

Research Paper

A novel approach for designing efficient and sustainable cooling cycles with low global warming potential refrigerants

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ABSTRACT

With the current legislation on the phase-out of 3rd generation refrigerants, new cooling cycles are expected to operate with 4th generation refrigerants, hence, the need for optimal system performance with these new working fluids. In this study, an innovative optimization approach was applied for the design of cooling cycles with 4th generation refrigerants based on integrating statistical analysis design of experiments (DoE) with molecular modeling using the polar soft-SAFT model. First, a detailed multi-criteria assessment was applied for the selection of 4th generation refrigerants in medium–low temperature applications. Results demonstrated the potentiality of *trans*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(E)) or *cis*-1,2,3,3,3-pentafluoroprop-1-ene (R1225ye(Z)) in terms of environmental, safety, and technical criteria in basic cooling cycles under specific operating conditions. Multi-objective optimization guided using statistical analysis tools were implemented to study potential enhancement in cooling cycle performance using these promising refrigerants in terms of energy and exergy efficiency. This included evaporator and condenser temperature, fluid choice, compression yield, superheating/subcooling degrees, and cycle type. The evaporation and condenser temperature, and the compressor efficiency are shown to monopolize more than three-quarters of the cumulative contribution on system efficiency for those operated with R1234ze(E) in advanced liquid-to-suction line heat exchangers (LL/SL-IHX). Further optimization through examining the effect of heat transfer phenomena assisted in determining optimal operating conditions for new systems operating with low GWP refrigerants, instilling annual cost savings of \$1.59 K and reduction in CO₂ emissions by 1.02 tCO₂-eq compared to the baseline system.

1. Introduction

The year 2022 marked the seventh consecutive year with global temperatures above pre-industrial era, with average global surface temperatures reaching 0.89 °C above the 20th century average [1]. The drastic warming patterns culminated in unprecedented heat waves sweeping across both Earth's poles, with temperatures reaching 40°C and 30°C above normal in Antarctic and Arctic areas, respectively [2]. These alarming climate anomalies, among many others, foreshadow with certainty the ranking of 2022 among the 10-warmest recorded years, and the incessant warming trends across the globe.

Expectedly, the warming climate and increasing global temperatures are sufficient drivers for increasing the demand for space cooling (e.g., domestic, industrial, etc.) and product refrigeration, with roughly 2 billion air-conditioning (AC) units in operation around the world in

2020, marking a 56 % increase since 2010. With the expected rise in living standards, population growth, and more frequent and extreme heatwaves, it is projected that the cooling demand will witness an additional 40 % increase by 2030 [3,4]. The rapid expansion of the cooling industry comes at the expense of increased energy consumption, tripling since 1990, accounting for 16 % of global electricity consumption and 1 gigatons (Gt) of CO₂ emissions in 2020, also projected to triple by 2050 [5].

The growth in space cooling and product refrigeration markets are blind spots in the energy and global warming debates on fronts related to (1) choice of refrigerants and their impact on global warming, and (2) energy-related efficiency of cooling cycles [6]. Transitioning towards climate-friendly, energy-efficient, and cost-effective cooling systems would avoid the resulting direct and indirect CO₂ emissions, and positively contribute to the United Nations (UN) Sustainable Development Goals (SDGs) on thermal comfort for sustainable cities (SDG 11) and

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Nomenclature*List of Abbreviations*

AC	Air-Conditioning
AcC	Activated Carbon
ANOVA	Analysis of Variance
AOT	Annual Operating Time
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
BBD	Box-Behnken Designs
BM	Binary Mixtures
CC	Cooling Capacity
CFCs	ChloroFluoroCarbons
CFD	Complete Factorial Designs
Comp	Compressor
Cond	Condenser
COP	Coefficient of Performance
c_p	Specific Liquid Heat Capacity
CSD	Carnahan-Starling-DeSantis
DLT	Discharge Line Temperature
DoE	Design of Experiments
DOF	Degrees of Freedom
DSH	DeSuperHeating
E_a	Energy Consumption
EES	Engineering Equation Solver
EoS	Equation of State
EU	European Union
Evap	Evaporator
FFD	Factional Factorial Design
GHG	GreenHouse Gas
GRA	Grey Relational Analysis
GWP	Global Warming Potential
H	Enthalpy
HCS	HydroCarbons
HCFOs	HydroChloroFluoroOlefins
HFCs	HydroFluoroCarbons
HFOs	HydroFluoroOlefins
HNPP	Half-Normal Probability Plot
ICA	Taguchi's Idle Column Array Method
IG	Ideal Gas
IHX	Internal Heat Exchanger
IS	Isentropic
L	Annual Leakage Rate
LJ	Lennard-Jones
LL/SL-IHX	Liquid Line-Suction Line - Internal Heat Exchanger
LMTD	Logarithmic Mean Temperature Difference
LPG	Liquefied Petroleum Gas
m	Refrigerant Charge Load
m_i	Chain Length
n	AC Lifetime

NBP	Normal Boiling Point
OA	Orthogonal Array
ODP	Ozone Depletion Potential
P_{cond}	Condenser Pressure
P_R	Pressure Ratio
PSR	Polynomial Surface Regression
Q_{cond}	Heat Released by the Condenser
RE	Refrigeration Effect
RSM	Response Surface Methodology
S	Entropy
SAFT	Statistical Associating Fluid Theory
S/N	Signal-to-Noise Ratio
T_0	Dead-State Temperature
TC	Total Cost
TEWI	Total Equivalent Warming Impact
TOPSIS	Technique for Order of Preference by Similarity to Ideal Solution
T_{pp}	Pinch Point Temperature
T_{Sub}	Degree of Subcooling
T_{Super}	Degree of Superheating
TXV	Thermostatic Expansion Valve
UA	Heat Transfer Coefficient
VCC	Volumetric Cooling Capacity
VCRC	Vapor Compression Refrigeration Cycles
x_p	Fraction of Polar Segments

Formulas, Units, and Greek Symbols

ψ_i	Availability or Specific Exergy of Stream i
Φ_{co}	Coil Capacity
η_s	Compressor Isentropic Efficiency
w_{cs}	Compressor Isentropic Work
$\dot{W}$	Compressor Power
w_c	Compressor Real Work
ε_i	Dispersive Energy between Segments
β_i	Effect to the Factor or Interaction i
η_{II}	Exergy Efficiency
μ_i	Experimental Dipole Moment in Vacuum
Q_i	Experimental Quadrupole Moment in Vacuum
ξ_i	Grey Relational Coefficient
γ	Grey Relational Grade
β	Indirect Emission Factor
ε^{IHx}	Intercooler Effectiveness
$\dot{m}$	Mass Flow
$\sum \dot{\chi}_{in}$	Rate of Exergy in the Input
α	Recovery Factor
σ_i	Segment Diameter
η_{th}	Thermal Efficiency
$\sum \dot{\chi}_d$	Total Exergy Destruction Rate
ρ_v	Vapor Density Exiting the Evaporator
ω_i	Weight Factors

increased climate action (SDG 13) [7]. Additionally, this transition indirectly ensures the sustenance of suitable delivery supply chains for perishable products such as food products for ending hunger (SDG 2), and access to medicines and vaccines for healthy lives (SDG 3) [7]. However, these are pending the determination of suitable low GWP refrigerants, alongside enhanced energy efficiency for cooling cycles.

The choice of refrigerant plays a role in the progression of global warming largely due to their atmospheric emissions either through leakage from existing units or charging of new units. For nearly three decades, since the ban on chlorofluorocarbons (CFCs) with the enactment of the Montreal protocol [8], 3rd generation hydrofluorocarbons (HFCs) were the dominant refrigerants of choice deployed in

commercial and residential cooling equipment with 86 % of total HFC consumption, most notably from 1,1,1,2-tetrafluoroethane (R134a) [9]. However, their high potency as greenhouse gases (GHGs) with global warming potentials (GWP) generally in order of 100 – 10000 s can result in 6 – 9 % of total CO₂ emissions by 2050, if left unchecked [10]. The passing of the Kigali's amendment in 2016 [11] and strict European Union (EU) regulations [12] on phasing-out the manufacture and consumption of HFCs with GWP > 150 by 2022, would cumulatively avoid 53 GtCO₂ equivalent emissions during 2020 – 2060 and reduce global temperatures by 0.4 °C; supporting the 1.5°C reduction goal of the Paris Agreement [9]. The realization of these environmental regulations would require the availability of low GWP alternative refrigerants, not

Table 1

Summary of systems, refrigerants, and statistical methodologies applied in the literature, including the type of DoE and outcomes/responses of the studies.

Ref.	System	Fluids	Experimentation	Type of DoE	Responses
[25]	CRS	R744, R404A, R410A, R717, R134a, R510A	Experimental	$L_{27}(3^{10})$ and ANOVA	COP, η_{II}
[26]	VCRC	R600a	EES and Experimental	$L_9(3^4)$ and ANOVA	$COP, \dot{m}, \eta_{II}$
[27]	VCRC-IHX	R600a and R134a	Experimental	$L_8(2^{2.4^1.2^2})$ and ANOVA	Exergy Analysis
[28]	VCRC	R290 and R600	Experimental	$L_{16}(4^5)$	$\dot{m}$
[20]	VCRC	13 CFCs	CSD EoS	FFD	COP, CC
[21]	VCRC	R410A	ASHRAE and Experimental	CFD	θ_{co}
[22]	VCRC	R134a	Experimental	BBD and ANOVA	COP, E_a
[23]	VCRC	R450A	Experimental	RSM and ANOVA	$COP, CC, P_{comp}, DLT, \dot{m}$
[24]	VCRC	R600a	Experimental	CFD	$\dot{m}$
[39]	VCRC	R600a and LPG	Experimental	ANOVA	$COP, CC, \omega_c, DLT, P_R$
[29]	VCHP	R11, R12, R22, and BM	Experimental	$L_{16}(4^5)$ and ANOVA	COP, η_{II}
[30]	VCHP	R22, R407C, and BM	Experimental	$L_{25}(5^6)$ and ANOVA	COP, η_{II}
[31]	VCHP	R22, R404A, and BM	Experimental	$L_{25}(5^6)$ and ANOVA	COP, η_{II}
[40]	MHP	R134a	Experimental	$L_{27}(3^9)$, RSM and ANOVA	COP
[32]	ORC-IHX	R123, R245fa, R600	Self-designed model	$L_{27}(3^9)$ and ANOVA	η_{th}
[33]	ORC-IHX	R123, R245fa, R600	Self-designed model	$L_{27}(3^9)$, GRA and ANOVA	η_{th}, η_{II}
[34]	ORC-IHX	R134a, R717, R718, R236fa, R245fa, R600a	NA	$L_{18}(6^{1.3^2})$ and ANOVA	η_{th}
[35]	ARS	NH_3-H_2O	Self-designed model	$L_{27}(3^8)$, GRA and ANOVA	$COP, eCOP$
[36]	ARS	NH_3-H_2O	EES	$L_{16}(4^5)$ and Linear Regression	COP, η_{II}
[37]	ARS	$LiBr-H_2O$	EES	BBD and ANOVA	COP
[38]	ARS	$LiBr-H_2O$	NA	$L_9(3^4)$ and ANOVA	COP
[41]	GCHP	R22	Experimental	$L_{27}(3^9)$ and ANOVA	COP
[42]	GSHP	R22	Experimental	$L_9(3^4)$ and ANOVA	COP
[43]	GSHP	R22	Experimental	$L_{18}(2^{1.3^7})$ and ANOVA	COP
[44]	SAR	$AcC-CH_3OH$, Zeolite- H_2O , $AcC-H_2O$	Statistical based on Experimental	FFD and ANOVA	COP
[45]	SAR	$AcC-CH_3OH$	Experimental	CFD and ANOVA	COP
[46]	LPGRS	LPG	Experimental	$L_{27}(3^9)$ and ANOVA	T_{evap}
[47]	TAR	Air/He (any inert gas)	Experimental	$L_9(3^4)$ and Regression	ΔT

*CRS – Cascade Refrigeration System; VCRC – Vapor Compression Refrigeration Cycle; IHX – Internal Heat Exchanger; VCHP – Vapor Compressor Heat-Pump; MHP – Mechanical Heat-Pump; ORC – Organic Rankine Cycle; ARS – Absorption Refrigeration System; GCHP – Ground Coupled Heat-Pump; GSHP – Ground Source Heat-Pump; SAR – Solar Adsorption Refrigeration; LPGRS – Liquefied Petroleum Gas Refrigeration System; TAR – Thermo Acoustic Refrigeration.

only with $GWP < 150$, but also with satisfactory safety-related properties (i.e., flammability and toxicity), technically efficient and cost-effective as direct replacements to existing HFC-operated cooling cycles. The search for such novel refrigerants spanned across natural refrigerants (i.e., water, alkanes, CO_2 , etc.) [13] and synthetic 4th generation refrigerants including hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) [14]. However, given the high safety performance and technical efficiency of HFCs, limited low GWP alternatives exist with suitable range of properties for direct replacement of the popular and efficient HFCs [15].

On another front, enhancing the efficiency of cooling cycles would directly contribute to reducing the CO_2 emissions resulting from energy consumption for operating the cooling cycle. These are primarily process-related considerations to the larger degree involving either the optimization of operating conditions or the design of novel cooling cycles with energy-saving potential [16–19], summarized in Table 1. However, this is not fully detached from the choice of refrigerant, as its thermodynamic properties have a direct impact on the maximum attainable system efficiency. Such a task is challenging due to the large search space for coupling potential low GWP refrigerants, cooling cycle designs, and operating conditions.

Recently, several studies aimed to design refrigeration systems with low energy consumption and high efficiency by optimizing multiple sets

of operating conditions, employing statistical analysis methods such as Taguchi, factorial designs and analysis of variance (ANOVA), to minimize the number of required experimental/modeling runs, as summarized in Table 1. Earlier works focused on capturing the trade-offs in selecting refrigerants for vapor compression refrigeration cycles (VCRC) operated with CFCs and HFCs, highlighting the role of fluid's critical temperature in enhancing the performance of the cycle on the expense of reduced cooling capacities [20,21]. Similar outcomes were pointed out from several works using a variety of statistical analysis tools such as Box-Behnken Designs (BBD) [22], Response Surface Methodologies (RSM) [23], and Complete Factorial Designs (CFD) [24] applied on hydrocarbon (HC)- or HFC-operated VCRCs. For more novel cooling cycle configurations, the role of evaporator and condenser temperatures of the lower cycle, and the isentropic compressor efficiency on the coefficient of performance and exergy of a vapor compression cascade cycle operated with HFC-based refrigerants were highlighted [25]. Similar analysis focused on minimizing exergy destruction and tuning control factors for R600a-operated vapor compression-based refrigeration [26,27], and optimum design of adiabatic capillary tubes in vapor compression systems using HCs refrigerants and their blends [28]. The application of statistical tools for system optimization even extended into heat pumps and organic Rankine cycles (ORCs) [29–34], and other novel technologies such as absorption refrigeration [35–38].

The preceding table of relevant literature highlights the limited application of system optimization based on statistical analysis for cooling cycles operated with 4th generation refrigerants, considering the deployment of new units would be solely operated with low GWP refrigerants, in line with imposed environmental and governmental regulations. This would depend on determining optimal low GWP refrigerants satisfying environmental, safety, and technical requirements for new cooling cycles, followed by determination of optimal operating conditions and cycle configurations for these promising refrigerants that would invariably maximize technical efficiency and minimize cost and environmental footprint. Additionally, the majority of the body of literature is merely focused on optimal energetic and exergetic performance, disregarding their possible effects on economic and environmental performance.

In this contribution, we aim to determine optimal 4th generation synthetic refrigerants (*i.e.*, HFOs, and HCFOs), cooling cycle configurations, and operating conditions suitable for low-medium temperature applications resulting in technically, economically, and environmentally efficient new systems readily deployable to the cooling market. This pioneering effort marks the first in the literature (see Table 1) to conduct a holistic 4E (Energy, Exergy, Economic, Environmental) analysis on low GWP refrigerants, integrating statistical methods with advanced equations of state (EoS). The selection of optimal 4th generation HFOs and HCFOs is based on a multi-criteria analysis spanning across environmental, safety, and technical criteria in a basic VCRC system, built on employing the polar soft-statistical associating fluid theory (soft-SAFT) [48], as a reliable platform to obtain relevant thermodynamic property data for technical evaluation, at conditions typically unavailable from experimental literature databases. The performance of selected promising refrigerants is further optimized through coupling statistical analysis tools with the molecular EoS to optimize the thermodynamic space characteristics [49,50], leading to optimized performance in terms of energy, exergy, cost-savings, and environmental footprint. This is applied in the case of operating these promising refrigerants in a basic VCRC, and its variant for energy savings, namely, liquid-to-suction line heat exchanger (LL/SL-IHX).

2. Methodology

2.1. Criteria for selecting promising low GWP refrigerants

A set of selection criteria have been applied to narrow down the feasible search space of promising refrigerants for further evaluation and performance optimization. We opted to limit the scope of this work to synthetic pure refrigerants, including 4th generation HFOs, and HCFOs, benchmarked to commonly used 3rd generation HFCs, R32 and R134a. The initial round of selection based on environmental and safety criteria in accordance with EU legislation No 517/2014 [12], allowed the

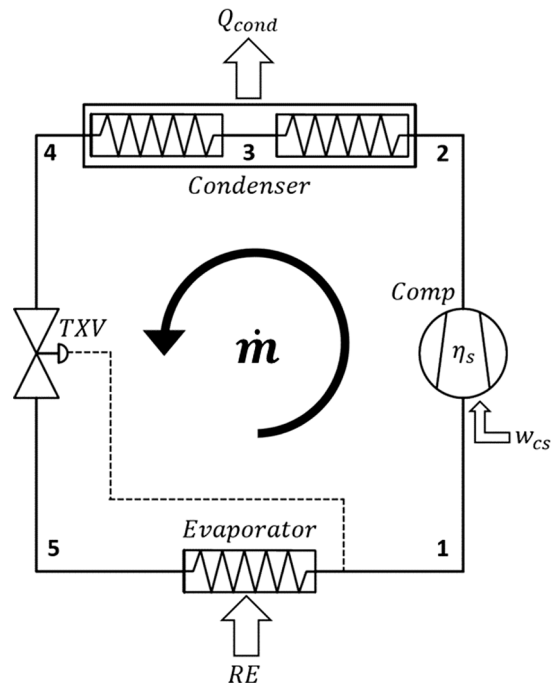


Fig. 1. Process flow diagram of the basic VCRC cycle studied in this work.

selection of refrigerants with (1) GWP < 150, (2) null ozone depletion potential (ODP) or ODP < 0.01, (3) non-toxic (A), and (4) either non- or low-flammability (1, or 2L), listed in Table 2.

Subsequently, their technical performance, benchmarked to R32 and R134a, was assessed in terms of key technical performance indicators (KPIs) for low-medium temperature applications in a standard VCRC, shown in Fig. 1, to determine the most promising refrigerants. The operation of the cycle starts with the isentropic compression of the refrigerant, resulting in a superheated vapor releasing its latent heat to the surrounding at the condenser's pressure. The resulting saturated liquid is expanded at isenthalpic conditions in the thermostatic expansion valve (TXV), resulting in a two-phase mixture that is evaporated at isobaric conditions in the evaporator reaching its saturated vapor phase.

A set of technical KPIs for evaluating promising 4th generation refrigerants were selected to determine the most promising two refrigerants computed using the methodology established in our earlier works for VCRC cycles [58,59]. The choice of KPIs was based on their impact on the design and operation of the cooling cycle, primarily affected by the thermodynamic properties of the refrigerant.

The size of the compressor is affected by the vapor density exiting the

Table 2

Shortlisted 4th generation refrigerants based on their environmental and safety impact.

ASHRAE Designation	IUPAC Name	GWP ₁₀₀ [*]	ODP [†]	Toxicity [‡]	Flammability [‡]
Accepted based on environmental and safety criteria					
R1123	1,1,2-trifluoroethene	0.005	0	A	2L
R1234yf	2,3,3,3-tetrafluoroprop-1-ene	0.501	0	A	2L
R1234ze(E)	<i>trans</i> -1,3,3,3-tetrafluoroprop-1-ene	1.370	0	A	2L
R1225ze(Z)	<i>cis</i> -1,2,3,3,3-pentafluoroprop-1-ene	0.344	0	NA ⁺	NA ⁺
R1336mzz(Z)	<i>cis</i> -1,1,1,4,4,4-hexafluoro-2-butene	2.080	0	A	1
R1233zd(E)	<i>trans</i> -1-chloro-3,3,3-trifluoroprop-1-ene	3.880	0.00024	A	1
R1224yd(Z)	<i>cis</i> -1-chloro-2,3,3,3-tetrafluoroprop-1-ene	< 1	0.00023	A	1
Benchmark refrigerants					
R32	Difluoromethane	771	0	A	2L
R134a	1,1,1,2-tetrafluoroethane	1530	0	A	1

^{*} GWP values from [51] for R1224yd(Z) and IPCC AR6 WGI Chapter 7 for remaining agents.

[†] ODP values from [52–54].

[‡] ASHRAE rating from [53–57].

⁺ ASHRAE official classification have not been published, yet generally regarded as mildly toxic and non-flammable.

evaporator (ρ_V), with higher ρ_V resulting in reduced compressor sizing. The compressor operating pressure and power consumption are affected by the normal boiling point (NBP), measure of the ease of vaporizing the refrigerant with heat absorption, and condenser pressure (P_{cond}), both should be minimized to ensure reduced compression power. The specific liquid heat capacity (c_p) denotes the amount of heat required for changing the temperature of the refrigerant at liquid state, which should be minimized.

Another technical indicator included the refrigeration effect (RE), which measures the cooling capacity of the refrigerant in terms of amount of latent heat absorbed in the evaporator, with maximum values preferred to ensure higher heat extraction and lower refrigerant mass flow rates. This is also related to the coefficient of performance (COP), which is a measure of the overall energy efficiency of the cooling cycle as the quantity of absorbed latent heat (i.e., RE) per unit of real work (w_c) inclusive of the compressor isentropic efficiency (η_s), as:

$$COP = \frac{RE}{w_c} = \frac{RE}{\frac{w_{ac}}{\eta_s}} = \frac{H_{evap,out} - H_{cond,out}}{\frac{H_{comp,out} - H_{evap,out}}{\eta_s}} \quad (1)$$

Additionally, the exergy efficiency (η_{II}) was included to gain additional insight on the effectiveness of the cycle [60–64], computed as the ratio of the total exergy destruction rate ($\sum \dot{\chi}_d$) and the rate of exergy input ($\sum \dot{\chi}_{in}$), using the mathematical formulation in **Section S1 in the Supporting Information (SI)** from our previous work [59].

$$\eta_{II} = 1 - \left(\frac{\sum \dot{\chi}_d}{\sum \dot{\chi}_{in}} \right) \quad (2)$$

Lastly, a techno-environmental indicator was included in the assessment, in the form of the total equivalent warming impact (TEWI) metric [65], as a measure of the contribution to global warming, with detailed description of its parameters and corresponding values within the European Union (EU) regional context included in **Section S2 in the SI**. The TEWI indicator accounts for the direct emissions of the refrigerant with their corresponding GWP (i.e., refrigerant leakage and end-of-life disposal) and indirect CO₂ emissions associated with energy consumption of the cooling cycle (E_d), related to its type and efficiency, given in terms of yearly tons of equivalent CO₂ emissions, as:

$$TEWI = TEWI_{direct} + TEWI_{indirect} \quad (3a)$$

$$TEWI_{direct} = GWP \cdot [(L \cdot m \cdot n) + (m \cdot (1 - \alpha))] \quad (3b)$$

$$TEWI_{indirect} = E_d \cdot \beta \cdot n = [\omega_c \cdot (CC/RE) \cdot AOT] \cdot \beta \cdot n \quad (3c)$$

where L is the annual leakage rate, m is the refrigerant charge load, n is the system operating life, α is the recovery factor, β is the indirect emission factor, AOT is the annual operating time, RE is the refrigeration effect, ω_c is the compressor real work, and CC is the cooling capacity.

Note that other life cycle stages can also result in CO₂ emissions such as refrigerant and cooling cycle manufacturing, however, their assessment is beyond the scope of this work, focused only on the operating phase of the cooling cycle.

2.2. The polar soft-SAFT EoS

The technical evaluation of the shortlisted refrigerants based on their environmental and safety performance (see **Table 2**) depends on the application of a reliable thermodynamic model for obtaining all relevant thermophysical properties. Accordingly, we opted to employ the polar soft-SAFT EoS [48], an extension of the original soft-SAFT EoS proposed by Blas and Vega [66,67]. In this molecular-based EoS, the residual Helmholtz energy density (a^{res}) of a fluid is obtained as the sum of Helmholtz energy density of various contributions accounting for different microscopic characteristics. For the particular case of fluorinated refrigerants, the equation reads:

$$a^{res} = a^{ref} + a^{chain} + a^{polar} \quad (4)$$

where, a^{ref} , is the reference term accounting for the repulsive and dispersive interactions between individual segments of the Lennard-Jones (LJ) reference fluid, and a^{chain} is the chain term accounting for the formation of chains from individual segments. Additional terms are added to the equation to explicitly account for dominant intermolecular interaction such as, in this case, the polar term (a^{polar}) for the contribution from multipolar interactions (i.e., dipole, or quadrupole). Further details on the different terms and applications can be found in the original contributions [48,66–70].

To apply the soft-SAFT model, a coarse-grain representation of the molecules descriptive of key structural and energetic characteristics through a set of molecular parameters is required. The basic three molecular parameters for any type of fluid include: the chain length (m_i), the LJ segment diameter (σ_i), and the LJ segments dispersive energy (ϵ_i). For fluids polar interactions, two additional parameters are needed, which include the dipole/quadrupole moment (μ/Q), and the fraction of polar segments (x_p). These molecular parameters are either fitted to pure fluid experimental saturated liquid density and vapor pressure or fixed *a priori* based on physical arguments.

Considering that the refrigerants examined in this work exhibit a permanent dipole moment from the asymmetrical charge distribution owed to the presence of the halogen atoms, we modeled them as LJ chain molecules explicitly taking into account their dipolar nature. Accordingly, the μ was fixed to the experimental value in vacuum, and x_p was determined *a priori* based on the molecular charge distribution [48,68], effectively fitting three parameters (i.e., σ_i , m_i , ϵ_i). Reliable and accurate molecular models for the studied refrigerants in **Table 2** have been previously developed by our group [58,71], and were used in this work in a transferable manner; they are included in **Table S2 in the SI** for completeness.

The polar soft-SAFT EoS was used to obtain all relevant thermo-physical properties required for the technical evaluation of the studied refrigerants. This also required estimating the pressure-enthalpy (PH) and temperature-entropy (TS) diagrams for the pure refrigerants from the equation under the imposed operating conditions, with values for the ideal gas enthalpy (H^G), and entropy (S^G) required for these predictions from the model taken from literature [53,72].

2.3. Optimization of the performance of cooling cycles with 4th generation refrigerants

The performance of the most promising two refrigerants from those listed in **Table 2**, based on the methodology highlighted earlier, was further optimized considering the effect of different operating conditions and cooling cycle configurations. In terms of cycle configuration, in addition to the basic VCRC cycle (see **Fig. 1**), we also examined the performance in the internal heat exchanger variation to the VCRC cycle (LL/SL-IHX VCRC) included in **Fig. 2**.

The LL/SL-IHX configuration operates in a similar manner to the basic VCRC cycle, with the main difference of introducing an internal heat exchanger between the suction and liquid lines in the basic VCRC, which cools the refrigerant at the condenser outlet (3 – 3') by heat rejection to the refrigerant from the evaporator (1 – 1'). This consequently increases the temperature in the compressor suction and discharge lines, while decreasing the condenser outlet temperature, promising enhanced RE, reduced compressor power consumption, and prolonged compressor lifetime [73]. Overall, this variation promises improved energy efficiency and reduced refrigerant mass flow rate [74]. The simulations for this cycle were done at equivalent conditions to the basic VCRC, with the additional assumption of intercooler effectiveness ($\epsilon^{IHx} = 60\%$) to ensure a minimum pinch point temperature (T_{pp}) of 4 K [75]. between the hot (3) and cold (1') streams in the internal heat exchanger, modeled as a counter-current one. The energy balance

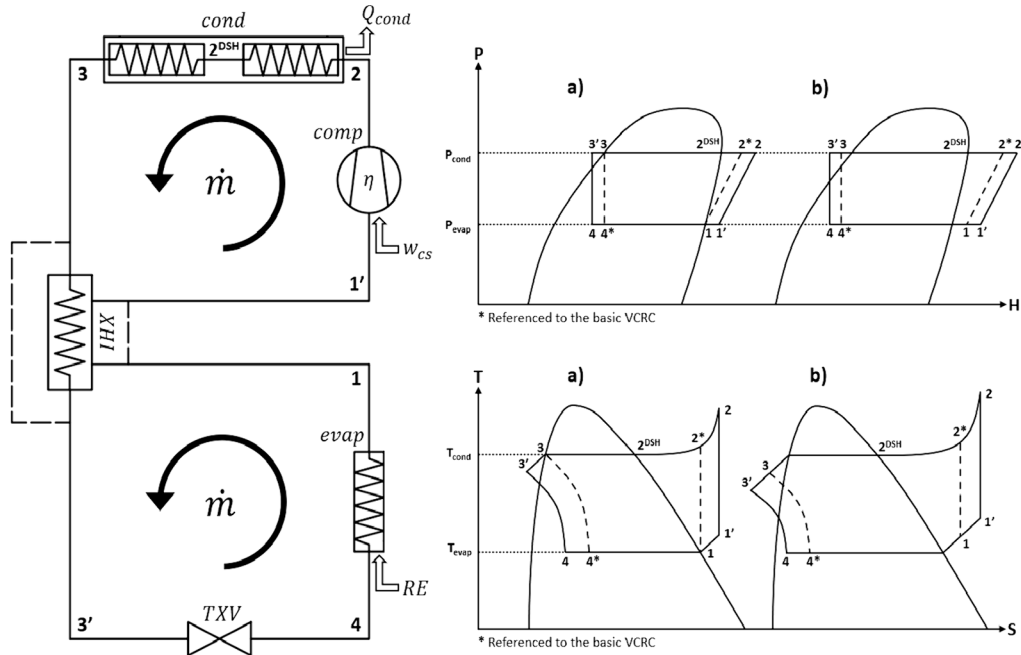


Fig. 2. Integrated view for the cooling cycles included in this work: basics VCRC in dashed lines, and LL/SL-IHX VCRC in solid lines, with superheating and sub-cooling effects in a) off, and b) on modes.

equations descriptive of the processing units in both cycles in Fig. 2 are included in Section S4 in the SI.

2.4. Statistical tools for cooling cycle performance optimization

To address the optimization problem to determine optimal operating conditions and cycle configurations suitable for the operation of promising 4th generation refrigerants, several statistical analysis tools were employed in this work. This was done to reduce the required computational time, while ensuring consistent and holistic mapping of the design search space, with minimal number of simulations runs. These include fractional factorial design (FFD) and Taguchi orthogonal array (OA) method to obtain the ranking of importance for the most influential design factors, with the addition of ANOVA and polynomial surface regression (PSR) model as validation tools for the ranking of importance, and lastly grey relational analysis (GRA) to build a consistent multi-objective optimization in a single expression.

2.4.1. Taguchi method and fractional factorial design

The Taguchi orthogonal array (OA) is a reliable statistical method utilized in design of experiments (DoE) and determination of impact of system parameters on performance for optimization problems. With this method, the most likely interactions are selected *a priori*, unlike the selection with FFD. The application of Taguchi and FFD depends on the selection of factors (design/operating conditions) and their levels (variation ranges), and accordingly the construction of the DoE structure that can best map the effect of individual factors on selected target functions (output responses) with minimal number of runs, depending on degrees of freedom (DOF) based on the number of factors and levels. The output from these tools is measured in the form of importance order ranking and contribution ratios of main factors to the target function. Additional details on the principles of developing Taguchi OAs and FFDs can be found elsewhere [76].

For the first iteration of the DoE in this work the main factors included: variation in evaporator and condenser temperatures (T_{evap} , T_{cond}), degrees of subcooling and superheating (T_{sub} , T_{super}), degree of isentropic compression efficiency (η_s) (fixed at a maximum of 95 % to avoid unrealistic scenarios [77]), choice of cooling cycle (*i.e.*, basic vs.

LL/SL-IHX), and choice of refrigerant (restricted to the two most promising based on the technical screening from the previous section). The level of variation for the selected factors was based on operating conditions suitable for use in common types of refrigeration and air-conditioning equipment [15]. These factors were examined on energy and exergy target functions. For energy-related target functions, COP (Eq. (1)) and volumetric cooling capacity (VCC) were chosen, as these are primary parameters indicative of energy efficiency (reflective of operating costs), and equipment size (reflective of capital costs) [49]. The VCC refers to the amount of cooling per unit volume of the refrigerant at the evaporator outlet impacting the efficiency of the cycle and the size of the compressor, with preference for high VCC values to ensure high RE while minimizing compression requirements [78]. The VCC of the cycle was computed as a function of ρ_v in the compressor suction line and the RE in the evaporator, as:

$$VCC|_{VCRC} = \rho_{v,1} \cdot RE; VCC|_{LL/SL-IHX} = \rho_{v,1'} \cdot RE \quad (5)$$

Conversely, η_{II} (see Eq. (2)) was chosen as the exergy-related target function to gain a more realistic perspective on the cycle's effectiveness by gauging the useful work available from the system. These target functions are applicable for both cooling cycle configurations (*i.e.*, basic vs. LL/SL-IHX). In the specific case for optimizing the LL/SL-IHX configuration, an additional target function was included, namely, the pinch point temperature (T_{pp}), which is a governing factor on the performance of waste heat recovery systems due to the inherent trade-offs between the heat exchanger area and the absorbed heat. In this case, low T_{pp} values were preferred leading to increased absorbed heat and thereby produced cooling, yet on the expense of increasing the heat transfer area and cost of the heat exchanger [75]. The T_{pp} was estimated as a function of the internal heat exchanger effectiveness (ϵ^{IHx}) and the condensation, evaporation, and suction line temperatures, as:

$$T_{pp} = \Delta T_1 = T_3 - T_{1'} = T_3 - (\epsilon^{IHx} \cdot [T_3 - T_1] + T_1) \quad (6)$$

2.4.2. Complementary validation tools

Other statistical tools were included in the form of ANOVA and PSR model to validate the importance of each factor, order, and contribution ratios obtained from the DoE.

For the ANOVA method, the importance of each factor on the target function was determined, and accordingly the rank for each factor was calculated by finding the statistical significance of the independent variable (factor) on the dependent variable (target function), with high F -test and low p -test values for a 95 % confidence level denoting statistical significance of the factor.

In the case of the PSR model, a 3D graphical hierarchical representation for the developed DoE is required to select a limited number of subset of experiments that are fully orthogonal and can fully map the responses. Further information on graphical presentation of factorial designs can be found in Barton *et al.*'s analysis [79]. The PSR model is formulated to correlate the main factors with the target responses in a manner where the number of coefficients is equal to the number of experiments based on the structure of the DoE. Note that a positive value for the coefficient is indicative of a high order of importance in the coefficient-set, reaffirming the results obtained from ANOVA. Moreover, the resulting correlation model can also enable prediction of the target responses at conditions not included in the limited experimental set.

2.4.3. Multi-objective optimization using grey relational analysis (GRA)

Considering that the developed DoEs were used to measure the effect of each factor on each target response separately, the GRA method was used to encompass multiple target functions into a single objective function, that can simultaneously optimize their performance [33,35]. To do so, the results of the responses were normalized between 0 and 1 using Eq. (7) and Eq. (8), followed by evaluating the grey relational coefficient (ξ_i) (Eqs. (9) and (10)) which expresses the relationship between desired and actual normalized value.

$$y_i(k) = \frac{x_i^o(k) - \min x_i^o(k)}{\max x_i^o(k) - \min x_i^o(k)} \quad (7)$$

$$y_i(k) = \frac{\max x_i^o(k) - x_i^o(k)}{\max x_i^o(k) - \min x_i^o(k)} \quad (8)$$

$$\begin{aligned} \xi_i(k) &= \frac{\Delta_{\min} + \varphi \Delta_{\max}}{\Delta_{oi}(k) + \varphi \Delta_{\max}} \\ &= \frac{(\min_{vj \in i} \min_{vk} [y_0(k) - y_i(k)]) + \varphi (\max_{vj \in i} \max_{vk} [y_0(k) - y_i(k)])}{(y_0(k) - y_i(k)) + \varphi (\min_{vj \in i} \min_{vk} [y_0(k) - y_i(k)])} \end{aligned} \quad (9)$$

$$\Delta_{oi} = y_0(k) - y_i(k) \quad (10)$$

where $y_i(k)$ is the GRA normalization value, $x_i(k)$ is the property value, $\xi_i(k)$ is the grey relational coefficient, Δ_{oi} is the deviation value between $y_0(k)$ and $y_i(k)$, φ is the identification coefficient set to 0.5, and $\Delta_{\min}$ and $\Delta_{\max}$ are the minimum and maximum value of the Δ_{oi} .

The single objective function or grey relational grade (γ) (see Eq. (11)) provides a single correlation encompassing the multiple target responses inclusive of different weight factors (ω_i) for each target function. The weight factors were obtained statistically as the ratio of each parameters' delta value to the total delta value of all assessed factors (see Eq. (12)).

$$\gamma_i = \frac{1}{n} \sum_{k=1}^n \omega_i \xi_i(k) \quad (11)$$

$$\omega_i = \frac{\sum_{j=1}^p \Delta_{i,j}}{\sum_{i=1}^m \sum_{j=1}^p \Delta_{i,j}} \quad (12)$$

The results are evaluated from the signal-to-noise ratios (S/N) to assess the reliability and accuracy of the developed DoE [80], with noise representing the variability of the characteristic, while signal accounts for the average value. The larger-is-better S/N type (Eq. (13)) was selected in this work with the aim of enhancing the system efficiency while minimizing the variability of the characteristic, aiming for high S/N values.

$$S/N = -10 \cdot \log_{10} \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (13)$$

being n the experiment replication number and y_i the data measured for the i^{th} performance characteristics.

3. Results and discussion

3.1. Determination of promising low GWP 4th generation refrigerants

Highlighted in Fig. 3 is the technical performance of the shortlisted refrigerants in a basic VCRC cycle (see Table 2) benchmarked to R32 and R134a based on the technical KPIs of Section 2.1. Note that this evaluation was done at arbitrary operating conditions to facilitate the comparison of the refrigerants under the same conditions, which might not be optimal for each refrigerant, yet sufficient for the purpose of their screening. These conditions include steady-state flow, fixed evaporator and condenser temperatures (i.e., $T_{\text{evap}} = 270$ K and $T_{\text{cond}} = 300$ K) ensuring a lift temperature of 30 K [15,81,82], negligible superheating and subcooling, zero pressure drop and isobaric conditions in both condenser and evaporator, and ideal isentropic compressor efficiency, similar to our previous work [71].

The trade-offs between the different factors affecting the design and efficiency of the VCRC clearly increase the difficulty in discerning the suitability of a single refrigerant over others. Accordingly, the most suitable refrigerant would be the one that achieves an acceptable compromise between the different criteria as demonstrated from the comparative assessment in Fig. 4. To this end, all technical KPIs were assessed with a scale from 1 to 9 denoting improved technical performance and suitability for the intended application.

The suitability of 3rd generation refrigerants, R32, and R134a is supported primarily by their low NBP , and high RE , COP , and η_{II} , while their low to moderate performance in environmental aspects is overshadowed by the alternative 4th generation refrigerants. In terms of techno-environmental impact, commercial refrigerants such as R134a present the highest $TEWI$ due to the substantial contribution of its direct emissions from its high GWP. A reduction in $TEWI$ is seen for all alternative low GWP refrigerants, due to diminished contribution from their direct emissions. Though presenting marginal variations in their indirect emissions levels, related to the effect of their properties on system efficiency and energy consumption (see Table S3 in the SI), the impact of these remains substantial considering the number of cooling cycles operated worldwide.

R1336mzz(Z), R1233zd(E), and R1224yd(Z) present the lowest condenser operating pressure ($P_{\text{cond}} < 0.2$ MPa). As such, limited reduction in the saturation temperature is expected resulting in reduced compressor temperature lift and, consequently, compressor work. This will potentially reduce the operating costs and improve the systems' efficiency (COP and η_{II}), as seen with R1233zd(E). Notwithstanding, very low condenser operating pressures as with R1336mzz(Z) ($P_{\text{cond}} < 0.1$ MPa) though preferential for reducing compressor work, might still prove problematic during refrigerant loading/unloading process, in addition to higher propensity for air leakage into the system [84]. Nonetheless, a trade-off ensued with their high suction densities, requiring large compressors associated with increased capital investments. Additionally, the inverse correlation between the energetic properties of these refrigerants (i.e., c_p and RE) revealed low specific energy requirements for subcooling (high c_p), yet with moderate cooling capacities (low-mid RE). Given its high NBP and reduced $TEWI$, these refrigerants might represent an attractive alternative for high temperature applications [82], even though their deployment in low-medium temperature applications is possible with the use of deep vacuum or multistage compressors, however, with significant capital and operating investments [85].

In terms of technical KPIs, R1123 is a potentially promising alter-

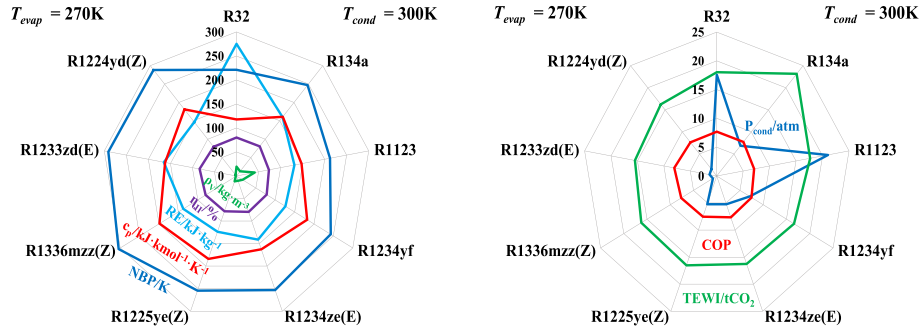


Fig. 3. Technical evaluation for promising environmentally friendly refrigerants, based on KPIs predicted using polar soft-SAFT. The calculated values for these KPIs are included in [Table S3](#) in the SI.

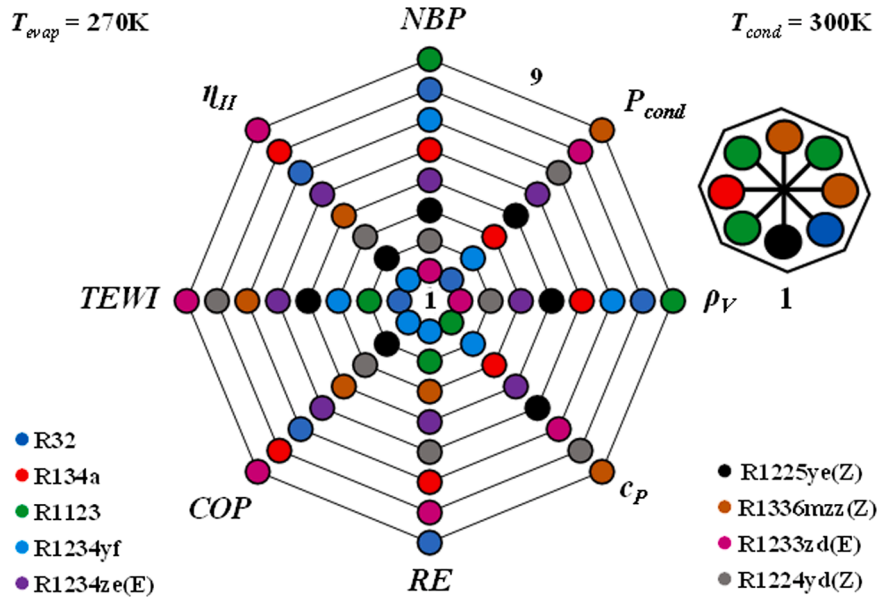


Fig. 4. Comparative assessment based on refrigerant characteristics for finding optimal refrigerant, with a scale of 1 – 9 (worst – best) denoting improved performance, based on results included in [Fig. 3](#), and [Table S3](#) in the SI. Refrigerants ranked as 1 are shown in the in-step in the right-hand side.

native refrigerant for low-medium temperature applications. Its low *NBP* value at atmospheric pressure is indicative of its ease of vaporization without the need for extremely low evaporator operating pressures, in addition to its high suction density and its impact on reducing compressors sizing; these are indicators of relatively reduced capital and operating investments. Moreover, R1123 energetic properties including c_p and *RE*, are within acceptable levels, with moderate specific energy demand to sub-cool the condenser liquid outlet, and moderate cooling capacity output. However, these benefits are partially offset with R1123 high condenser operating pressure ($P_{cond} > 1.5$ MPa) that can increase operating expenditure, while reducing the system energy and exergy efficiencies [83], case and point R1123's having the lowest *COP* and η_{II} .

Among the remaining fluids, R1234yf stands out due to its higher suction density at the evaporator outlet, which contributes to enhance its volumetric cooling capacity. However, this refrigerant offers a lower performance in other important KPIs, such as the *RE*, to *COP*, η_{II} , c_p , and P_{cond} . In particular, R1234yf emits substantially higher indirect GHGs emissions throughout its lifespan compared to systems functioning with R1234ze(E) or R1225ye(Z), due to its lower efficiency in terms of refrigeration effect at constant cooling capacity requirements [86], resulting in higher mass flow rates contributing to its high indirect GHGs emissions [87]. Another aspect to consider is the indirect effect caused by an increase in the net power output of compressed vapor even at similar *RE* values, as seen for R1234yf compared to R1225ye(Z).

The final tier of possible alternatives, which has been finally chosen in this work, include R1234ze(E) and R1225ye(Z) as potential refrigerants for the selected temperature range with acceptable compromise in terms of technical KPIs. R1234ze(E) excels over 3rd generation refrigerants in terms of *TEWI* and key technical metrics such as c_p and P_{cond} , whereas R1225ye(Z) exhibits a mix of outcomes, balancing operating costs with performance efficiency. A slight concern was in terms of R1234ze(E) mid-flammability (A2L) based on ASHRAE standard safety class [88]. However, this was recently adjusted to non-flammable (A1) by Honeywell and the U.S. Department of Transportation (DOT) [89], owing to the dependency of its flammability ratio on the experimental operational conditions [90].

3.2. Parametric evaluation and optimization of cooling cycle design and working conditions

With the demonstrated potentiality of R1234ze(E) and R1225ye(Z) as promising low GWP refrigerants for air conditioning applications, we aim to further optimize their performance by assessing the effect of main cycle design features and operating conditions on energy and exergy savings. This is done employing a DoE strategy with the main cooling cycle parameters (factors) provided in [Section 2.4.1](#) and their variation levels examined in this work listed in [Table 3](#). The selected operating conditions are representative of cooling cycles in North America,

Table 3

Design factors and variation levels employed in the FFD analysis.

Code	Factors	Level [-1]	Level [+1]
A	T_{evap}	263 K	268 K
B	T_{cond}	293 K	288 K
C	System	Basic VCRC	LL/SL-IHX
D	η_s	80 %	95 %*
E	T_{Sub}	3 K	5 K
F	T_{Super}	3 K	5 K
G	Refrigerant	R1225ze(Z)	R1234ze(E)

* Ideal compression is considered at 95% to account for real scenarios only.

Europe, and Japan, designed to operate at cooling loads suitable for domestic air-conditioners [91]. The impact of these factors was assessed on three target functions, with COP and VCC for energy, and η_{II} for exergy.

The initial design of the DoE was done using a Taguchi $L_8(2^7)$ orthogonal array, equivalent to a 2^{7-4} FFD, as shown in Fig. S1 in the SI, which can estimate the effect of individual factors, however, aliased (connected) with two-factor interactions. This implies that the main effects of the factors can be identified only if the two-way interactions are insignificant [92], possibly leading to inconclusive results. Accordingly, for the sake of reliability, though on the expense of more computationally taxing DoE, we opted for a resolution IV 2^{7-3} FFD to separately consider the main effects of individual factors as well as two-factor interactions, with the DoE structure in Fig. S2a in the SI. As such, the DoE requires 16 cases (see Fig. S2b in the SI) to reliably estimate effects of all individual factors using only one-eighth of the number of

runs for a complete factorial design, since higher-order interactions (i.e., three-way, and higher) are considered insignificant. Notice that the effect of individual factors were assembled in separate columns (1 – 7) from the two-factor interactions (8 – 15) to avoid any possible ambiguity in the alias pattern typically arising in resolution IV designs from aliasing two-factor interactions with each other [93]. Additional details on the principles of developing fractional factorial designs can be found elsewhere [76].

Provided in Fig. 5 and Table S4 in the SI are the results of the FFD analysis on the effect of the cooling cycle factors on their energy and exergy performance. For a more energetically preferred performance (i.e., enhanced COP, and VCC), the evaporator temperature was found to be the most influential, while superheating and refrigerant-type were insignificant factors. The evaporator temperature resulted in a Pareto principle (or 80/20 rule) for optimizing VCC (see Fig. 5b), with 94.6 % of the overall contribution ratio attributed solely to this design factor. In the case of optimizing COP, aside from evaporator temperature, the condenser temperature and compression yield were also found to be effective factors (see Fig. 5a), with the three design factors accounting for 97.9 % of the total cumulative contribution, consistent with similar analysis results [94]. Similar importance orders and contribution ratios were obtained using the ANOVA analysis (see Table S5 in the SI).

Same design factors, though with differing orders, were obtained for improving exergy efficiency (see Fig. 5c) with larger impact seen with condenser temperature and compression yield, and lower contribution owed to evaporator temperature, similar to previous contributions [33], and confirmed with the ANOVA (see Table S5 in the SI) and HNPP analysis (appreciate zoom regions within Fig. 5). Conversely, a

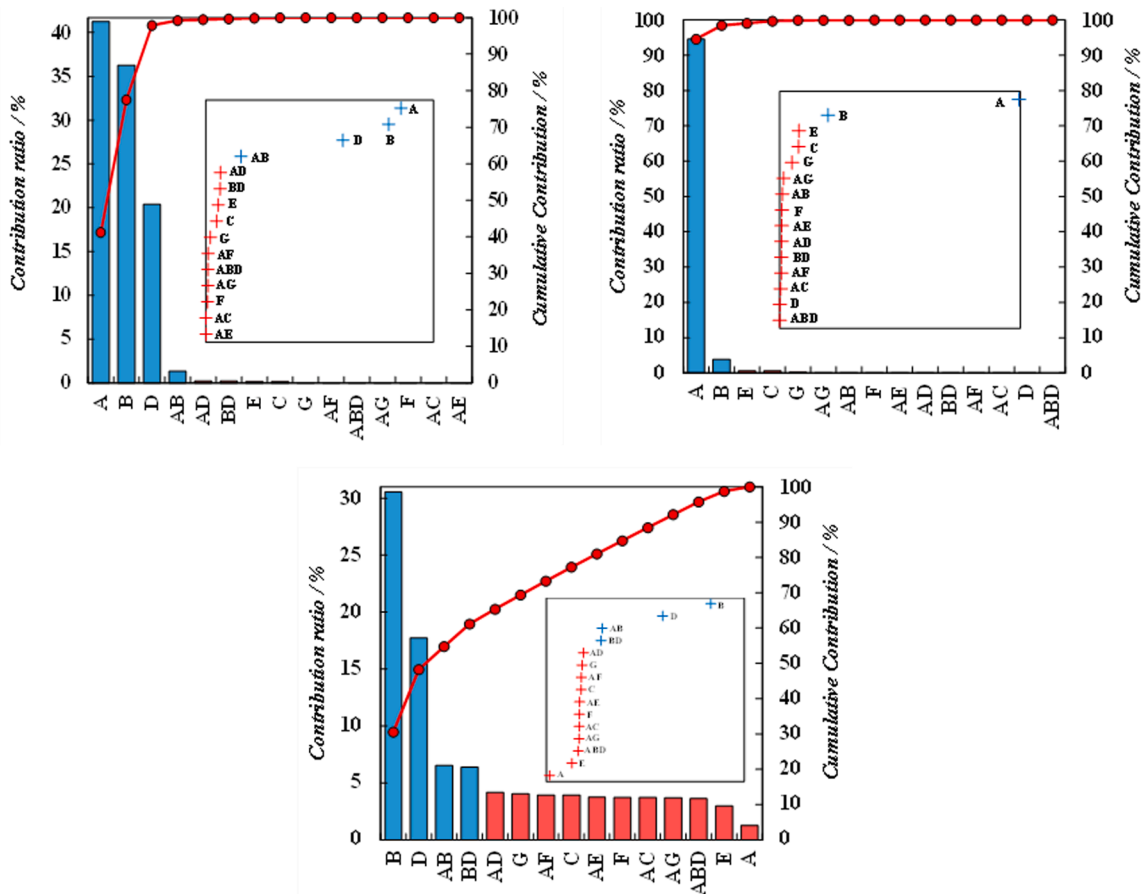


Fig. 5. Cumulative contribution and contribution ratio of design factors in Table 3 on a) COP, b) VCC, and c) η_{II} . Note that bars denote the individual contribution of corresponding factors according to its Alias structure (see Fig. S2a) while red dots indicate the cumulative contribution. The Half-Normal Probability Plot (HNPP), with a zoomed view, showcases the absolute values of the standardized effects of factors in correlation with the normal scores or labels presented on the y-axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

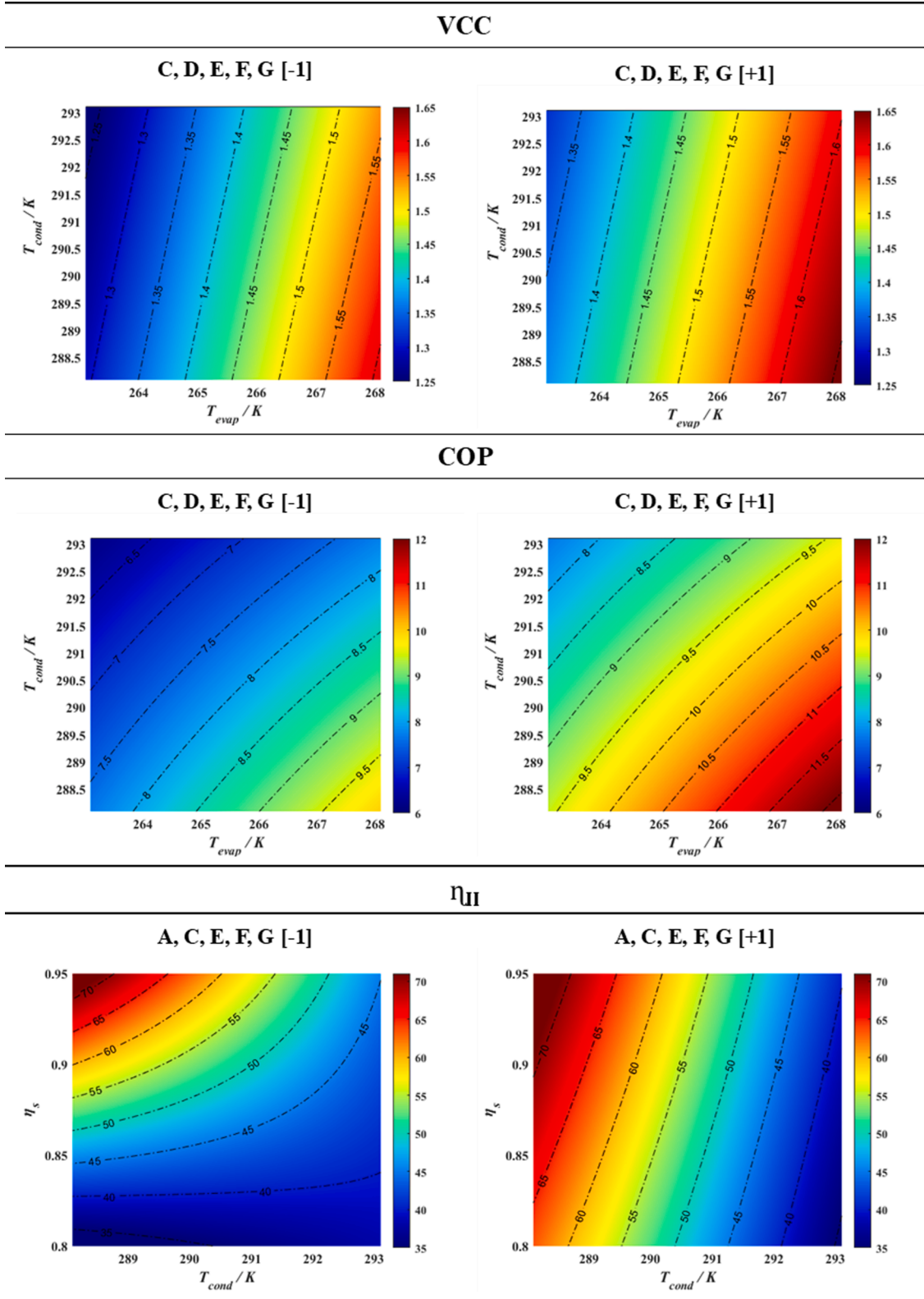


Fig. 6. Polynomial regression model for VCC, COP, and η_{II} as a function of the T_{evap} (A), T_{cond} (B), or η_s (D). Letters refer to the factors provided in Table 3.

diminished role was seen for superheating and fluid-type also previously observed with the energy target functions, highlighted in the in-step probability plots in Fig. 5 for the three target functions. The insignificance of refrigerant-type in this work, otherwise a crucial factor in performance of VCRC systems, is attributed to the similar molecular structure and functional groups for both refrigerants (*i.e.*, R1234ze(E)

and R1225ye(Z)), with their relatively similar critical temperatures (within 2.5 K) [20] resulting in equivalent performance.

Based on the FFD and ANOVA results, the top two influential factors for each target response function are in the order of: $T_{evap} > T_{cond}$ for COP and VCC, and $T_{cond} > \eta_s$ for η_{II} . Although some other common factors are influential among the three target functions, their order of importance

was rather diverging.

An orthogonal 3D projection of the DoE was developed (see Fig. S3 in the SI) to generate a polynomial surface regression model (see Eq. (14)), as an additional validation test to the FFD and ANOVA results, as well as to enable quantifying the effect of the design factors on the target functions for the full-factorial experiments using only one-eighth of the total runs shown in Fig. S4 in the SI. The order of the adopted hierarchy is described as: factors A and B constitute a two-dimensional medium, while the three-dimensional cube is built through the orthogonal projection of factor C. This first level or inner design representation is completed through the inclusion of multi-directional line segments for factors D, E, F and G. The location on the multi-directional line segment tells the levels of factors (*i.e.*, -1 or $+1$) excluded from the hierarchy first level, holding these linking connections parallel to the coordinate axes.

$$y = \beta_0 + A \cdot \beta_1 + B \cdot \beta_2 + C \cdot \beta_3 + D \cdot \beta_4 + E \cdot \beta_5 + F \cdot \beta_6 + G \cdot \beta_7 + AB \cdot \beta_8 + AC \cdot \beta_9 + AD \cdot \beta_{10} + AE \cdot \beta_{11} + AF \cdot \beta_{12} + AG \cdot \beta_{13} + BD \cdot \beta_{14} + ABD \cdot \beta_{15} \quad (14)$$

where β_0 the average theoretical value, $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7$ the factor effects, and $\beta_8, \beta_9, \beta_{10}, \beta_{11}, \beta_{12}, \beta_{13}, \beta_{14}, \beta_{15}$ the interaction effects corresponding to AB, AC, AD, AE, AF, AG, BD and ABD, as described in the characteristic Alias structure in Figure S2a in the SI.

The estimated coefficients for the regression model are provided in Table S6 in the SI. The values of the regression coefficients set (*e.g.*, positive values indicative of synergetic effects) further validate the same observations from the FFD and ANOVA results on the importance of T_{evap} , T_{cond} , and η_s with varying orders of importance for the three response functions. Additionally, the study of high-order interactions revealed the insignificant effect of all kinds of interactions, apart from AB, AD, and BD interactions, finding significance for optimizing the three response targets.

The sparsity assumption [95] was employed to determine the degree of overfitting, by neglecting the contribution of factors with little to no-effect on measured responses provided in Fig. S5 in the SI. The results affirm that 99 % of COP variability is explained by evaporator and condenser temperature and compression yield, while 94.6 % of VCC variability is attributed to evaporator temperature alone, while the remainder can be attributed to condenser temperature. Conversely, 75.2 % of exergy efficiency is on account of condenser temperature and compression yield. These results highlight the major contribution and role of these design factors (*i.e.*, T_{evap} , T_{cond} , η_s) on maximizing each of the three target responses, with varying degrees of importance.

Accordingly, the regression model was used to assess the effect of interactive interactions between these main three factors with statistically significant effects on each response function. The resulting 3D surface graphs in Fig. 6 are built on the basis of keeping the levels of remaining factors at the fixed values specified for the FFD in Table 3, while discretizing the top two factors for each target response within the limits of levels ± 1 . Considerable improvement is observed with fixing the non-discretized factors to the upper bound with level $+1$ across all target functions, similar to that seen earlier with FFD and ANOVA. Enhanced performance for all target responses is seen with reducing the condenser temperature due to the increase in the compressor discharge pressure, at the expense of ensuring lower temperature lifts between heat-exchanging units. The opposite trend is seen with increasing the evaporator temperature, being more influential on energy rather than exergy performance, requiring higher thermal gradients to achieve comparable performance enhancement ratios. Lastly, the system's η_{II} is more sensitive to the degree of compressor yield as opposed to VCC.

Notwithstanding, three statistical analysis methods clearly establish the optimality of setting all design factors to the upper level (*i.e.*, level $+1$ in Table 3), attributed to the 16th case in the DoE, ensuring maximizing the three target functions, however with diverging order of importance for statistically significant design factors when investigating

their impact on the target responses separately. The GRA method is employed to encompass the three target functions into a single objective function, that can simultaneously attain the optimal performance of the three objectives. The grey relational grade (γ) was developed with weight factors obtained statistically from each parameters' S/N ratio prior to estimating the total delta value of all assessed factors, as:

$$\gamma = 0.11 \cdot \gamma_{COP} + 0.05 \cdot \gamma_{VCC} + 0.85 \cdot \gamma_{\eta_{II}} \quad (15)$$

The computed γ are represented in Fig. 7a, highlighting the optimality of the 16th case ($A_1B_1C_1D_1E_1F_1G_1$) as seen with FFD and ANOVA. Other cases with notably high performance are in the order of 12th $>$ 11th $>$ 15th, obtained under $[+1, +1, -1, +1, -1, -1, -1]$, $[-1, +1, -1, +1, +1, -1, +1]$, and $[-1, +1, +1, +1, -1, +1, -1]$ factor levels, respectively. However, it should be stressed that the 12th case is potentially the most cost-effective owing to the implementation of a basic VCRC (C_{-1}), in addition to reduced degrees of subcooling (E_{-1}) and superheating (F_{-1}) for streams departing the condenser and evaporator units.

Additionally, the GRA method is a potent tool for determining a consistent importance order for the design factors among diverging targets, in the order of T_{cond} (B) $\gg \eta_s$ (D) $\gg T_{evap}$ (A) $>$ refrigerant-type (G) $>$ System-type (C) $> T_{Super}$ (F) $> T_{Sub}$ (E). The order of importance is relatively consistent with the collective results obtained from the previous statistical analysis methods. The top-three factors (*i.e.*, T_{evap} , T_{cond} , η_s) monopolize more than 93 % of the cumulative contribution, while the remaining factors have almost identical impact on the response function with ~ 3 % contribution ratios. The degree of superheating and refrigerant (*i.e.*, R1234ze(E) vs. R1225ye(Z)) were the least effective factors on optimizing performance characteristics, with contribution ratios $\ll 1$ %, with additional tests benchmarked to the 16th case confirming the slight significance of refrigerant-type over superheating on inducing larger variation in target responses.

Provided in Fig. 7b, is a comparative plot between the inverse of COP and VCC obtained earlier from FFD, with high-performance cases in the lower left quadrant similar to the approach of Domanski *et al.* [49] in order to analytically engineer optimal cooling processes. The fundamental trade-off between COP and VCC points to 4th, 8th, 10 – 12th, and 14 – 16th cases (see Fig. S2b in the SI) as the optimum combination of factors to maximize both target functions based on energy savings. However, only the 11th, 12th, 15th, and 16th cases contribute to increasing the cycle's energy/exergy performance because of a significant throttling irreversibility drop. This consequently contributes to reducing the indirect CO₂-equivalent emissions associated with electricity emission factors. In particular, the transition from an underperforming system (3rd case) to the most efficient system (16th case) would result in 56.22 % emissions reduction (from 47.86 tCO₂-eq to 30.63 tCO₂-eq) computed in terms of the indirect TEWI when using R1234ze(E) (GWP = 1.4) in an LL/SL-IHX VCRC cycle with nearly 95 % compression yield and applying 5 K subcooling and superheating at evaporator and condenser temperatures of 268 K and 288 K, respectively.

3.3. Optimization for performance of low GWP refrigerant in advanced cooling cycle

Thus far, the most optimal performance from the preceding section can be expected with R1234ze(E) using an LL/SL-IHX advanced cooling cycle. However, specific operating conditions for this configuration were fixed *a priori*, which we aim to adjust for additional enhancements in the cycle's performance. Accordingly, a three-level DoE using Taguchi OA is applied considering factors that have direct implications on the heat transfer phenomena in the IHX. This design excludes factors previously assessed including evaporator and condenser temperature and compression yield. It can be argued that evaporator and condenser temperatures play a role in the heat transfer phenomenon, however, they were fixed to level $+1$ (see Table 3) responsible for optimal

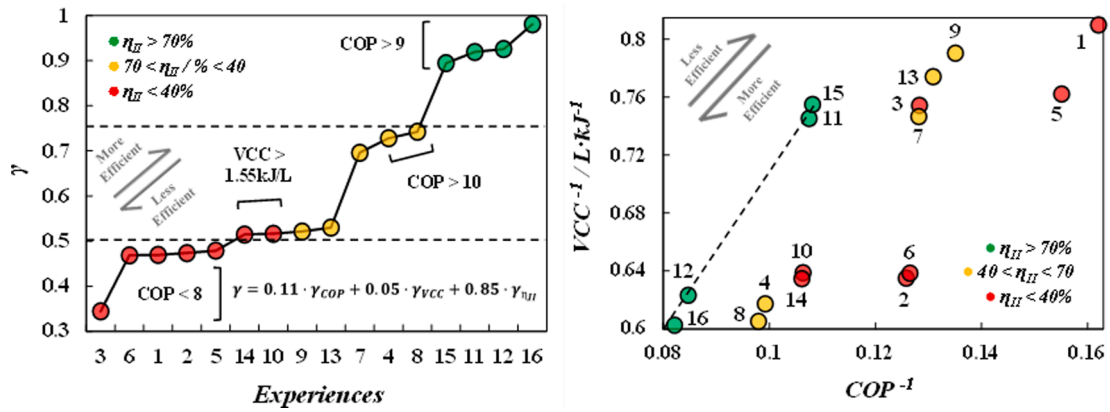


Fig. 7. Efficiency plot for maximum performance based on GRA (a), and FFD simulations (b).

Table 4

Design factors and variation levels employed in the Taguchi OA analysis.

Code	Factors	Level [1]	Level [2]	Level [3]
A'	CC	5 kW	7.5 kW	10 kW
B'	η^{IHX}	0.5	0.6	0.7
C'	T_{Sub}	2.5 K	5.0 K	7.5 K
D'	T_{Super}	2.5 K	5.0 K	7.5 K

performance based on the previous DoE. The same level is applied to isentropic efficiency, with the addition to its minor role in optimizing heat transfer given its intrinsic connection to the compressor device.

Alternatively, levels were applied to design factors including cooling

load, intercooler efficiency, and degrees of superheating and subcooling, as provided in Table 4, considered as key performance factors in enhancing the heat transfer phenomena in IHX-based systems. The cooling load (A') was varied in the range of 5 – 10 kW based on requirements for low-medium temperature cooling applications for cold-stores and freezers with dimensions between 20 – 40 m². Additionally, intercooler efficiency (B') was capped at 70 % to avoid extremely reduced pinch point temperature differences in the intercooler under the specified evaporator and condenser temperatures, that can incur excessive capital costs. The chosen target response functions for this DoE were focused on capital costs-related factors including VCC and T_{pp-IHX} , and operating costs related including COP and η_{II} through the usage of the Taguchi and Pareto ANOVA approaches.

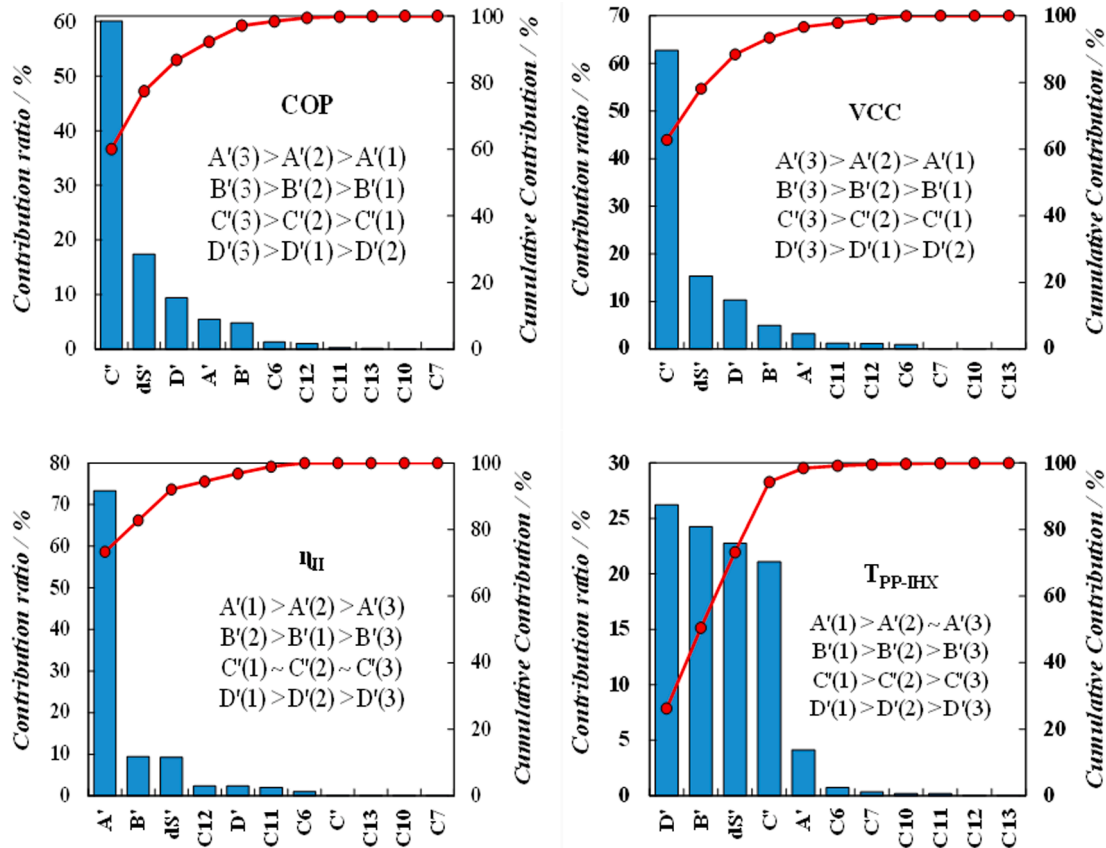


Fig. 8. Cumulative contribution and contribution ratio of design factors in Table 4 on a) COP, b) VCC, c) η_{II} , and d) T_{pp-IHX} . Note that bars denote the individual contribution of corresponding factors, while red dots account for the cumulative contribution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For this three-level DoE, a variety of Taguchi OAs can be formulated, as shown in Table S7 in the SI, with $L_{27}(3^{13})$ OA as the most technically beneficial choice. However, this is computationally expensive with an exhaustive number of cases required for a complete analysis. Alternatively, $L_{16}(2^{15})$ OA can effectively accommodate the required degree of freedom for the three-level factors, while reducing the number of total cases to sixteen, yet with a visible loss of orthogonality. This is resolved with an internal re-shaping and re-allocating process to successfully assign three-level factors ($A' - D'$) to orthogonal arrays premeditatedly constructed to two-level factor settings [96], using the Taguchi's idle column array (ICA) technique [97], with the structure shown in Fig. S6 in the SI. With this approach, the resulting DoE can be described as nearly orthogonal [98] (with OA loss of 4.4 %), given special attention when collapsing the pairs of OA columns onto the levels of the new three-level factor [98]. Certainly, all factors are pre-allocated to avoid confusion between main-factors and second-order interactions, clustering interactive effects in alike columns. Details on the procedure for the ICA approach in the DoE are elsewhere [99].

The S/N ratio from the DoE (Fig. S7 in the SI) are converted into the Pareto-ANOVA plots in Fig. 8 to determine the importance order and effect of main factors on optimizing the selected target functions. For enhanced energy performance with high COP and VCC values, the degree of subcooling was found to be the most influential with a cumulative ratio ≥ 60 %, followed to a lesser extent by the degree of superheating, and lastly, intercooler efficiency and cooling load. Interestingly, this ranking is reversed in the case of enhancing exergy performance, with more dominant impact associated with cooling load (cumulative ratio > 70 %) compared to other factors, following the ranking of $CC \gg \epsilon^{HX} > T_{Super} > T_{Sub}$. The narrative is rather different for impacting T_{pp-IHX} , with larger contribution seen with the degree of superheating and intercooler efficiency compared to the other factors, otherwise influential for energetic and exergy performance. It should be noted that the idle column (dS') from the ICA procedure to enhance the orthogonality of the DoE is present for all target functions, as its level served as the basis for the modification of the Taguchi OA, with those columns housing multi-factor interactions, yet with minimal contribution ratios ~ 2.4 %.

The analysis above demonstrated the divergent ranking of importance for the selected factors for the performance of the chosen target functions. This is also exasperated when considering the levels of the factors, with optimal performance for COP and VCC when settling the design factors at the highest values (level 3) (COP: $C_3D_3A_3B_3$, VCC: $C_3D_3B_3A_3$), while η_{II} is optimized at mixed values for levels 1 and 2 ($A_1B_2D_{1,2}C_1$), and T_{pp-IHX} is optimized with factors at level 1 ($D_1B_1C_1A_1$). In summary, if one chooses to enhance the energy performance of the cycle through increasing the set values for the design factors, the impact will be detrimental for the system's IHX pinch temperature, while compromising its exergy efficiency.

Considering the trade-off between the impact of the design factors and their levels on the target functions for enhancing the performance of LL/SL-IHX cycle configuration, we have applied the GRA method to encompass the multiple target responses in a single objective function, focused on the energy and exergy responses, while T_{pp-IHX} was settled as a constraint either equal to or higher than the value set for the 16th case from the two-level DoE (see Section 3.2), at 8 K, as:

$$\gamma = 0.17 \cdot \gamma_{COP} + 0.16 \cdot \gamma_{VCC} + 0.67 \cdot \gamma_{\eta_{II}} \quad (16)$$

Provided in Fig. 9 are the results of the multi-objective GRA optimization organized in ascending order per experience from low to high performance. Note that the optimum operating conditions are also computed through the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) procedure in Table S8 in the SI, achieving similar outcomes regardless of the employed multi-criteria decision-making tool. An opposing behavior is obtained from the analysis, with high performance cases (run 10') being associated with reduced T_{pp-IHX} ,

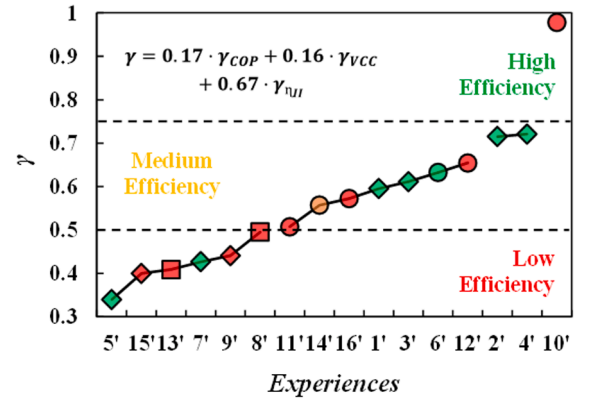


Fig. 9. Grey-relational grade for the maximum performance characteristic. Note that symbols correspond to the degree of enhancement regarding experience number sixteen: ● for enhancement in 100% of energy/exergy outcomes, ■ for enhancement in 66% of energy/exergy outcomes, and ◆ for enhancement in 0–33% of energy/exergy outcomes. Green, orange and red denote intercooler's pinch temperatures that respectively exceed, match, and fall below the benchmark.

while low performing cases (run 5') is associated with appropriate T_{pp-IHX} value. The only acceptable trade-off is seen with case 4' with factors set to ($A_1B_2C_2D_1$) while maintaining the set T_{pp-IHX} constraint, although case 10' is expected to operate more efficiently, yet its low T_{pp-IHX} may prove to be inconvenient in cooling cycle operations. For the best performing case (i.e., case 4') the optimal design factors include: $CC = 5.0$ kW (A_1), $\epsilon^{HX} = 60$ % (B_2), and T_{Sub} and T_{Super} of 5.0 K (C_2) and 2.5 K (D_1), respectively. Under these conditions, the performance of the cycle is relatively similar in terms of energy efficiency to its baseline (case 16 in Section 3.2), however, with 21 % improved exergy efficiency and expanded pinch temperature in the intercooler, giving more room for waste-heat recovery and system optimization. In terms of extracting definitive ranking for design factors on target responses, it can be discerned that intercooler efficiency needs to be operated at 60 % due to its common impact on all target responses. For the other design factors, distinct trends are seen depending on the target response, with larger impact on T_{pp-IHX} associated with lowering the degree of superheating, enhanced energy performance with degree of subcooling, and linkage of cooling capacity to maximizing exergy.

To demonstrate the effect of enhanced exergy efficiency, we have estimated the total cost (TC) and associated CO₂ emissions (TEWI) of the examined cases, provided in Fig. 10, based on data in Table S1 and S9 in the SI. These results are over the 15 years lifespan of the system.

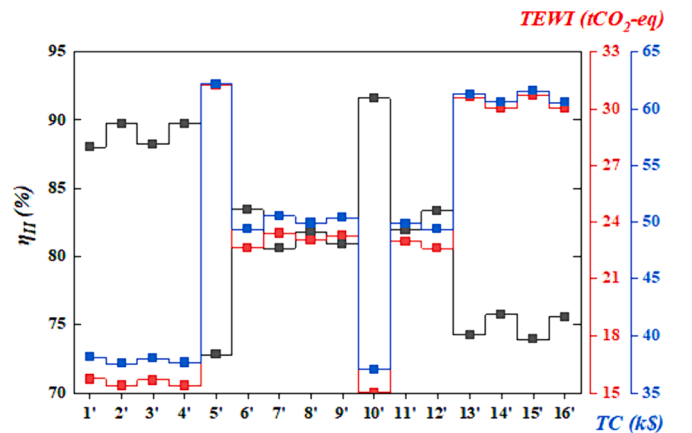


Fig. 10. Relation between exergy efficiency (grey) and its impact on total cost over 15 years (blue) and TEWI (red) for the DoE. See text for details.

Cases with the highest η_{II} (cases 1'–4' and 10') resulted in the lowest TC and TEWI, denoting reduced cooling cycle cost and environmental impact. The opposite trend is seen with cases with least η_{II} (case 5') resulting in the highest TC and TEWI. Considering that the optimal cycle design is set to case 4' with factors set to $(A'_1 B'_2 C'_2 D'_1)$, associated with total cost of \$ 37.58 k (\$2.51 k-yr⁻¹) and emissions of 15.38 tCO₂-eq (1.0256 tCO₂-eq-yr⁻¹), its operation compared to the baseline case 16 ($A'_3 B'_2 C'_2 D'_2$) associated with total cost of \$ 61.40 k (\$4.08 k-yr⁻¹) and emissions of 30.63 tCO₂-eq (2.04 tCO₂-eq-yr⁻¹) would result in net saving of \$ 23.82 k (\$1.59 k-yr⁻¹) and reduced carbon footprint of 15.25 tCO₂-eq (1.02 tCO₂-eq-yr⁻¹). In this manner designing a cost-effective, efficient, and environmentally friendly cooling cycle operated with low GWP R1234ze(E) in an LL/SL-IHX configuration would be readily deployable to the market.

4. Conclusions

In this work, a statistical analysis built on the use of the molecular-based polar soft-SAFT EoS was adopted to evaluate the effect of design factors on the energy and exergy performance of air-conditioning cooling cycles operated with low GWP 4th generation synthetic refrigerants.

The multi-criteria screening framework based on environmental, safety, and technical KPIs employed allowed determine promising low GWP refrigerants, highlighting the appropriateness of R1234ze(E) and R1225ye(Z) for low-medium temperature applications. Subsequently, a two-level DoE using fractional factorial design, ANOVA, and polynomial response surface regression models were employed to analyze the effect of design factors on multi-objective energy and exergy-related targets including COP, VCC, and η_{II} . The collective results from the statistical analysis determined the critical importance of evaporator and condenser temperature alongside isentropic efficiency in enhancing the performance of the system, while revealing the negligible effect associated with superheating and fluid-type on the cycle, of valuable importance for the design of new cooling cycles with alternative refrigerants. A grey-relational analysis was developed to merge the three target functions into a single objective function, establishing a clear hierarchy of design factors based on their impact on cooling cycle efficiency: $T_{cond} \gg \eta_s \gg T_{evap} > \text{refrigerant-type} > \text{system-type} > T_{super} > T_{sub}$. Optimal performance, marked by a 56 % reduction in CO₂-eq emissions was achieved using an LL/SL-IHX cycle with R1234ze(E), applying 95 % isentropic compression, 5 K superheating and subcooling, and setting evaporator and condenser temperatures at 268 K and 288 K, respectively.

Further optimization via a three-level DoE enhancing heat transfer in the LL/SL-IHX cycle based on the optimal conditions established from the previous design, highlighted the role of intercooler efficiency, degrees of superheating and subcooling, and cooling loads in reducing capital costs and enhancing performance. The best-case scenario, meeting pinch demands for industrial processes, was projected to deliver 21 % higher exergy efficiency compared to the base case, maintaining energy requirements and yielding significant cost (\$1.59 k-yr⁻¹) and CO₂ emission (1.02 tCO₂-eq-yr⁻¹) savings over a 15-year system lifespan. It was found that, while the superheating and intercooler efficiency are key factors to reduce capital costs in terms of heat transfer area, subcooling operation plays a more predominant role on the assessed performance characteristics.

Based on a compromise among all studied factors, the best-case scenario was reached using R1234ze(E) and implementing the following process conditions: a cooling load of 5 kW, intercooler efficiency of 60 %, and subcooling and superheating temperatures of 5.0 K and 2.5 K, respectively.

Overall, this work demonstrated the effective integration of molecular modeling and statistical tools for designing and optimizing cost-effective, efficient, and environmentally friendly cooling cycles operated with 4th generation cooling agents, ready for market deployment. This methodology can be easily tailored to analyze additional variables

(i.e. impact of lubricant) and integrated into a more general life cycle analysis (LCA) to guide the development of sustainable cooling systems.

CRedit authorship contribution statement

Carlos G. Albà: Conceptualization, Investigation, Writing – original draft. **Ismail I.I. Alkhatib:** Methodology, Writing – review & editing. **Fèlix Llorell:** Funding acquisition, Supervision, Writing – review & editing. **Lourdes F. Vega:** Supervision, Writing – review & editing.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.applthermaleng.2024.122895>.

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