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Thermodynamic evaluation of CO_2 for ultra-low temperature refrigeration

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ABSTRACT

Carbon dioxide (CO_2, R744) is the only refrigerant in the safest class by the ASHRAE 34 Standard in the group of natural refrigerants, with zero ozone depletion potential and a global warming potential of 1. It has been recently proposed for commercial refrigeration and heat pumps. Ultra-low temperature (ULT) refrigeration considers two-stage cascades with hydrofluorocarbon synthetic refrigerants (R404A/R23 high and low-temperature stages, HTS and LTS, respectively) and, lately, hydrocarbons (R290/R170). This paper examines the potential of R744 in ULT refrigeration cascade configurations in combination with other promising refrigerants. R744 is proposed in the medium temperature stage (MTS) of a three-stage cascade and the HTS of a two-stage transcritical operation (subcritical and transcritical with and without ejector, respectively). The operational and energy performance are compared with standard two- and three-stage ULT refrigeration cascades. Also, the cycles have been optimized, changing the main parameters as cascade heat changer temperatures or gas cooler pressure to maximize COP. This optimization and all the models have been made with Python, extracting the thermodynamic properties of REFPROP. The results show that in the HTS, the coefficient of performance (COP) is 39 % lower than the same two-stage cascade cycle with R290. In the MTS of a three-stage cascade, COP is 10 % lower than the same three-stage cascade cycle with R290. The ejector increases the COP by 38 % in the transcritical HTS, but remains below the hydrocarbon two-stage cascade. The choice of alternative refrigerants in the other stages does not significantly vary the COP results. Technological advancements in single subcritical and transcritical R744 configurations should be transferred to ULT refrigeration cascades to increase competitiveness and take advantage of its environmental and safety characteristics.

Introduction

Refrigeration consists of cooling a particular ambient or product to a specific temperature, usually employing systems based on vapour compression cycles. Below –50 °C, it is considered ultra-low temperature (ULT) refrigeration and cascade or auto-cascade cycles are typically considered [1]. Liu et al. [2] studied pull-down, stable operation performance, temperature drop, air temperature fluctuation, and power consumption under controlled ambient conditions of a ULT refrigeration unit using an R290 and R170 cascade (high-temperature stage, HTS, and low-temperature stage, LTS, respectively). Wang et al. [3] assessed the pull-down performances at 26 °C ambient temperature. The superheating degree was the main factor influencing LTS compressor discharge temperature during the rapid cooling phase. In contrast, the evaporation and condensation pressures influenced the stable cooling phase more. Rodriguez-Criado et al. [4] retrofitted a standard R290 packaged unit to develop a ULT indirect cascade system with R170 in the LTS. The operational behaviour was adequate, exhibiting a COP (Coefficient of Performance) from 0.6 to 1.6 and acceptable discharge temperature for cold room temperatures between –80 °C and –65 °C. Li et al. [5] modified a ULT cascade refrigeration unit to introduce an ejector. The ejector pressure lift ratio increased when the ambient temperature rose, while the entrainment ratio was insensitive. The energy consumption with the ejector was 4.8 % lower than the baseline at 25 °C ambient temperature.

Excessive temperature lifts between condensation and evaporation temperatures (as it happens in ULT refrigeration) require cascade configurations and it can be based on two, three or more stages. In ULT refrigeration, the energy performance of current cycles is deficient due to the high-temperature lift [6] and solutions must be found.

Udroiu et al. [6] proposed cascade cycles based on six different

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Nomenclature

$\dot{m}$	Refrigerant mass flow rate (kg s^{-1})
$\dot{Q}$	Heat transfer (kW)
h	Enthalpy (kJ kg^{-1})
P	Pressure (MPa)
$\dot{W}$	Power consumption (kW)
u	Velocity (m/s)
S	Entropy (kJ kg^{-1} K^{-1})
X	Vapour title (-)
m	Refrigerant mass charge (kg)
L	Annual percentual refrigerant leakage (-)
n	Lifetime of a refrigeration installation (years)
E	Annual energy consumption (kWh)

Greek symbols

η	Efficiency (-)
μ	Entrainment ratio (-)
α	Percentual recycling refrigerant at the end of the lifetime (-)
β	Carbon emission factor (kgCO_2 kWh^{-1})

Subscripts

ref	Refrigerant
evap	Evaporator
in	Inlet
out	Outlet
hot	Hot fluid of heat exchanger
cold	Cold fluid of heat exchanger
is	Isentropic
suc	Suction
disc	Discharge
comp	Compressor
sec	Secondary fluid line
prim	Primary fluid line
nozzle	Nozzle of ejector
mixing	Mixing chamber of ejector
dif	Diffuser of ejector
anual	Per year

Abbreviations

ULT	Ultra-low temperature
COP	Coefficient of performance
LTS	Low-temperature stage
MTS	Medium-temperature stage
HTS	High-temperature stage
HT	High-temperature
LT	Low-temperature
HFC	Hydrofluorocarbon
GWP	IPCC AR5 100-yr global warming potential
CR	Compression ratio
TEWI	Total equivalent warming impact

configurations: single-stage with and without internal heat exchanger, vapour injection, liquid injection, and parallel compression with and without economizer (42 different combinations) and R290 (propane) and R170 (ethane) for HTS and LTS, respectively. A vapour injection in the LTS can increase the COP to 0.89 (40 % higher than standard conurations). An optimal intermediate cascade temperature, depending on the configuration was proved optimal. Udroiu et al. [7] extended the configurations to include ejectors. An ejector in both stages increases COP by 21% than the standard configurations. Also, R290/R170 outperforms R23 and R507A by 13.6 % in the same cycle. The proposal emits less than half of the equivalent CO_2 than current cycles.

The refrigeration sector focuses on the fourth generation of refrigerants, where the low global warming potential (GWP) must be the lowest possible. The GWP index indicates how much heat can be captured by a greenhouse gas relative to CO_2 (designed with R744 when used as a refrigerant). Hydrofluorocarbon (HFC) refrigerants like R134a present significantly higher GWP values than CO_2, 1430. As it is happening for standard refrigeration and heating applications, low GWP refrigerants must be found for the ULT refrigeration sector, for which there is a lack of available information [8]. Most ULT units use refrigerants like R23 or R508B in the LTS, with GWP in the order of 14000.

The following presents a theoretical analysis of low GWP refrigerants for ULT. Sun et al. [9] compared R404A/R41 with R404A/R23. Under the same condition, the theoretical analysis indicates that R404A/R41 is the most convenient pair. Aktemur and Ozturk [10] considered an internal heat exchanger using R41 with R601, R602A and cyclopentane. The refrigerant pairs ranked by thermodynamic performance are R601/R41, cyclopentane/R41, and R602A/R41, respectively. Kilicarsan and Hosoz [11] simulated the energy and irreversibility efficiencies employing R23 with R152a, R290, R507, R134a, R717 and R404A for a −40 °C refrigerated space temperature and 27 °C ambient temperature. R717/R23 has the highest COP and lowest irreversibility except for the limited range of polytropic efficiency (50–60 %) and ΔT (13 K–16 K). Deymi-Dashtebayaz et al. [12] proposed six low GWP refrigerant pairs, R161, R1234yf, and R1234ze(E), combined with R41 and R744, at 40 °C condensation temperature and −30 °C evaporation temperature. R161/R41 and R1234ze(E)/R41 are optimal refrigerant pairs with the highest COP, exergy efficiency and lowest total cost rate. Mota-Babiloni et al. [13] highlighted the potential of R170, R1150, R290 and R744 in mixtures to reduce the GWP value and increase COP. A3 refrigerants are required to obtain the maximum COP.

Three-stage cascade refrigeration configurations are considered to reach lower evaporation temperatures. Gupta [14 15] made one of the first proposals for three-stage cascades to reach temperatures down to −60 °C. Sun et al. [16] recommended R717/R41/R1150, R152a/R41/R1150, R161/R41/R1150, R717/R170/R1150, R152a/R170/R1150 and R161/R170/R1150 for from −120 °C to −80 °C evaporation temperatures. Walid Faruque et al. [17] conducted a parametric analysis with four hydrocarbons in a 10 kW system. The m-Xylene/Heptane/1-butene (HTS, MTS (medium temperature stage), LTS) combination offers the maximum performance at −120 °C and −110 °C evaporation temperature, and m-Xylene/Heptane/1-butene at −100 °C and −90 °C. Johnson et al. [18] proposed methane, ethylene and propylene reaching −163 °C with a three-stage cascade. Qin et al. [19] proposed utilizing an intermediate pressure regulator obtaining an improvement between 32.93 % and 15.38 %. In other vapour compression systems applications, Badra et al. [20] combined R1243zf, R1224yd(Z), and R1233zd (E) in multilevel high-temperature heat pumps to operate up to 160 °C.

R744 is A1 in the ASHRAE Std 34 classification, meaning it does not propagate a flame and is included among the lower toxicity fluids (when tested as per the standard). This is a substantial benefit compared with other ultralow GWP fluids, such as R290 or R170, which are A3, highly flammable refrigerants. Besides, it is chlorine and fluorine-free, and its acquisition cost is relatively lower than the rest of synthetic refrigerants. Also, R744 has a high latent heat of vaporization and high volumetric refrigeration capacity, allowing a smaller compressor [21] and reducing the unit's initial cost. These characteristics make R744 a refrigerant interesting for next-generation refrigeration and heat pump applications [22].

R744 is being massively introduced in large commercial refrigeration systems to comply with European regulations [23]. R744 has also been proposed in the LTS of standard temperature cascade refrigeration. Several investigations were published with promising results. In a designed initially R134a/R744 system, Blanco-Ojeda et al. [24] obtained 46 %, 42.1 % and 22.5 % less carbon footprint emissions for R436A, R1234yf and R513A, when compared with the R134a baseline. Zhang et al. [25] investigated an R134a/R744 cascade air source heat pump system. The system can supply water above 50 °C with COP up to 3.07 and 1.60 when the ambient air temperature is −5 °C and −45 °C, respectively. Regarding ULT refrigeration, Yamaguchi et al. [26] experimentally studied the dry ice blockage in a CO_2-solid-gas-flow-based ULT cascade refrigeration system. Dry ice sedimentation occurs after the expansion valve in low flow velocity, at low condensation temperature and heating power input. At a higher mass flow rate, blockage occurs in the expansion tubes. At suitable operating conditions, −62 °C can be achieved continuously and stably. Only the work of Tan and Erişen [27] proposed R744 in the HTS together with R404A and R410A; and R1150, R170, and R23 in the LTS. The lowest overall COP values were obtained with R744 in the HTS because the cascade was not optimized. The LTS refrigerant selected also influenced the resulting cycle design.

R744 has a relatively low critical point, 30.98 °C. Over this temperature, the refrigerant is in the transcritical region. In such a case, the conventional condenser is replaced by a gas cooler [28] while the evaporator remains with a similar function to conventional cycles [29]. Llopis et al. [30] compared R404A two-stage with cascades and R744 transcritical and subcritical cycles. They concluded that R744 transcritical/subcritical has the worst energy performance. Because of that, modifications were proposed to improve the cycle efficiency in recent years. In transcritical operation, Gullo et al. [31] highlighted that ejector-based "R744 only" is promising but needs to overcome a few drawbacks, high cost, complexity and maintenance operations. Mature supermarket applications can be applied to small applications. Song et al. [22] highlighted the benefits of transcritical R744 technology in terms of adaptability to broad working conditions, energy consumption, equivalent carbon content and environmental benefits. The future development of transcritical R744, including smart systems and expansion work recovery techniques such as expander, ejector, and vortex tube, were carefully analyzed.

Several configuration technological advancements are proposed to increase its energy performance and reduce total greenhouse gas emissions, such as including ejectors, which are commercially available today [32]. Expósito-Carrillo et al. [33] presented an optimization methodology for a two-stage R744 refrigeration unit with and without an ejector. The ejector configuration showed up to a 13% COP increase and proved that the operating region of the control variables is limited due to the use of the ejector. Yang et al. [34] studied the performance of a transcritical R744 refrigeration cycle with an ejector, reaching a 2.3 times higher COP than without an ejector.

Literature reveals that R744 use is being extended in different refrigeration and heat pump applications. However, this natural refrigerant must also be considered for ultra-low temperature refrigeration cycles to reduce the final carbon footprint and increase the safety of ULT cascade configurations. Currently, R744 has not been considered for this application, so assessing its feasibility is important for its introduction in future commercial units optimized for the highest energy efficiency. Because of that, this work proposes transcritical and subcritical R744 cycles for ULT cascades to study R744 viability. The R744 transcritical cycle is considered in the HTS while using R170 in the LTS. Moreover, using an ejector in the R744 transcritical cycle is also studied to increase overall COP. Regarding the subcritical R744 cycle, it is placed in the MTS of a three-stage cascade, with R170 and R290 in LTS and HTS, respectively. These configurations have been optimized to maximize COP. All configurations are compared with a reference cycle, the R290/R170 two-stage cascade. R23 and R170 in LTS are combined with the transcritical R744 cycle. On the other hand, R290, R600a, R1234yf and R717 are compared in HTS for the three-stage cascade configuration.

Materials and methods

This section presents the configurations this article is based on and the strategy used, from the assumptions to the final model.

Configurations

Two cycles have been comprehensively assessed, a transcritical R744 (HTS) two-stage cascade and a subcritical R744 (MTS) three-stage cascade. Also, the improvement of the R744 transcritical (HTS) two-stage cascade with an ejector. These configurations are represented in Fig. 1, including the main components necessary for the operation. Also, Fig. 2 shows the temperature-entropy diagrams of each cycle.

Refrigerants

If not specified the contrary, the thermodynamic approach considers the natural refrigerants R744, R290 and R170, whose characteristics are shown in Table 1. In subsequent sections, other refrigerants like R23, R1234yf, R600a and R717 are simulated for comparison with the proposed solution based on natural refrigerants. The database for calculations with these refrigerants is from REFPROP 10.0 and NIST Standard Reference database 23. Python 3.10 has been used for the computational model.

Equations

The gas cooler exit temperature is set at 35 °C to simulate controlled or standard ambient conditions. Regarding evaporation temperature, –80 °C has been set for simulating ULT refrigeration. The simulation comprises medium-capacity refrigeration conditions, with 10 kW as the cooling capacity. Also, the evaporator superheating degree is 5 K, and the condenser subcooling degree is 2 K.

The equations of the main components are the same in all cycles. The mass flow rate ($\dot{m}_{ref}$) of LTS can be calculated using the proposed cooling capacity ($\dot{Q}_{evap}$) and the enthalpy difference in the evaporator ($h_{evap,\,in} - h_{evap,out}$), Eq. (1).

$$\dot{m}_{ref} = \frac{\dot{Q}_{evap}}{\left(h_{evap,\,in} - h_{evap,out}\right)} \tag{1}$$

The mass flow rate of the other stages (HTS and MTS, when necessary) can be calculated by a heat balance at the cascade heat exchanger between the cold and the hot sides, Eq. (2). A difference of 5 K between cold and hot fluid has been considered.

$$\dot{m}_{hot}\ \left(h_{hot,in} - h_{hot,out}\right) = \dot{m}_{cold}\ \left(h_{hot,out} - h_{hot,in}\right) \tag{2}$$

The total power consumption ($\dot{W}$) is the sum of each compressor's power consumption ($\dot{W}_{comp}$), Eq. (3).

$$\dot{W} = \sum \dot{W}_{comp} \tag{3}$$

Using the mass flow rate and the enthalpy difference in the compressor ($h_{disc} - h_{suc}$), the compressor power consumption can be calculated, Eq. (4).

$$\dot{W}_{comp} = \dot{m}_{ref}\ \left(h_{disc} - h_{suc}\right) \tag{4}$$

The compressor isentropic efficiency (η_{is}) is used for the compressor discharge enthalpy (h_{disc}) through the compressor suction enthalpy (h_{suc}) and the isentropic compressor discharge enthalpy ($h_{is,disc}$), Eq. (5).

$$h_{disc} = \frac{h_{is,disc} - h_{suc}}{\eta_{is}} + h_{suc} \tag{5}$$

The isentropic efficiency depends on the compressor considered.

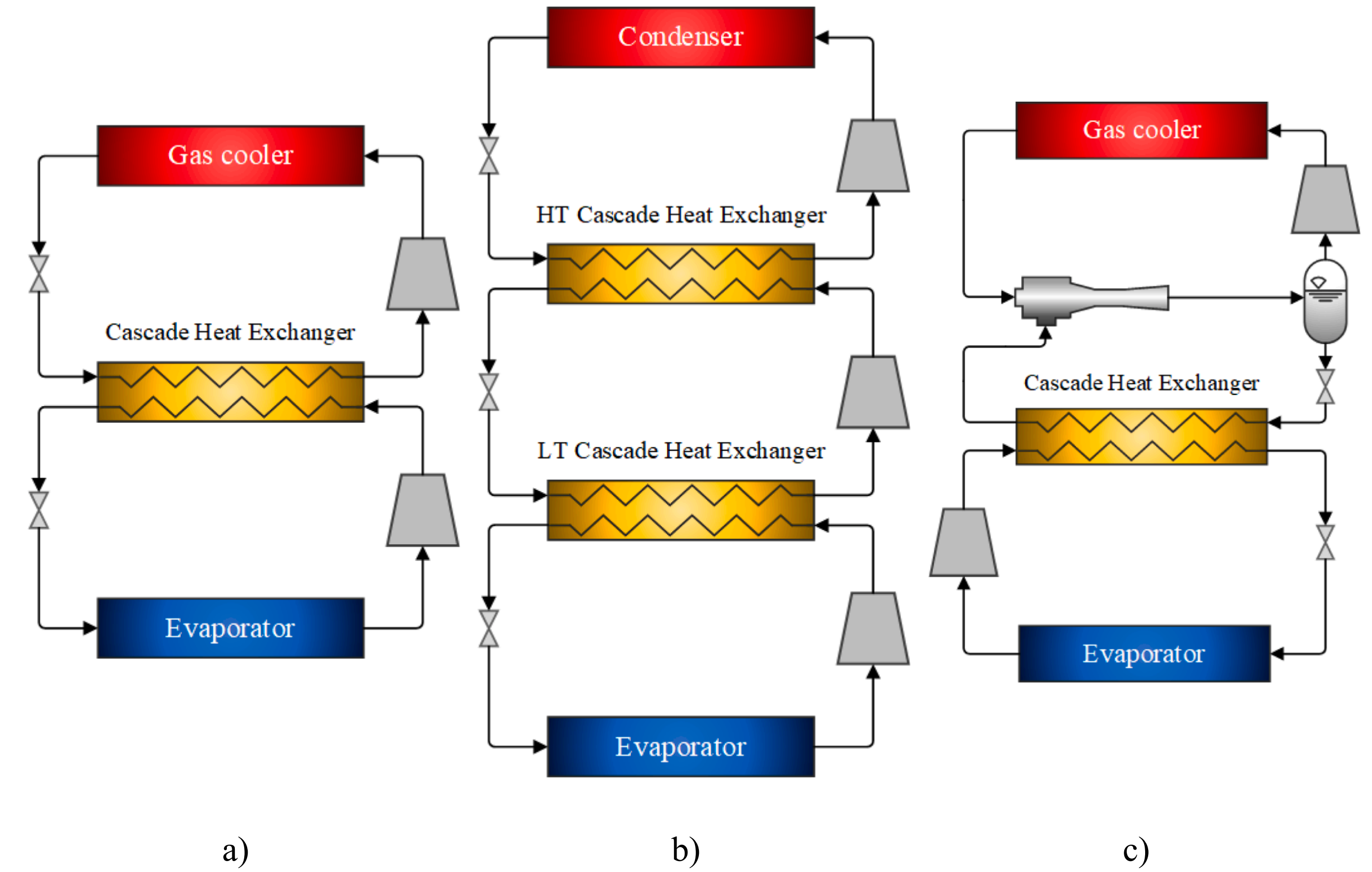

Fig. 1. Schematic diagrams of ULT configurations: a) Transcritical two-stage cascade, b) three-stage cascade, and c) transcritical two-stage cascade with ejector.

Criado et al. [4] demonstrated that R290 and R170 isentropic efficiency simulation could be based on the same equation, so the correlation of Udroiu et al. has been used [6 7] using the compression ratio (*CR*) as the input, Eq. (6).

$$\eta_{is} = -0.0669\ CR^4 + 1.6971\ CR^3 - 15.569\ CR^2 + 57.082\ CR - 0.9003 \quad (6)$$

For R744, another correlation is developed using compressor manufacturer data, Eq. (7). Data for developing an isentropic compressor equation was obtained from a commercial scroll compressor with an 8.04 m^3/h displacement and a 14.54 kW nominal cooling capacity. Moreover, the main information about the steady state conditions used for the equation is shown in Table 2.

$$\eta_{is,R744} = -1.3092\ CR^4 + 18.983\ CR^3 - 102.74\ CR^2 + 241.45\ CR - 144.01 \quad (7)$$

Both equations are expressed in terms of compression ratio, which is the ratio of the discharge and suction pressures (P_{disc} and P_{suc}, respectively), Eq. (8).

$$CR = \frac{P_{disc}}{P_{suc}} \quad (8)$$

Fig. 3 shows the validation of the proposed equation for R744 isentropic compressor efficiency using manufacturer data.

Finally, the overall coefficient of performance (*COP*), which quantifies the energy performance of the configuration, is the ratio between the LTS cooling capacity and the total power consumption, Eq. (9).

$$COP = \frac{\dot{Q}_{evap}}{\dot{W}} \quad (9)$$

The cycles have been optimized to maximize the COP. For that purpose, the COP has been determined with the variation of gas cooler pressure and intermediate cascade temperature in the transcritical cascade. Additionally, the gas cooler pressure has been set over the critical point (74 bar) to the maximum pressure that can reach the cycle considering the compression ratio. The intermediate cascade temperature has been set from evaporation to condensation temperatures with a 20 K difference (above and below, respectively). In the three-stage cascade simulations, the COP has been calculated by varying both intermediate cascade temperatures from evaporation to condensation temperature with a 20 K difference. Moreover, the difference between intermediate cascade temperatures must be above 20 K. In all cases, the maximum compression ratio for R744 has been set to 5 because of R744 commercial compressors' limitations. Similarly, the maximum compression ratio using R290 and R170 has been set to 10.

Ejector

The ejector is a fluid dynamic device used in refrigeration to improve the cycle energy efficiency. It uses a high-pressure fluid to compress a low-pressure fluid, effectively boosting the pressure of the low-pressure fluid. It allows the compressor to work more efficiently by reducing the pressure ratio.

Ejector model is based on an existing proposal [7], validated with literature data. A constant-pressure mixing model is adopted, meaning the mixed flows are unified without pressure variation. The ejector efficiencies are constant at 0.8, nozzle, mixing chamber and diffuser have been considered 0.8.

Determining the entrainment ratio (μ), the ratio of the secondary and primary fluid mass flow rates ($\dot{m}_{sec}$ and $\dot{m}_{prim}$, respectively), is the main factor to be considered in the ejector model. The initial value is assumed to be adjusted in subsequent calculations using Eq. (10).

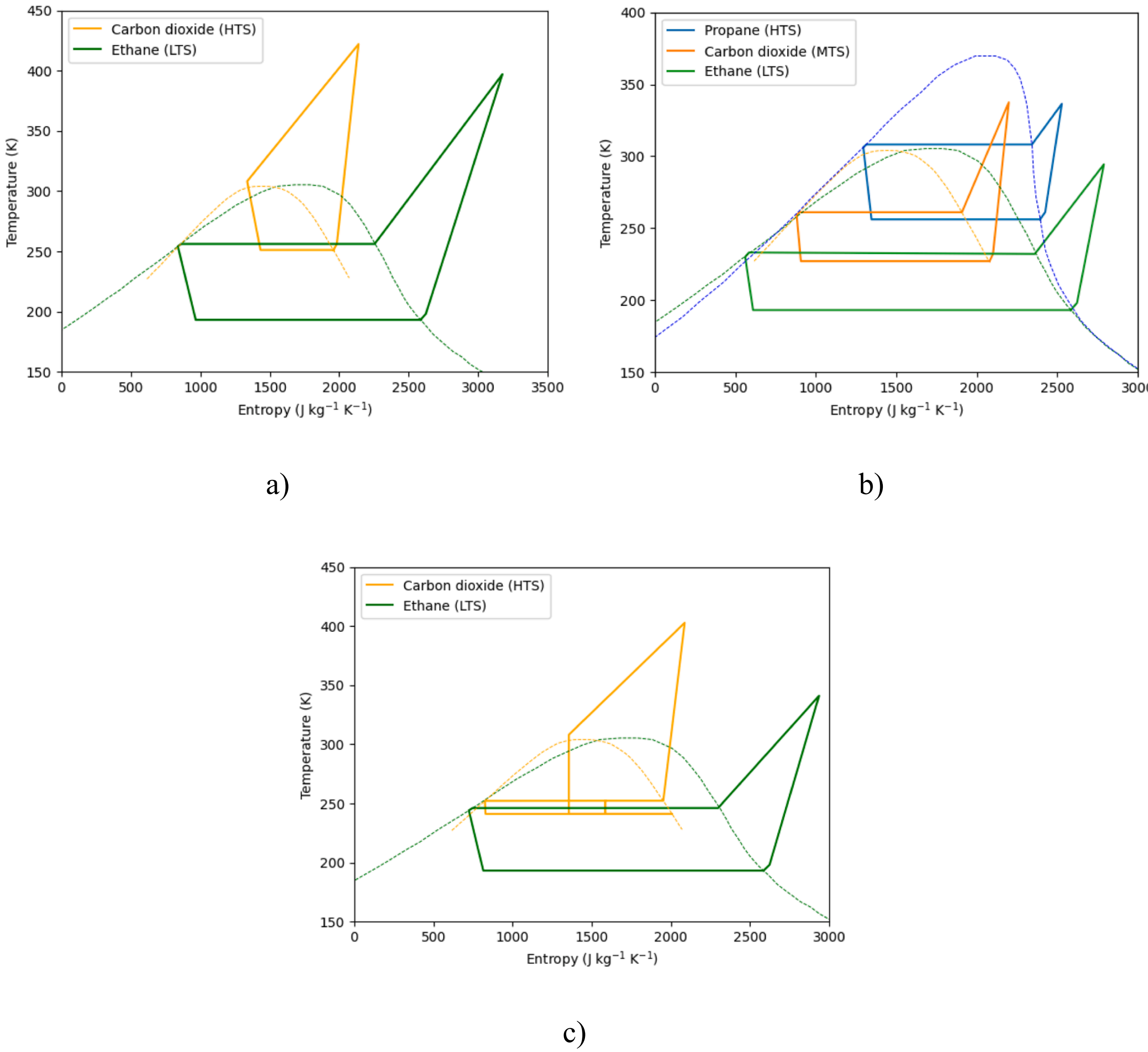

Fig. 2. Ts diagrams of ULT configurations: a) Transcritical two-stage cascade, b) three-stage cascade, and c) transcritical two-stage cascade with ejector.

Table 1
Refrigerants' main properties.

Refrigerant designation	R290	R170	R744
Stage	High	Low	High
CAS Number	74-98-6	74-84-0	124–38-9
Linear Formula	CH3CH2CH3	CH3CH3	CO2
Molecular weight	44.1 g mol^{-1}	30.1 g mol^{-1}	44.0 g mol^{-1}
Boiling point	−42.1 °C	−88.6 °C	−78.46 °C
Critical temperature	96.55 °C	32.17 °C	30.98 °C
Critical pressure	4.25 MPa	4.87 MPa	7.38 MPa
Latent heat of vaporisation	400.8 kJ kg^{-1} [a]	477.7 kJ kg^{-1} [b]	282.44 kJ kg^{-1} [a]
Vapour density	5.50 kg m^{-3} [a]	3.09 kg m^{-3} [b]	51.7 kg m^{-3} [a]
ASHRAE Std 34 classification	A3	A3	A1
OEL	1000 ppm	1000 ppm	5000 ppm
Refrigerant Concentration Limit	5300 ppm	7000 ppm	40000 ppm
$GWP_{100\text{-}yr}$	<1	<1	1

[a] at −20 °C, [b] at −80 °C.

Table 2
Operational conditions for the compressor data.

Parameter	Value
Refrigerant	R744
Evaporation temperature	From –50 to –25 °C
Condensation temperature	From –20 to 10 °C
Frequency	50 Hz
Superheating degree	5 K

$$\mu = \frac{\dot{m}_{sec}}{\dot{m}_{prim}} \tag{10}$$

The ejector model is based on the enthalpy and velocity of its different sections. Initially, the outlet velocity of each nozzle (u_{nozzle}) can be determined by using the inlet enthalpy (h_{in}) and the outlet isentropic enthalpy ($h_{out,is}$) with the nozzle efficiency (η_{nozzle}), as shown in Eq. (11)

$$u_{nozzle} = \sqrt{2\,\eta_{nozzle}\left(h_{in} - h_{out,is}\right)} \tag{11}$$

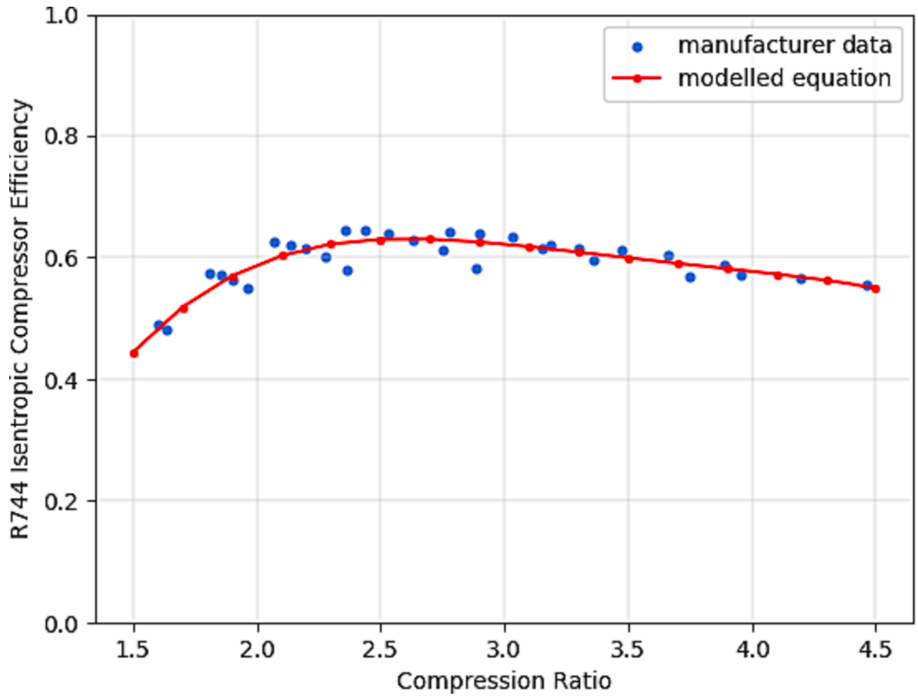

Fig. 3. Validation of R744 isentropic compressor efficiency correlation.

The operational conditions and thermodynamic stages can be calculated in the mixing chamber using energy and momentum conservation equations, as shown in Eq. (12) and (13).

$$u_{mixing} = \left(u_{nozzle,prim}\frac{1}{1+\mu} + u_{nozzle,sec}\frac{1}{1+\mu}\sqrt{\eta_{mixing}}\right) \quad (12)$$

$$h_{mixing} = \frac{1}{1+\mu}\left(h_{out,is,prim} + \frac{{u_{nozzle,prim}}^2}{2}\right) + \frac{\mu}{1+\mu}\left(\left(h_{out,is,sec} + \frac{{u_{nozzle,sec}}^2}{2}\right) - \frac{{u_{mixing}}^2}{2}\right) \quad (13)$$

To determine the diffuser enthalpy (h_{out}) and the diffuser outlet pressure (P_{out}), Eq. (14) to (17) are utilized, which involve the ideal specific enthalpy ($h_{out,is}$), ideal entropy ($s_{out,is}$), and the outlet conditions of the mixing process (h_{mixing}, u_{mixing}, P_{mixing}). It is assumed that the pressure in the mixing process remains constant.

$$h_{out} = h_{mixing} + \frac{{u_{mixing}}^2}{2} \quad (14)$$

$$P_{out} = f(h_{out,is}, s_{out,is}) \quad (15)$$

$$h_{out,is} = \eta_{dif}\left(h_{out} - h_{mixing}\right) + h_{mixing} \quad (16)$$

$$s_{out,is} = f(h_{mixing}, P_{mixing}) \quad (17)$$

Ultimately, the initial value is adjusted by iteratively performing calculations until the condition based on the vapour quality at the ejector outlet (x_{out}), as illustrated in Eq. (18), is satisfied. This process is repeated until convergence is achieved. The vapour quality at the ejector outlet is the function of pressure and enthalpy, Eq. (19).

$$\frac{1}{1+\mu} = x_{out} \quad (18)$$

$$x_{out} = f(P_{out}, h_{out}) \quad (19)$$

For a better understanding, Fig. 4 shows all calculation models.

TEWI

Reducing greenhouse gas emissions is a priority of the refrigeration and heat pump sector. The Total Equivalent Warming Impact (TEWI) metric assesses the environmental impact of these systems considering two types of greenhouse gas emissions: direct and indirect emissions, Eq. (20).

$$TEWI = GWP\ m\ L_{anual}\ n + GWP\ m\ (1-\alpha) + (E_{anual}\ \beta\ n) \quad (20)$$

The GWP parameter varies depending on the specific refrigerant used. Direct emissions from accidental leakages are calculated with the amount of refrigerant (m), the annual refrigerant leakage rate (L_{anual}), and the number of years the system operates (n). The second part of the equation concerns the emissions from losses while recycling, also considering the GWP with the amount of refrigerant and the fraction of the refrigerant charge that is recovered and recycled at the end of the system's lifetime ($1-\alpha$). The third part is the indirect emissions regarding the annual energy consumption of the system expressed in kilowatt-hours (E_{anual}). Also, the carbon intensity factor considers (β) the amount of greenhouse gases released when the system generates and absorbs electricity.

A leakage percentage of 5% has been taken into account for the calculation, which is a common assumption in the refrigeration industry. Additionally, a lifetime period of 15 years has been considered, which is the expected lifetime of a typical refrigeration system. After the end of the lifetime period, a recycling rate of 85% has been proposed based on data from the International Institute of Refrigeration [35]. Regarding the emission factor, this proposal assumes the emission factor of the European Union, which has been set at 0.229 $kgCO_{2e}\,kWh^{-1}$ [36]. Table 3 shows all the assumptions of TEWI parameters.

The TEWI metric for a cascade cycle involves the accumulation of the stages (MTS if required), Eq. (21).

$$TEWI = TEWI_{HTS} + TEWI_{LTS} + TEWI_{MTS} \quad (21)$$

The TEWI equation provides a single metric for quantifying the environmental impact of a refrigeration system over its entire life cycle.

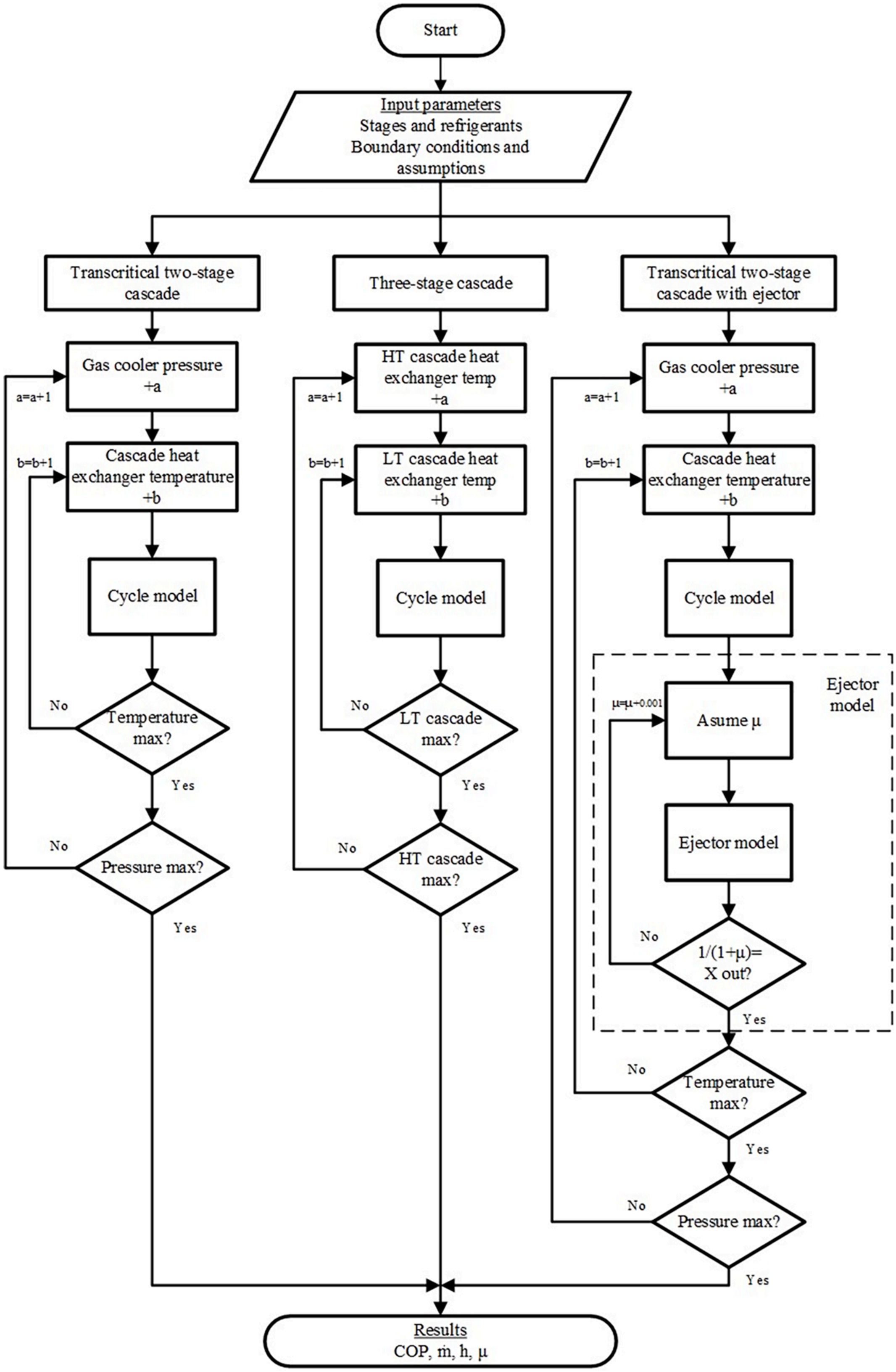

Fig. 4. Methods flow diagram.

This allows the comparison of different refrigerant options and system designs and can be used to identify opportunities for improvement in efficiency and environmental performance.

Results and discussion

This section presents the main results of the R744 configurations, focusing on the performance of the cycles and the main parameters of

Table 3
TEWI parameters.

Parameter	Value
L_{anual} (%)	5
n (years)	15
α(%)	85
β($kgCO_{2e}$ kWh^{-1})	0.229

interest: entrainment ratio, mass flow rate, enthalpic lift, COP, volumetric cooling capacity, intermediate cascade temperature, and equivalent carbon dioxide.

Transcritical R744 two-stage cascade

The first configuration analyzed is the two-stage cascade using transcritical R744 in the HTS. Fig. 5 shows the overall cascade COP results depending on the HTS gas cooler pressure and the HTS cascade heat exchanger temperature.

As said before, the cycle has been optimized, changing the gas cooler pressure from 74 bar to the maximum it can reach and the cascade heat exchanger from –50 °C to 5 °C. The compressors also have a maximum compression ratio that can reach because of their mechanical characteristics. Because of that, it has been set the condition that the maximum compression ratio for R744 must be 5 and for R170 must be 10. That condition improves the data integrity and reliability of the results. An example of that can be seen in cascade heat exchanger temperatures. The minimum temperature is –28 °C, and the maximum is –22 °C, temperatures above or under those involve compression ratios that standard compressors cannot reach. Also, the combination of particular gas cooler pressures and cascade temperatures causes a similar issue, the white colour in Fig. 5.

The highest COP reached is 0.34, below the one obtained with the same cycle but with R290 as HTS subcritical refrigerant (0.56). This lower COP is principally because of the characteristics of transcritical R744. First, the compressor efficiency of the stage with R744 is lower than the same stage with R290 with the same conditions because of the high-pressure lift of R744, which causes an increase in energy consumption in the compressor. On the other hand, a more significant parameter that causes the low performance is the low enthalpy lift in the stage evaporator. The difference between the two refrigerants is approximately double. The substantial enthalpy lift causes the mass flow rate necessary for the cooling capacity to be higher, and consequently, that mass flow rate causes a more considerable energy consumption in the compressor. The results show that the optimum pressure is around 86 bar for gas cooler pressure.

Three-stage cascade with subcritical R744 MTS

For subcritical conditions, a three-stage cascade is proposed using the R744 in the MTS. Fig. 6 can be seen as the graph of the results, the maximum value of the colorbar is 0.77 only for a better comparison with Fig. 7.

The performance of a three-stage cascade with R744 in MTS is significantly higher than that of a two-stage cascade with transcritical

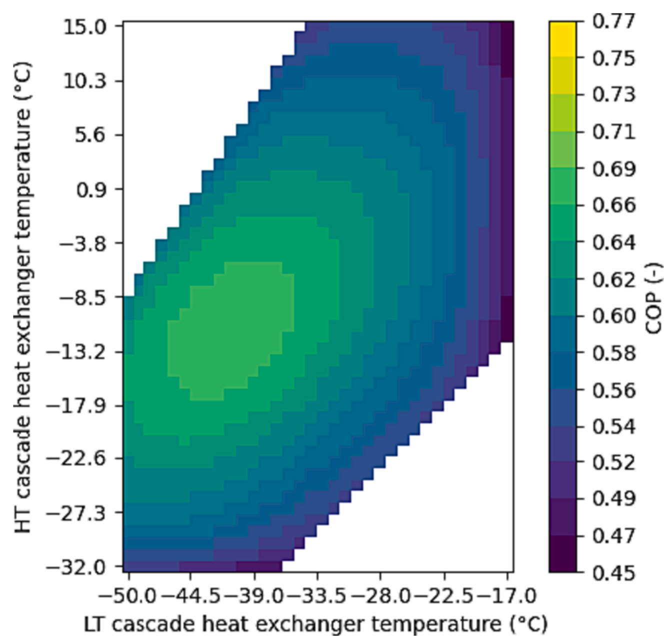

Fig. 6. Three-stage cascade COP.

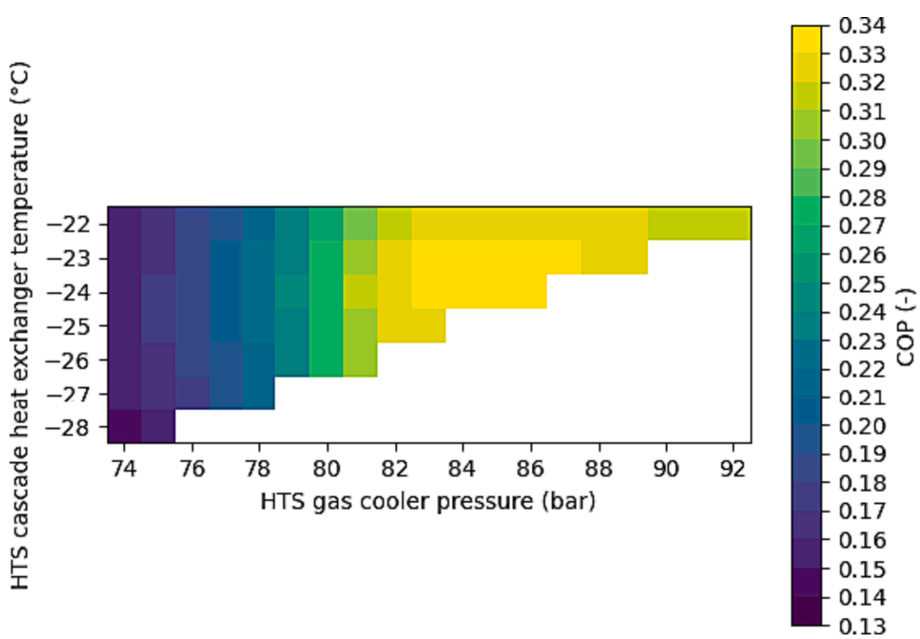

Fig. 5. Transcritical two-stage cascade COP.

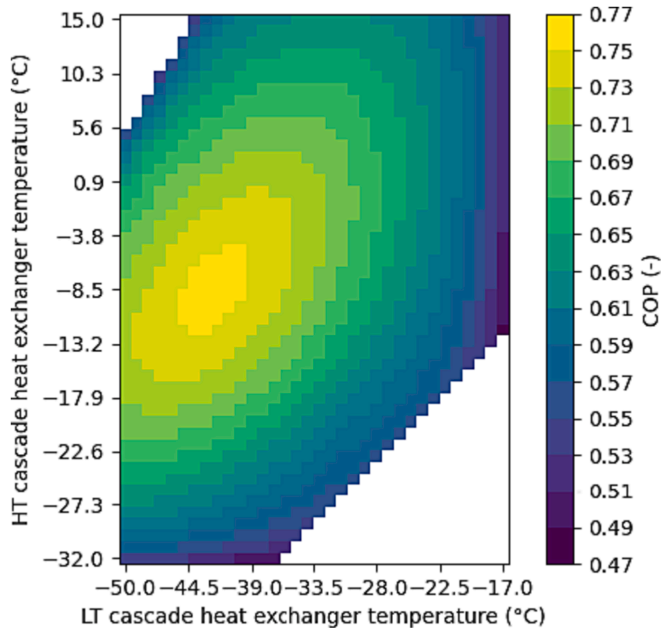

Fig. 7. Three-stage cascade with R290 COP.

R744. In this case, the maximum COP reached is 0.68, higher than the transcritical R744 two-stage cascade and also with R290. This higher COP is because of a higher compressor efficiency, having three stages instead of two. The thermal lift of each one is lower. Because of that, the compression rate can be lower, and consequently, the compressor efficiency is beneficial for the ULT observed temperature lift (–80 evaporation temperature to 35 °C gas cooler temperature). Besides, the problem with mass flow rate because of the evaporator's enthalpy lift, explained in the previous section, disappears.

Regarding the cascade heat exchanger temperatures, the maximum COP is observed at around –40 °C in the low-temperature (LT) cascade heat exchanger and around –10 °C in the high-temperature (HT) heat exchanger. That means the R744 stage only covers 30 °C, 26 % of the total temperature lift, R170 covers 40 °C, and R290 covers 45 °C.

Also, it is interesting to compare the three-stage cascade with subcritical R744 MTS with another refrigerant in the same stage, as R290, Fig. 7. As can be seen, the maximum COP using R290 in the MTS is 0.76, 11.7 % higher. Also, the R290 has a higher range of operational temperatures because of the lower compression ratio than the R744. That allows a movement of optimal cascade heat exchanger temperatures, in this case, the optimum temperatures are in the HT cascade heat exchanger at –9 °C and –44 °C in the LT one.

Transcritical R744 two-stage cascade with ejector in the HTC

The ejector is a component that can improve the cycle efficiency due to increasing compressor suction pressure, so the ejector can help reduce the compressor's work. Also, increasing the suction pressure causes a reduction in compression ratio, which is crucial in R744 cycles due to the considerable outlet pressures and the low compression ratio of R744 compressors. Fig. 8 shows efficiency considering gas cooler pressure and the cascade heat exchanger temperature.

In this case, the optimum cascade heat exchanger temperature is around –33 °C with a maximum COP of 0.47. This maximum COP is 38 % higher than the same cycle without ejector (0.34) presented in section *3.1* but is 16 % lower than the two-stage cascade with R290 and R170 (0.56).

As explained in section 2.4, the entrainment ratio is the most critical parameter in the ejector model and is adjusted by iteratively performing calculations until the condition is satisfied. Because of that, there is a different entrainment ratio at every cascade heat exchanger and every gas cooler pressure. Fig. 9 shows the different entrainment ratio values.

As can be seen, the entrainment ratio has a pattern in which the higher the pressure of the gas cooler and the higher the evaporation temperature of HTS, the higher it is. The HTS gas cooler is also the pressure of primary fluid in the ejector, and the HTS evaporator temperature is the stage of the secondary fluid, which can be expressed in terms of pressure.

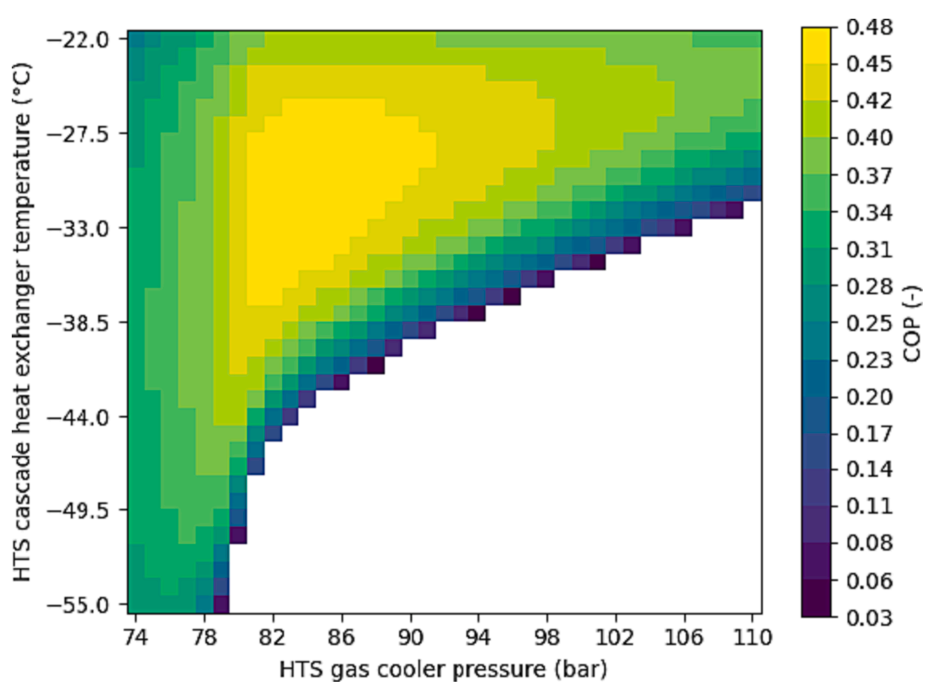

Fig. 8. Two-stage cascade with transcritical ejector COP.

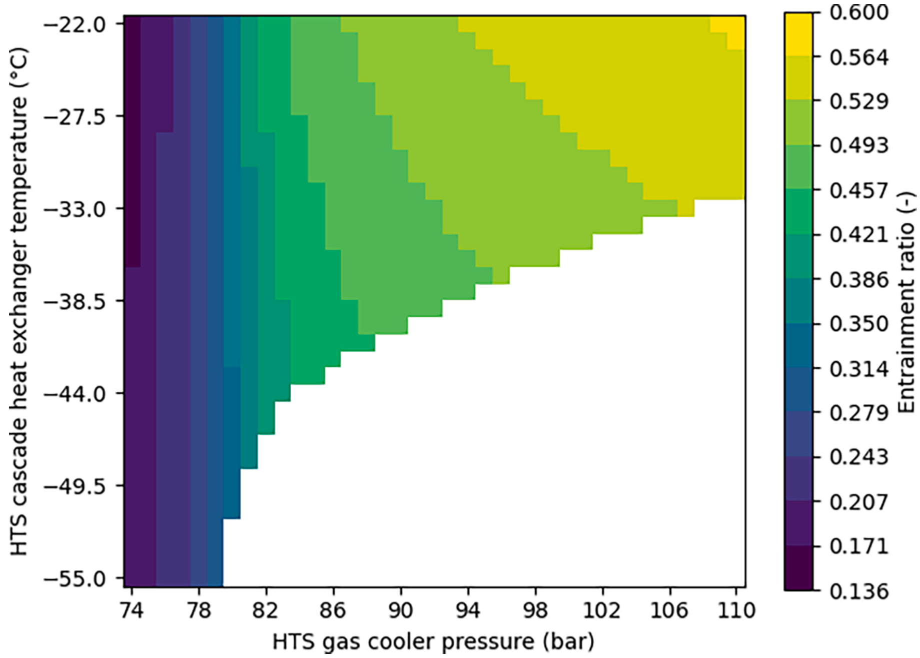

Fig. 9. Ejector entrainment ratio values.

Comparison of refrigerants for the rest of the stages

The selection of refrigerants is an important aspect in the design of refrigeration systems, as it can significantly impact their energy efficiency, environmental impact, or safety. This section will compare different refrigerants for two- and three-stage cascade refrigeration systems.

In the two-stage cascade, the use of R170 and R23 as refrigerants in LTS is compared, while maintaining R744 as the refrigerant in the HTS. In the three-stage cascade, the use of R290, R600a, R1234yf, and R717 as refrigerants in the high-temperature stage is compared, while maintaining R744 as the refrigerant in the medium temperature stage and R170 in the low-temperature stage. Additionally, compressor efficiency will be constant at 0.7, as the compression rate of the refrigerants is significantly different and using an individual equation for each would distort the comparative analysis. Fig. 10 shows the COP comparison between R23 and R170 in LTS transcritical R744 cascade. Fig. 11 compares R290, R600a, R717 and R1234yf in the HTS three-stage cascade.

As can be seen, R170 allows a greater operational range because of the higher compression ratio of R23. Even having expanded the maximum compression ratio to 15 in this case, R170 still allows similar or higher COP. The maximum COP of R170 is 0.54 at a cascade heat exchanger temperature of –10 °C and pressure of 90 bar. In the case of R23, the maximum COP is 0.53 at a cascade heat exchanger temperature of –14 °C and a pressure of 91 bar. Considering the significant difference in GWP of the two refrigerants presented, R170 is a better option for LTS.

For the HTS, the COP is also similar for the four refrigerants, around 0.74 (R290, 0.742; R600a, 0.754; R717, 0.755; R1234yf, 0.729). The results show that with the proper optimization, the refrigerant selection in a single temperature stage does not significantly influence the overall COP of the HTS of the three-stage cascade.

Gas cooler temperatures comparative

The gas cooler outlet temperature is important and depends on the environmental temperatures. Because of that, a comparison between

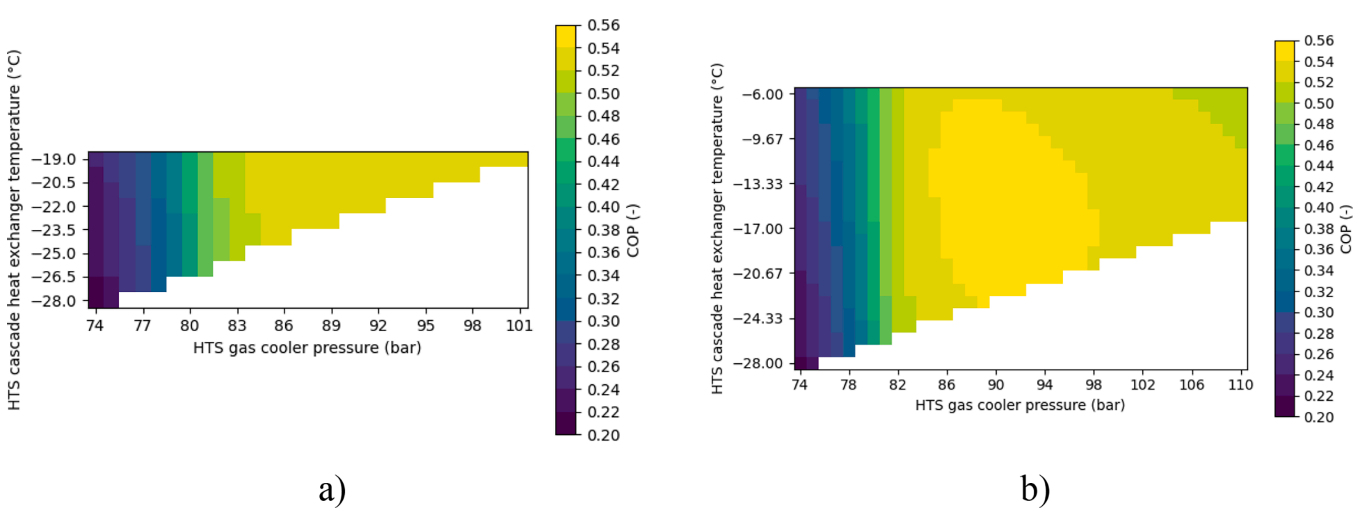

Fig. 10. Comparative refrigerants in LTS transcritical cascade: a) R23 and b) R170.

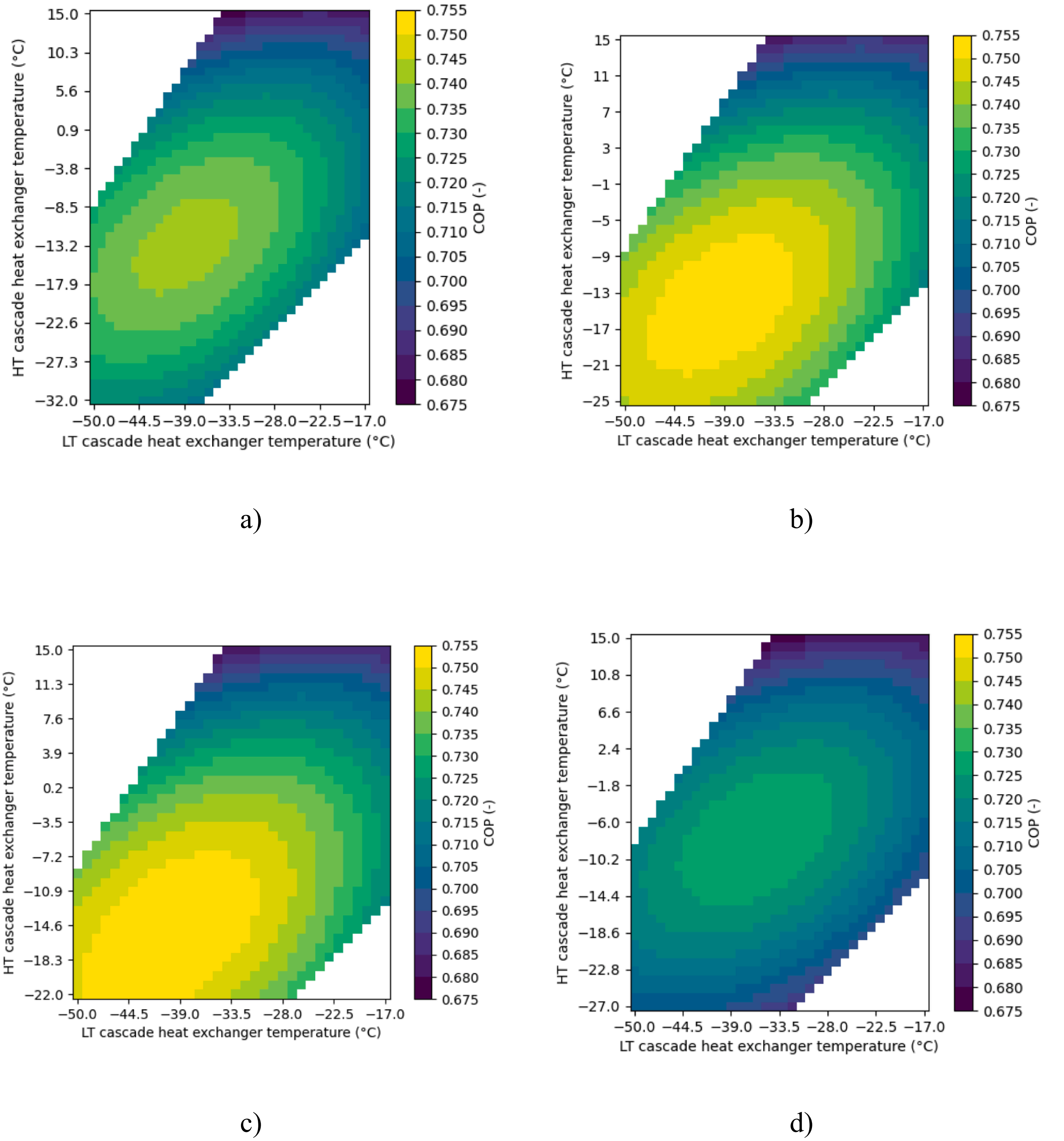

Fig. 11. Comparative refrigerants in HTS three-stage cascade: a) R290, b) R600a, c) R717 and d) R1234yf.

different gas cooler temperatures is important to analyze in this cycle. Fig. 12 shows the COP of different gas cooler temperatures depending on the gas cooler pressure. Also, the cascade heat exchanger temperature has been optimized.

The initial analysis shows that each temperature exhibits an optimal pressure for gas cooling, wherein the magnitude of this optimal pressure increases with the gas cooler temperature. Notably, the coefficient of performance (COP) varies considerably between the critical pressure and the optimal pressure, depending on the temperature of the gas cooler. However, once this optimum pressure threshold is surpassed, performance differentials stabilize, diminishing the magnitude of variations.

Carbon footprint assessment

TEWI analysis can identify opportunities for reducing emissions through improving energy efficiency, reducing refrigerant leakage, and utilizing alternative refrigerants with lower GWP.

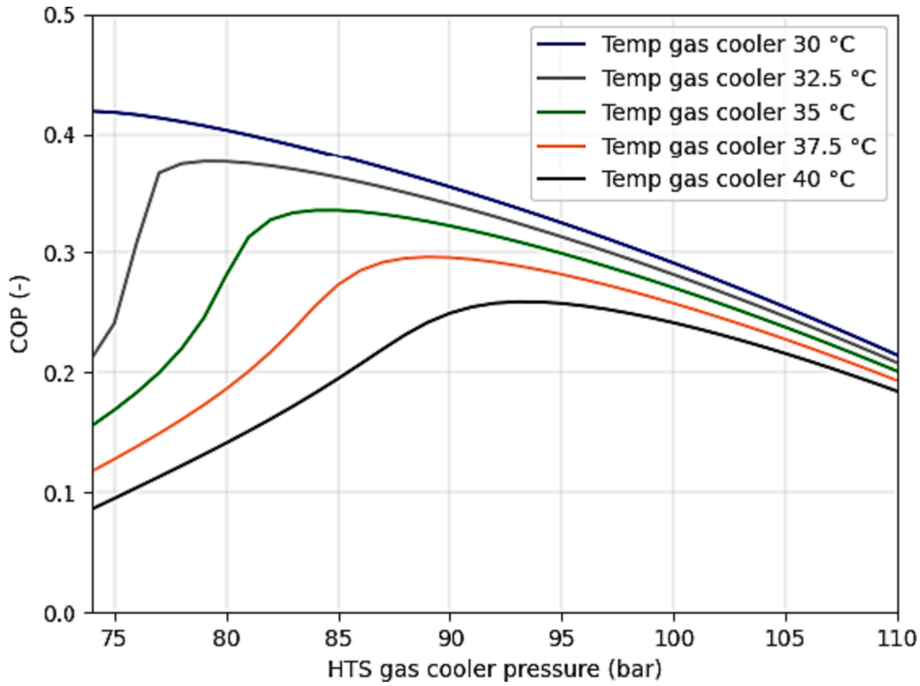

Fig. 12. Gas cooler temperature comparative.

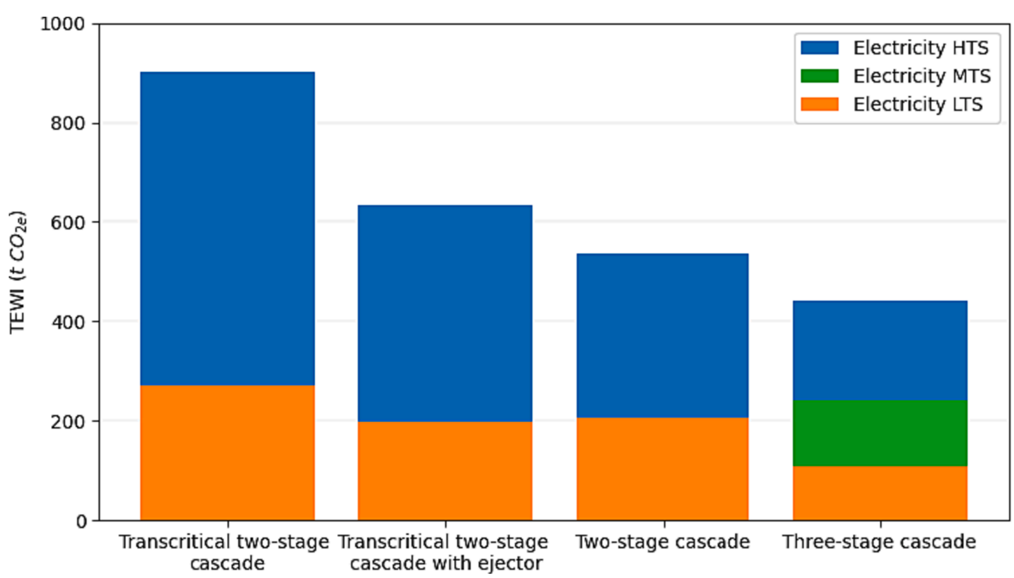

Fig. 13. Carbon footprint results for proposed configurations.

Fig. 13 shows the graph of TEWI results classified by configuration and source of carbon emissions according to the stage. TEWI values have been determined with the three cycles proposed and one two-stage cascade with R290 and R170. The results indicate that the transcritical R744 two-stage cascade cycle has the highest environmental impact with 902.3 tCO_{2e}, followed by the transcritical R744 two-stage cascade with ejector (634.5 tCO_{2e}). The simple two-stage cascade is in third place (536.8 tCO_{2e}) and then the three-stage cascade with subcritical R744 with 441.631 tCO_{2e}. Analysing further the results, the most significant contributor to the TEWI in all three cycles is the electricity consumption of the HTS, even in the case of a three-stage cascade. The leakage and recycling contributions are practically insignificant because of low GWP refrigerants. For example, the leaking carbon emissions for the transcritical cycle are for HTS 3.9 $kgCO_{2e}$, the recycling carbon emissions are 0.78 $kgCO_{2e}$, and the electricity emissions in the same stage are 630,668 $kgCO_{2e}$.

Conclusion

In this study, the performance of various refrigeration cycles with CO_2 (R744) was compared in terms of their coefficient of performance (COP) and environmental impact using TEWI analysis. R744 in transcritical and subcritical operation for two- and three-stage cascades are simulated and optimised to maximize the overall COP. Several refrigerants are compared for the other stages and the influence of the ejector in the transcritical cycle is assessed.

The results indicate that the performance of all the calculated R744 transcritical cycles is inferior compared to a common two-stage cascade ethane-propane cycle, with a 39 % lower COP (0.34 for transcritical R744 two-stage cascade and 0.56 for two-stage cascade R290/R170 cycle). Adding an ejector improves the performance of the transcritical R744 cycle by 38 % (COP of 0.47) compared to the same cycle without an ejector. However, its performance remains inferior to the reference cycle. On the other hand, the three-stage cascade cycle with subcritical R744 in the MTS (COP of 0.68) improves the performance of a two-stage propane-ethane cascade cycle, but the same cycle using R290 instead of R744 offers an improvement of 11.7 % in COP (0.76).

When comparing refrigerants in the other stages, the results show that their performances are quite similar. However, the enormous difference in GWP in the low-temperature stage makes ethane (R170) clearly preferable if flammable refrigerants can be used. The differences are insignificant in the high-temperature stage, making GWP a reference value.

Finally, when comparing the equivalent carbon emissions (TEWI), the three-stage cascade cycle with propane (R290), CO_2 (R744), and ethane (R170) offers a lower TEWI than the other cycles. Also, transcritical R744 two-stage cascade offers the highest TEWI due to the lower performance. R744 is in the safest class of the ASHRAE 34 Standard and is an important aspect to consider if natural refrigerants are prioritized in future environmental regulations. Current technology advancement in commercial refrigeration is required in ULT cascade configurations to increase efficiency and reduce carbon emissions from electricity production.

This study aims to approximate the behaviour of CO_2 in ultra-low temperature cycles at a theoretical level. CO_2 compressors are designed for specific applications used today. To give the most accurate results possible, the behaviour of the compressor has been modelled according to the data offered by the manufacturers. In addition, limitations have been added such as the compression rate according to the limitations of the market models.

CRediT authorship contribution statement

Cosmin-Mihai Udroiu: Conceptualization, Software, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **Adrián Mota-Babiloni:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Supervision, Project administration. **Pau Giménez-Prades:** Software, Investigation, Resources, Data curation, Visualization. **Ángel Barragán-Cervera:** Conceptualization, Investigation, Writing – review & editing. **Joaquín Navarro-Esbrí:** Conceptualization, Formal analysis, Investigation, Writing – review & editing, Funding acquisition.

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.

Data availability

Data will be made available on request.

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References

[1] C. M. Udroiu, A. Mota-Babiloni, C. Espinós-Estévez, and J. Navarro-Esbrí, “Energy-Efficient Technologies for Ultra-Low Temperature Refrigeration,” pp. 309–322, 2022, doi: 10.1007/978-981-16-9101-0_22.
[2] Liu Z, Bai M, Tan H, Ling Y, Cao Z. Experimental test on the performance of a −80 °C cascade refrigeration unit using refrigerants R290–R170 for COVID-19 vaccines storage. J Build Eng Jan. 2023;63:105537. https://doi.org/10.1016/J.JOBE.2022.105537.
[3] Wang H, Song Y, Cao F. Experimental investigation on the pull-down performance of a -80°C ultra-low temperature freezer. Int J Refrig Nov. 2020;119:1–10. https://doi.org/10.1016/J.IJREFRIG.2020.04.030.
[4] Rodriguez-Criado JC, Expósito-Carrillo JA, Peris Pérez B, Dominguez-Muñoz F. Experimental performance analysis of a packaged R290 refrigeration unit retrofitted with R170 for ultra-low temperature freezing. Int J Refrig 2022;134:105–14.
[5] Li Y, Yu J, Qin H, Sheng Z, Wang Q. An experimental investigation on a modified cascade refrigeration system with an ejector. Int J Refrig Dec. 2018;96:63–9. https://doi.org/10.1016/j.ijrefrig.2018.09.015.
[6] Udroiu C-M, Mota-Babiloni A, Navarro-Esbrí J. Advanced two-stage cascade configurations for energy-efficient –80 °C refrigeration. Energy Convers Manag 2022. https://doi.org/10.1016/J.ENCONMAN.2022.115907.
[7] Udroiu C-M, Mota-Babiloni A, Giménez-Prades P, Barragán-Cervera Á, Navarro-Esbrí J. Two-stage cascade configurations based on ejectors for ultra-low temperature refrigeration with natural refrigerants. Int J Thermofluids 2023;17:100287.
[8] Mota-Babiloni A, Mastani Joybari M, Navarro-Esbrí J, Mateu-Royo C, Barragán-Cervera Á, Amat-Albuixech M, et al. Ultralow-temperature refrigeration systems: Configurations and refrigerants to reduce the environmental impact. Int J Refrig 2020;111:147–58.
[9] Sun Z, Liang Y, Liu S, Ji W, Zang R, Liang R, et al. Comparative analysis of thermodynamic performance of a cascade refrigeration system for refrigerant couples R41/R404A and R23/R404A. Appl Energy 2016;184:19–25.
[10] Aktemur C, Ozturk IT. Energy and Exergy Analysis of a Subcritical Cascade Refrigeration System with Internal Heat Exchangers Using Environmentally Friendly Refrigerants. J Energy Resour Technol Trans ASME 2021;143(10):Oct. https://doi.org/10.1115/1.4049271/1091953.
[11] Kilicarslan A, Hosoz M. Energy and irreversibility analysis of a cascade refrigeration system for various refrigerant couples. Energy Convers Manag Dec. 2010;51(12):2947–54. https://doi.org/10.1016/j.enconman.2010.06.037.
[12] Deymi-Dashtebayaz M, Sulin A, Ryabova T, Sankina I, Farahnak M, Nazeri R. Energy, exergoeconomic and environmental optimization of a cascade refrigeration system using different low GWP refrigerants. J Environ Chem Eng Dec. 2021;9(6):106473. https://doi.org/10.1016/J.JECE.2021.106473.
[13] Mota-Babiloni A, Fernández-Moreno A, Giménez-Prades P, Udroiu C-M, Navarro-Esbrí J. Ternary refrigerant blends for Ultra-Low Temperature Refrigeration. Int J Refrig 2023;148:108–16.
[14] Gupta VK. Numerical optimization of multi-stage cascaded refrigeration-heat pump system. J Heat Recover Syst Jan. 1985;5(4):305–19. https://doi.org/10.1016/0198-7593(85)90005-0.
[15] Gupta VK. Optimum design of multi-stage cascaded refrigeration-heat pump system. J Heat Recover Syst Jan. 1986;6(3):235–44. https://doi.org/10.1016/0198-7593(86)90007-X.
[16] Sun Z, Wang Q, Dai B, Wang M, Xie Z. Options of low Global Warming Potential refrigerant group for a three-stage cascade refrigeration system. Int J Refrig Apr. 2019;100:471–83. https://doi.org/10.1016/J.IJREFRIG.2018.12.019.
[17] Walid Faruque Md, Hafiz Nabil M, Raihan Uddin M, Monjurul Ehsan M, Salehin S. Thermodynamic assessment of a triple cascade refrigeration system utilizing hydrocarbon refrigerants for ultra-low temperature applications. Energy Convers Manage: X 2022;14:100207.
[18] Johnson N, Baltrusaitis J, Luyben WL. Design and control of a cryogenic multi-stage compression refrigeration process. Chem Eng Res Des May 2017;121:360–7. https://doi.org/10.1016/j.cherd.2017.03.018.
[19] Qin Y, Li N, Zhang H, Liu B. Study on the performance of an energy-efficient three-stage auto-cascade refrigeration system enhanced with a pressure regulator. Energy Nov. 2022;258:124872. https://doi.org/10.1016/J.ENERGY.2022.124872.
[20] B. B. E., M. B. A., G. M., and K. R.,. Theoretical study of a multilevel heat pump for multi-source heating. 6th IIR Conf Thermophys Prop Transf Process Refrig 2021. https://doi.org/10.18462/IIR.TPTPR.2021.2206.
[21] Ma Y, Liu Z, Tian H. A review of transcritical carbon dioxide heat pump and refrigeration cycles. Energy Jun. 2013;55:156–72. https://doi.org/10.1016/J.ENERGY.2013.03.030.
[22] Song Y, Cui C, Yin X, Cao F. Advanced development and application of transcritical CO2 refrigeration and heat pump technology—A review. Energy Rep Nov. 2022;8:7840–69. https://doi.org/10.1016/J.EGYR.2022.05.233.
[23] Hart M, Austin W, Acha S, Le Brun N, Markides CN, Shah N. A roadmap investment strategy to reduce carbon intensive refrigerants in the food retail industry. J Clean Prod Dec. 2020;275:123039. https://doi.org/10.1016/J.JCLEPRO.2020.123039.
[24] Blanco Ojeda FWA, Almeida Queiroz MV, Marcucci Pico DF, dos Reis Parise JA, Bandarra Filho EP. Experimental evaluation of low-GWP refrigerants R513A, R1234yf and R436A as alternatives for R134a in a cascade refrigeration cycle with R744. Int J Refrig 2022;144:175–87.
[25] Zhang H, Geng X, Shao S, Si C, Wang Z. Performance analysis of a R134a/CO2 cascade heat pump in severe cold regions of China. Energy Jan. 2022;239:122651. https://doi.org/10.1016/J.ENERGY.2021.122651.

[26] Yamaguchi H, Niu XD, Sekimoto K, Neks P. Investigation of dry ice blockage in an ultra-low temperature cascade refrigeration system using CO2 as a working fluid. Int J Refrig Mar. 2011;34(2):466–75. https://doi.org/10.1016/J.IJREFRIG.2010.11.001.

[27] H. Tan and A. Erişen, "Novel Design and Thermodynamic Analyses of Cascade Refrigeration System at Ultra-Low Temperature," *Int. J. Thermodyn.*, vol. 25, no. 1, pp. 142–150, Mar. 2022, doi: 10.5541/IJOT.1017282.

[28] Yu B, Yang J, Wang D, Shi J, Chen J. An updated review of recent advances on modified technologies in transcritical CO2 refrigeration cycle. Energy Dec. 2019; 189:116147. https://doi.org/10.1016/J.ENERGY.2019.116147.

[29] Groll EA, Kim JH. Review article: Review of recent advances toward transcritical co2 Cycle Technology. HVAC R Res 2007;13(3):499–520. https://doi.org/10.1080/10789669.2007.10390968.

[30] Llopis R, Sánchez D, Sanz-Kock C, Cabello R, Torrella E. Energy and environmental comparison of two-stage solutions for commercial refrigeration at low temperature: Fluids and systems. Appl Energy Jan. 2015;138:133–42. https://doi.org/10.1016/j.apenergy.2014.10.069.

[31] Gullo P, Hafner A, Banasiak K. Transcritical R744 refrigeration systems for supermarket applications: Current status and future perspectives. Int J Refrig Sep. 2018;93:269–310. https://doi.org/10.1016/J.IJREFRIG.2018.07.001.

[32] Pardiñas Á, Selvnes H, Banasiak K, Hafner A. Next generation of ejector-supported R744 booster systems for commercial refrigeration at all climates. Int J Refrig Apr. 2023;148:168–78. https://doi.org/10.1016/J.IJREFRIG.2022.10.027.

[33] Expósito-Carrillo JA, Sánchez-de La Flor FJ, Perís-Pérez B, Salmerón-Lissén JM. Thermodynamic analysis of the optimal operating conditions for a two-stage CO2 refrigeration unit in warm climates with and without ejector. Appl Therm Eng Feb. 2021;185:116284. https://doi.org/10.1016/J.APPLTHERMALENG.2020.116284.

[34] Yang D, Zhu J, Wang N, Xie J. Experimental study on the performance of transcritical CO2 two-stage compression refrigeration system with and without an ejector at low temperatures. Int J Refrig Nov. 2022. https://doi.org/10.1016/J.IJREFRIG.2022.11.019.

[35] "Guideline for Life Cycle Climate Performance," 2016. [Online]. Available: www.iifiir.org.

[36] Greenhouse gas emission intensity of electricity generation in Europe. https://www.eea.europa.eu/ims/greenhouse-gas-emission-intensity-of-1.