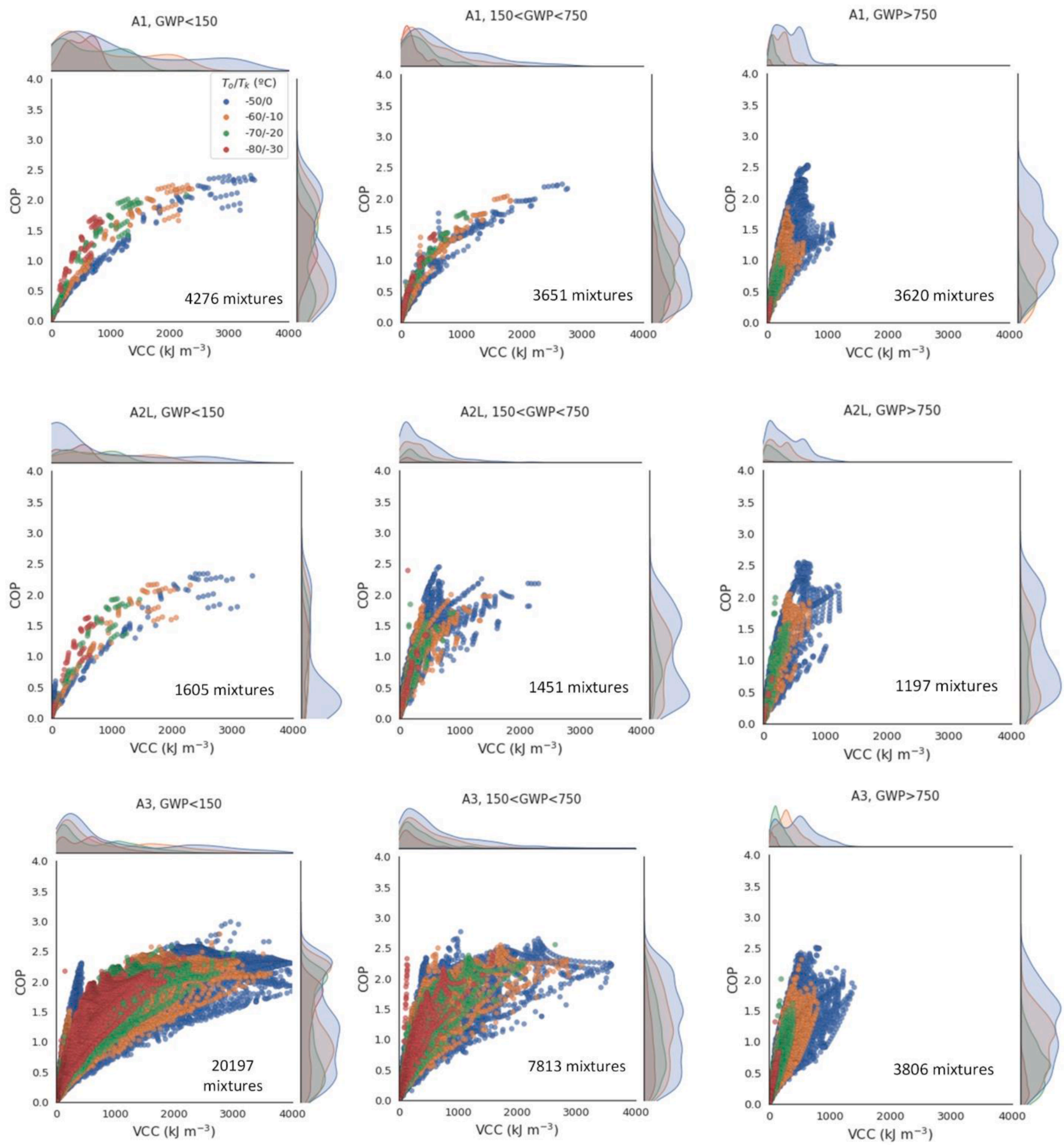


**Fig. 1.** Scatter plot of the VCC against the COP. Colour means temperature range, divided into nine subplots depending on the GWP and flammability restrictions.

R-41, R-290, or R-170. In this figure, the lower the evaporation temperature, the higher the trade-off in flammability is. Therefore, the COP is reduced a 15% in the −80 °C evaporation temperature condition transiting from A3 to A2L and 34% in the −50 °C condition. The reduction is almost negligible for the A2L to A1 transition, so it is recommended to use A1 instead of A2L in energy terms. Globally, the COP varies from 2.44 for the flammable class to 1.66 for the A1 class.

Regarding VCC, there is a remarkable decrease in most of the conditions transiting from A3 to A2L, except for the −70 °C evaporation temperature. Indeed, this is the only condition in which the A2L blend results in a higher VCC than the A1.

As for temperature glide, the highest obtained value is 6.2 K for the A3 mixture considering an evaporation temperature of −80 °C due to a remarkable presence of R-1150. Despite that, all obtained values are considered low enough not to affect system performance.

Table 4 shows the results of COP and VCC of the obtained optimal mixtures and the commonly used refrigerants in the LTS for the different evaporation and condensation temperatures. As can be seen, the highest

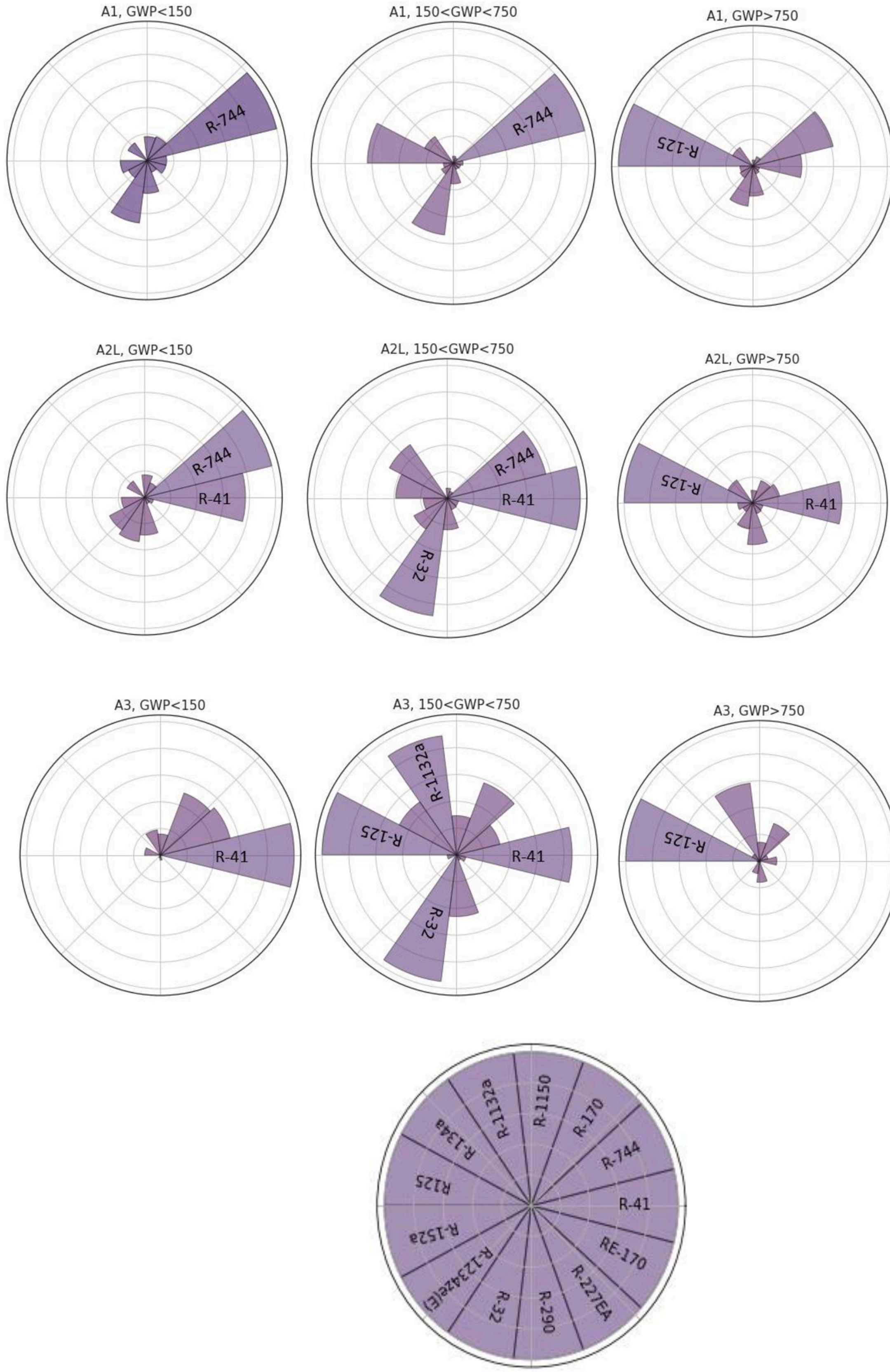


**Fig. 2.** Radial histogram of the prevalence of refrigerants in the nine subplots. The lower subplot is aligned with the subplots for each refrigerant.

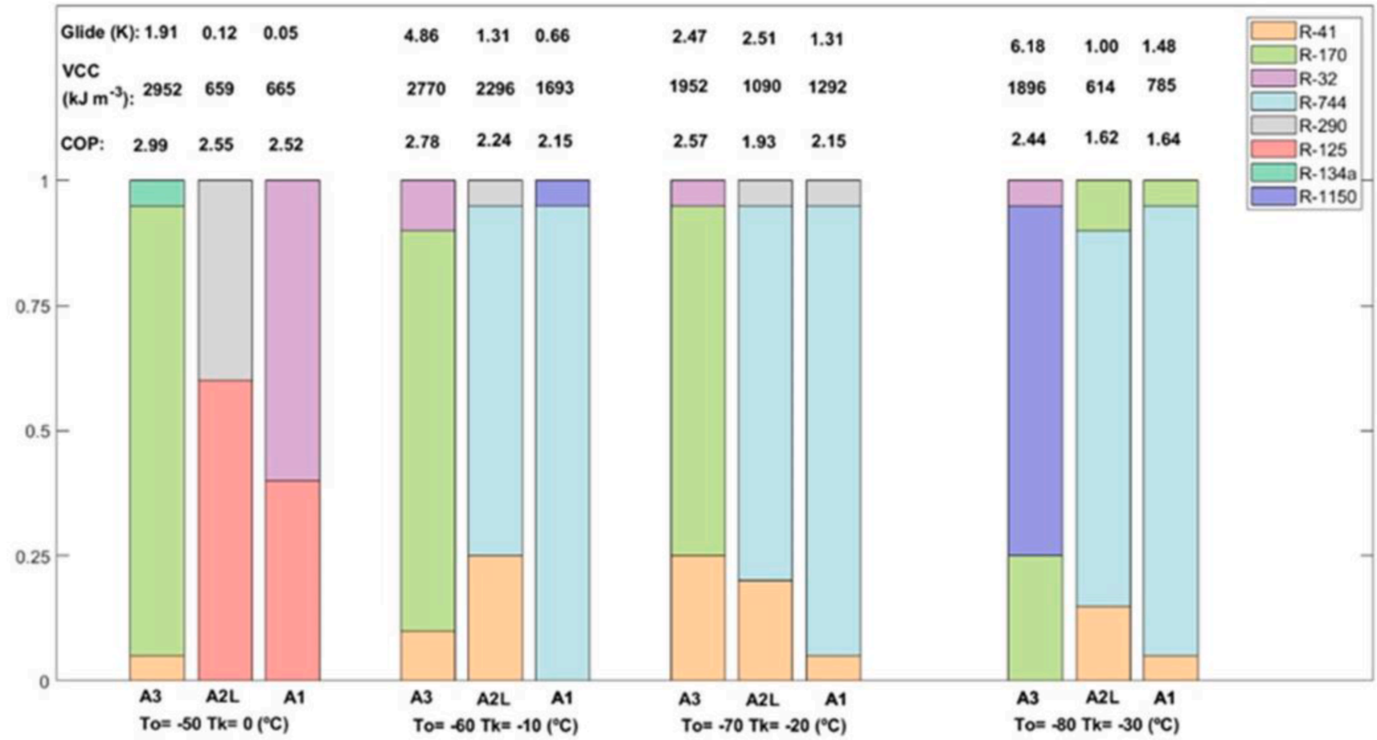


**Fig. 3.** Optimum mixture in terms of energy performance for each ULT condition.

**Table 4**
COP and VCC comparison between potential and existing blends in LTS.

| COP | R-469A | R-472A | R-473A | R-23 | R-170 | Highest COP in Fig. 3 | Lowest COP in Fig. 3 |
|---|---|---|---|---|---|---|---|
| $T_o$=−50 °C $T_k$=0 °C | 1.30 | 0.28 | 2,03 | 2.49 | 2.68 | 2.99 | 2.52 |
| $T_o$=−60 °C $T_k$=−10 °C | 0.91 | NC | 1.81 | 2.36 | 2.57 | 2.78 | 2.15 |
| $T_o$=−70 °C $T_k$=−20 °C | 0.39 | NC | 1.51 | 2.14 | 2.40 | 2.57 | 1.93 |
| $T_o$=−80 °C $T_k$=−30 °C | NC | NC | 1.11 | 1.84 | 2.16 | 2.44 | 1.62 |

| VCC (kJ $m^{-3}$) | R-469A | R-472A | R-473A | R-23 | R-170 | Highest VCC in Fig. 3 | Lowest VCC in Fig. 3 |
|---|---|---|---|---|---|---|---|
| To=−50 °C $T_k$ = 0 °C | 567 | 134 | 1945 | 2234 | 2399 | 2952 | 659 |
| To=−60 °C $T_k$ =−10 °C | 266 | NC | 1243 | 1532 | 1748 | 2770 | 2296 |
| $T_o$=−70 °C $T_k$=−20 °C | 73 | NC | 708 | 971 | 1201 | 1952 | 1090 |
| To=−80 °C $T_k$ =−30 °C | NC | NC | 334 | 557 | 769 | 1896 | 614 |

NC=not converged with selected boundary conditions.

COP and VCC of obtained optimal mixtures are higher than that of existing refrigerants in all cases. However, flammability must be considered for a correct analysis of the results.

A3 optimal mixtures increase COP from 7.1% to 13.0% and VCC from 23% to 147% compared to R-170, being the most considerable improvement of both parameters at the evaporation temperature of −80 °C, where the main mixture component is R-1150. It is then concluded that mixtures based on R-1150 can notably improve the performance of A3-designed systems. Regarding A1 optimal mixtures, COP varies from −10.8% to +1.2%, and VCC varies from −70.5% to +40.9% regarding R-23, which has the highest performance values amongst the A1 existing refrigerants.

Finally, Fig. 4 shows the results of a complete cascade system simulation for different refrigerant pairs of HTS/LTS. As can be seen, COP values are lower than those obtained in the previous analysis due to the electrical consumption of the HTS compressor.

As can be seen, HTS lowers the COP. At for the evaporation temperature of −50 °C, all refrigerant pairs have comparable COP. However, the VCC of the A3 refrigerant pair is up to 345% higher than the other refrigerant pairs with these conditions. At the evaporation temperature of −60 °C, the highest COP is still obtained for A3 refrigerants. But at this temperature, A1 refrigerants have 16% lower COP, maintaining a similar VCC compared with A3 mixtures. The same happens with the evaporation temperature of −80 °C, where A1 mixtures have a 30% lower COP but a similar VCC to A3 mixtures.

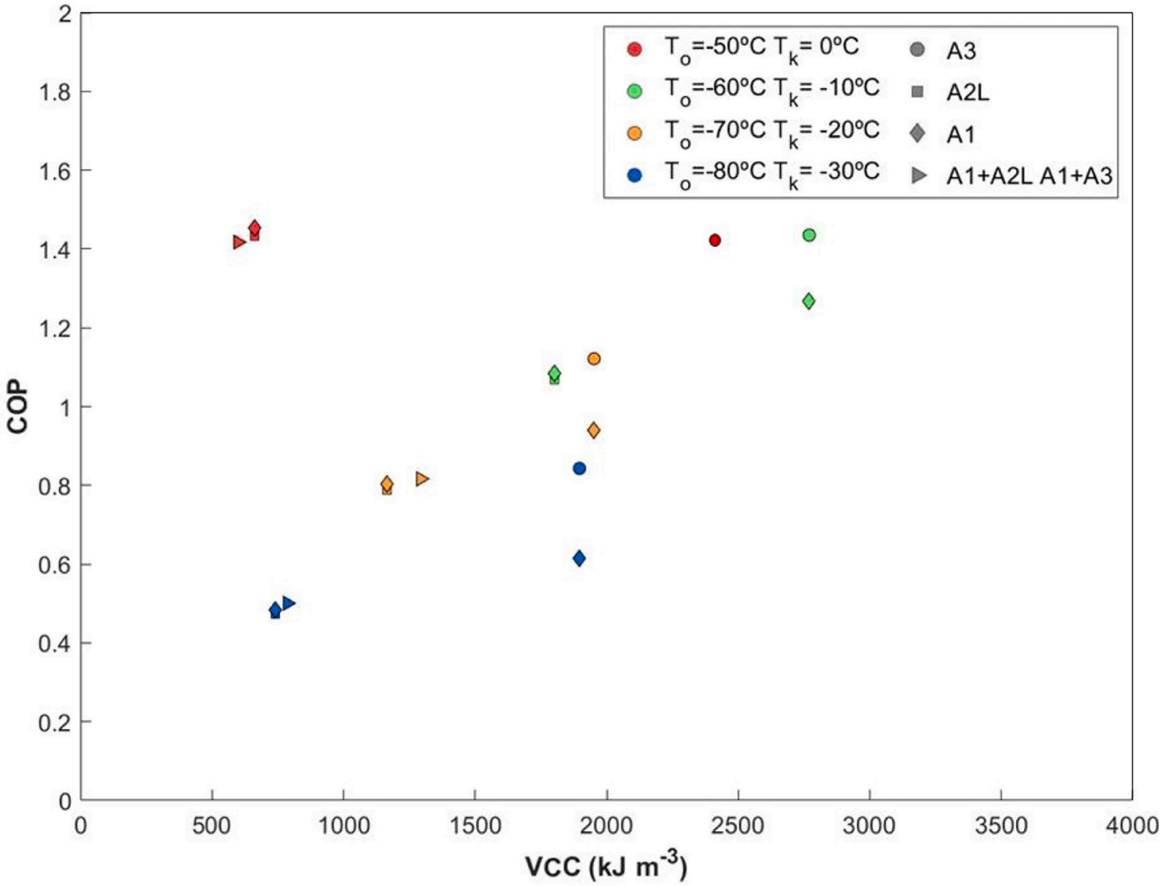


**Fig. 4.** COP and VCC for a complete cascade system (HTS/LTS) for different refrigerant pairs (A1: R-448A/optimal A1 mixture, A2L: R-454C/optimal A2L mixture, A3: R-290/optimal A3 mixture, A1+A2L A1+A3: R-448A/optimal A2L or A3 mixture).

## 4. Conclusions

This work presents the first approach to mixtures in ULT refrigeration, which application only have three mixtures registered today. These systems usually work with two CRS, so the focus is on the LTS, as the HTS has been much studied previously in works covering alternatives to R-134a and R-404A. LTS is critical as few refrigerants have suitable thermodynamical properties (such as low NBP) for this temperature. The different trade-offs and candidates are presented for four temperature ranges.

The mixing process was done with a mole variation of 5% for the presented refrigerants. Those mixtures with predicted NBP higher than the evaporation temperature were discarded. The saturated states were selected with a conservative approach favouring low glides mixtures.

Firstly, it was found that flammability is a big concern for all temperature ranges, as for non-flammable mixtures, the performance significantly decreases. For example, for an evaporation temperature of −80 °C, the COP approximately falls 33% if non-flammability is necessary. The volumetric cooling capacity also decreases notably for non-flammable conditions.

On the other hand, GWP is critical in the −50 °C evaporation temperature, as R-125 was a promising component in this condition, but its high GWP limits the candidates. In the other ranges, lower than −60 °C, R-744 outperforms other possibilities, reducing the GWP concern. It is mixed with flammable refrigerants such as R-41, which boosts its performance.

Then, potential candidates are R-170/41/134a (0.9/0.05/0.05) for −50 °C, but it is highly flammable (A3), mildly flammable (A2L) R-744/41/290 (0.7/0.25/0.05) for −60 °C, and no flame propagation (A1) R-744/1150 (0.95/0.05). For −60 °C, R-744/41/290 is the most convenient options are obtained at 0.75/0.2/0.05 and 0.9/0.05/0.05 for the mildly flammable and no flame propagation conditions, respectively. Similar mixtures but replacing R-290 with R-170 are the best options for the −80 °C evaporation temperature.

This article gives an initial insight into potential three-component mixtures in ultra-low refrigeration. Mixtures considered in the future will reduce the use of high GWP refrigerants as a component because of the lack of availability. Then, they should analyse the complete cascade system for different temperature lifts and refrigerants. Moreover, the heat exchange process using zeotropic mixtures can be studied experimentally in the evaporator, condenser and cascade heat exchanger. Finally, a comprehensive life cycle climate performance analysis could enrich the environmental point of view.

## 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.

## Acknowledgements

This publication is part of the $R + D + i$ project PID2020–117865RB-I00, funded by MCIN/AEI/10.13039/501100011033. Adrián Mota-Babiloni acknowledges grant IJC2019–038997-I funded by MCIN/AEI/10.13039/501100011033. Cosmin Mihai Udroiu acknowledges grant PRE2021-097369 funded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in your future". Pau Giménez-Prades acknowledges grant CIACIF/2021/182, funded by the Generalitat Valenciana (GV) and the European Social Fund (ESF).

## References

Aktemur, C., Ozturk, I.T., Cimsit, C., 2021. Comparative energy and exergy analysis of a subcritical cascade refrigeration system using low global warming potential refrigerants. Appl. Therm. Eng. 184, 116254 https://doi.org/10.1016/J.APPLTHERMALENG.2020.116254.

Albà, C.G., Vega, L.F., Llovell, F., 2020. A consistent thermodynamic molecular model of n-hydrofluoroolefins and blends for refrigeration applications. Int. J. Refrig. 113, 145–155. https://doi.org/10.1016/j.ijrefrig.2020.01.008.

American Society of Heating, R. and A.-C.Engineers, 2018. ASHRAE Handbook : Refrigeration.

ASHRAE, 2019. ANSI/ASHRAE standard 34-2019 designation and safety classification of refrigerants.

Bai, T., Li, D., Xie, H., Yan, G., Yu, J., 2021. Experimental research on a Joule-Thomson refrigeration cycle with mixture R170/R290 for −60°C low-temperature freezer. Appl. Therm. Eng. 186, 116476 https://doi.org/10.1016/J.APPLTHERMALENG.2020.116476.

Bai, T., Yan, G., Yu, J., 2022. Influence of internal heat exchanger position on the performance of ejector-enhanced auto-cascade refrigeration cycle for the low-temperature freezer. Energy 238, 121803. https://doi.org/10.1016/J.ENERGY.2021.121803.

Bell, I.H., Domanski, P.A., McLinden, M.O., Linteris, G.T., 2019. The hunt for non-flammable refrigerant blends to replace R-134a. Int. J. Refrig. 104, 484–495. https://doi.org/10.1016/j.ijrefrig.2019.05.035.

Calleja-Anta, D., Nebot-Andres, L., Sánchez, D., Cabello, R., Llopis, R., 2022. Drop-in substitutes for R-600a. Experimental evaluation and optimisation of a commercial fridge. Appl. Therm. Eng. 211, 118490 https://doi.org/10.1016/j.applthermaleng.2022.118490.

Deymi-Dashtebayaz, M., Sulin, A., Ryabova, T., Sankina, I., Farahnak, M., Nazeri, R., 2021. Energy, exergoeconomic and environmental optimisation of a cascade refrigeration system using different low GWP refrigerants. J. Environ. Chem. Eng. 9, 106473 https://doi.org/10.1016/J.JECE.2021.106473.

Di Nicola, G., Giuliani, G., Polonara, F., Stryjek, R., 2005. Blends of carbon dioxide and HFCs as working fluids for the low-temperature circuit in cascade refrigerating systems. Int. J. Refrig. 28, 130–140. https://doi.org/10.1016/J.IJREFRIG.2004.06.014.

Faugeroux, D., 2016. Ultra-low temperature freezer performance and energy use tests stirling ultracold SU78UE Eppendorf Cryocube 570h thermo fisher TSX600.

Granryd, E., Ekroth, I., Lundqvist, P., Melinder, Å., Palm, B., Rohlin, P., 2011. Refrigerating engineering. Department of Energy Technology, Division of Applied Thermodynamics and Refrigeration. Royal Institute of Technology, KTH, Stockolm (Sweden).

Halon, T., Gil, B., Zajaczkowski, B., 2022. Comparative investigation of low-GWP binary and ternary blends as potential replacements of HFC refrigerants for air conditioning systems. Appl. Therm. Eng. 210, 118354 https://doi.org/10.1016/j.applthermaleng.2022.118354.

Kauffeld, M., Maurath, T., Germanus, J., Askar, E., 2020. N2O/CO2-mixtures as refrigerants for temperatures below -50°C. Int. J. Refrig. 117, 316–327. https://doi.org/10.1016/J.IJREFRIG.2020.04.026.

Lemmon, E.W., Bell, I.H., Huber, M.I., McLinden, M.O., 2018. NIST standard reference database 23: reference fluid thermodynamic and transport properties – REFPROP, version 10.0. NIST.

Linteris, G.T., Bell, I.H., McLinden, M.O., 2019. An empirical model for refrigerant flammability based on molecular structure and thermodynamics. Int. J. Refrig. 104, 144–150. https://doi.org/10.1016/j.ijrefrig.2019.05.006.

Logesh, K., Baskar, S., Md Azeemudeen, M., Reddy, B.P., Jayanth, G.V.S.S., 2019. Analysis of cascade vapour refrigeration system with various refrigerants. Mater. Today: Proceed. 18, 4659–4664. https://doi.org/10.1016/J.MATPR.2019.07.450.

Massuchetto, L.H.P., Nascimento, R.B.C.do, de Carvalho, S.M.R., de Araújo, H.V., d'Angelo, J.V.H., 2019. Thermodynamic performance evaluation of a cascade refrigeration system with mixed refrigerants: R744/R1270, R744/R717 and R744/RE170. Int. J. Refrig. 106, 201–212. https://doi.org/10.1016/J.IJREFRIG.2019.07.005.

McLinden, M.O., Radermacher, R., 1987. Methods for comparing the performance of pure and mixed refrigerants in the vapour compression cycle. Int. J. Refrig. 318–325.

Mota-Babiloni, A., Mastani Joybari, M., Navarro-Esbrí, J., Mateu-Royo, C., Barragán-Cervera, Á., Amat-Albuixech, M., Molés, F., 2020a. Ultralow-temperature refrigeration systems: configurations and refrigerants to reduce the environmental impact. Int. J. Refrig. 111, 147–158. https://doi.org/10.1016/J.IJREFRIG.2019.11.016.

Mota-Babiloni, A., Mastani Joybari, M., Navarro-Esbrí, J., Mateu-Royo, C., Barragán-Cervera, Á., Amat-Albuixech, M., Molés, F., 2020b. Ultralow-temperature refrigeration systems: configurations and refrigerants to reduce the environmental impact. Int. J. Refrig. 111, 147–158. https://doi.org/10.1016/J.IJREFRIG.2019.11.016.

Qin, Y., Li, N., Zhang, H., Jin, B., Liu, B., 2022. Experimental characterisation of an innovative refrigeration system coupled with Linde-Hampson cycle and auto-cascade cycle for multi-stage refrigeration temperature applications. Energy 240, 122498. https://doi.org/10.1016/J.ENERGY.2021.122498.

Qin, Y., Li, N., Zhang, H., Liu, B., 2021a. Energy and exergy analysis of a Linde-Hampson refrigeration system using R170, R41 and R1132a as low-GWP refrigerant blend components to replace R23. Energy 229, 120645. https://doi.org/10.1016/J.ENERGY.2021.120645.

Qin, Y., Li, N., Zhang, H., Liu, B., 2021b. Thermodynamic performance of a modified −150°C refrigeration system coupled with Linde-Hampson and three-stage auto-cascade using low-GWP refrigerants. Energy Conversion and Manag. 236, 114093 https://doi.org/10.1016/J.ENCONMAN.2021.114093.

Ramírez-Hernández, H.G., Morales-Fuentes, A., Sánchez-Cruz, F.A., Méndez-Díaz, S., García-Lara, H.D., Martínez-Martínez, S., 2022. Experimental study on the operating characteristics of a display refrigerator phasing out R134a to R1234ze(E) and its binary blends. Int. J. Refrig. 138, 1–12. https://doi.org/10.1016/j.ijrefrig.2022.03.004.

Rodriguez-Criado, J.C., Expósito-Carrillo, J.A., Pérez, B.P., Dominguez-Muñoz, F., 2021. Experimental performance analysis of a packaged R290 refrigeration unit retrofitted with R170 for ultra-low temperature freezing. Int. J. Refrig. https://doi.org/10.1016/J.IJREFRIG.2021.11.015.

Rodríguez-Jara, E.Á., Sánchez-de-la-Flor, F.J., Expósito-Carrillo, J.A., Salmerón-Lissén, J.M., 2022. Thermodynamic analysis of auto-cascade refrigeration cycles, with and without ejector, for ultra low temperature freezing using a mixture of refrigerants R600a and R1150. Appl. Therm. Eng. 200, 117598 https://doi.org/10.1016/J.APPLTHERMALENG.2021.117598.

Sivakumar, M., Somasundaram, P., 2014. Exergy and energy analysis of three stage auto refrigerating cascade system using Zeotropic mixture for sustainable development. Energy Conversion and Manag. 84, 589–596. https://doi.org/10.1016/J.ENCONMAN.2014.04.076.

Sobieraj, M., 2021. Development of novel wet sublimation cascade refrigeration system with binary mixtures of R744/R32 and R744/R290. Appl. Therm. Eng. 196, 117336 https://doi.org/10.1016/J.APPLTHERMALENG.2021.117336.

Sobieraj, M., Rosiński, M., 2019. Experimental study of the heat transfer in R744/R600a mixtures below the R744 triple point temperature. Int. J. Refrig. 103, 243–252. https://doi.org/10.1016/J.IJREFRIG.2019.03.038.

Song, Y., Wang, H., Cao, F., 2021. Principal effective factors on the dynamic pull-down performance of a zeotropic mixture based ultra-low temperature freezer. Appl. Therm. Eng. 183, 116070 https://doi.org/10.1016/J.APPLTHERMALENG.2020.116070.

Sun, Z., Liang, Y., Liu, S., Ji, W., Zang, R., Liang, R., Guo, Z., 2016. Comparative analysis of thermodynamic performance of a cascade refrigeration system for refrigerant couples R41/R404A and R23/R404A. Appl. Energy 184, 19–25. https://doi.org/10.1016/J.APENERGY.2016.10.014.

Sun, Z., Wang, Q., Dai, B., Wang, M., Xie, Z., 2019a. Options of low global warming potential refrigerant group for a three-stage cascade refrigeration system. Int. J. Refrig. 100, 471–483. https://doi.org/10.1016/J.IJREFRIG.2018.12.019.

Sun, Z., Wang, Q., Xie, Z., Liu, S., Su, D., Cui, Q., 2019b. Energy and exergy analysis of low GWP refrigerants in cascade refrigeration system. Energy 170, 1170–1180. https://doi.org/10.1016/J.ENERGY.2018.12.055.

The MathWorks Inc, 2019. MATLAB R2019a.

Udroiu, C.-.M., Mota-Babiloni, A., Navarro-Esbrí, J., 2022. Advanced two-stage cascade configurations for energy-efficient –80°C refrigeration. Energy Conversion and Manag. 267, 115907 https://doi.org/10.1016/j.enconman.2022.115907.

Walid Faruque, M., Hafiz Nabil, M., Raihan Uddin, M., Monjurul Ehsan, M., Salehin, S., 2022. Thermodynamic assessment of a triple cascade refrigeration system utilising hydrocarbon refrigerants for ultra-low temperature applications. Energy Conversion and Management X 14, 100207. https://doi.org/10.1016/j.ecmx.2022.100207.

Wang, H., Song, Y., Cao, F., 2020. Experimental investigation on the pull-down performance of a -80°C ultra-low temperature freezer. Int. J. Refrig. 119, 1–10. https://doi.org/10.1016/J.IJREFRIG.2020.04.030.