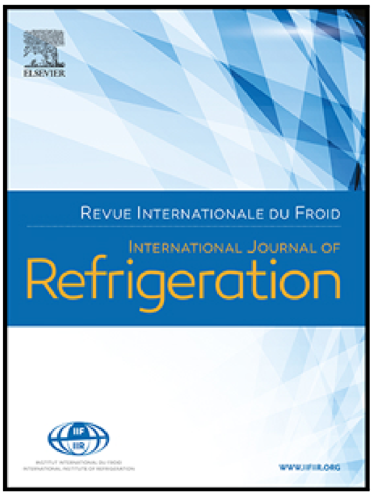

Ultralow-temperature refrigeration systems: Configurations and refrigerants to reduce the environmental impact

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Highlights

- Existing regulations do not limit GWP of refrigerants used for ULT applications.
- Very low operating temperatures limit the possible low GWP candidates.
- Cascade and auto-cascade refrigeration systems seem promising with ejector.
- Compared to other hydrocarbons, flammability of R170 and R1150 is not widely studied.
- R1132a is a promising candidate but requires further study.

Review

Ultralow-temperature refrigeration systems: Configurations and refrigerants to reduce the environmental impact

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Abstract

Several environmental protection policies have been enforced restricting working fluids with high global warming potential (GWP) values used in many types of refrigeration and heat pump systems. However, ultralow-temperature (ULT) refrigeration has not been included, which commonly uses refrigerants with very high GWP values (such as R23 and R508B). Therefore, publicly available research programs seeking low GWP alternative refrigerants do not cover this application and the transition to more environmentally friendly fluids is slowed down. This work presents a comprehensive review that summarizes and discusses the available studies about ULT refrigeration systems. The current status of the technology, system architectures and refrigerants are analyzed. Moreover, the transition towards low GWP refrigerants is proposed, presenting the most promising low GWP alternatives. The most commonly used architectures for ULT refrigeration are the two-stage cascade and auto-cascade, in which the use of ejector has recently been considered in research papers. R170 and R1150 are the available natural refrigerants suitable for ULT, but they have not yet been included in many flammability and risk assessment studies. The A2 hydrofluoroolefin R1132a has been recently proposed as a blend component to avoid problems of stability. However, more information is still necessary to start with simulation and experimental studies. R41 could be an alternative due to its low GWP and suitable normal boiling point, but it has not been thoroughly investigated yet. Overall, there is a gap in the literature in terms of developing alternative refrigerants for ULT refrigeration. This study aims at shedding light on this gap to direct future research in this field towards reliable, environmentally friendly and marketable alternative refrigerants.

Keywords

Ultra-low temperature (ULT), sustainable cooling, low GWP refrigerants, global warming, energy performance, cascade refrigeration

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Nomenclature

NBP	normal boiling point (°C)
P	pressure (MPa)
T	temperature (°C)
Subscripts	
crit	critical
sat,vap	saturated vapor
Abbreviatures	
A5	Article 5 countries of the Montreal Protocol
AB	alkyl benzene
AHRI	air-conditioning, heating and refrigeration institute
ANN	artificial neural network
AREP	alternative refrigerants evaluation program
ASHRAE	American society of heating, refrigeration and air-conditioning engineers
CO_2-eq.	carbon dioxide equivalent
COP	coefficient of performance
CSP	corresponding-states correlation
GWP	global warming potential
EPC	exergetic performance coefficient
HCs	hydrocarbons
HFCs	hydrofluorocarbons
HFOs	hydrofluoroolefins
HS	high stage
HT	high temperature
HTHP	high temperature heat pump
IS	intermediate stage
LS	low stage
LT	low temperature
MO	mineral oil
N.A.	not applicable/available
ODP	ozone depletion potential
OEL	occupational exposure limit (ppm)
OEM	original equipment manufacturer
PAG	polyalkyl glycol
PAO	polyalphaolefin
POE	polyol ester
RACHP	refrigeration, air-conditioning and heat pump
RCL	refrigerant concentration limit (ppm)
REL	relative exposure limit
SNAP	significant new alternative policy
ULT	ultralow-temperature

1. Introduction

Regulation (EU) No 517/2014 of the European Parliament and of the Council (commonly known as F-gas) banned the use of hydrofluorocarbons (HFCs) in the most widely extended types of refrigeration, air-conditioning and heat pump (RACHP) equipment (European Commission and The European Parliament and the Council of the European Union, 2014). The limits, based on 100-years global warming potential ($GWP_{100\text{-yr}}$) (IPCC, 2013), and the date of prohibition were established according to the availability of more environmentally friendly alternatives (shown in its Annex III). Therefore, a GWP limit of 150 came into effect since 2015 for domestic refrigerators and freezers where the low refrigerant charge makes it ideal for hydrocarbons (HCs), especially R600a (Belman-Flores et al., 2015). Other applications include different commercial refrigeration systems, with varied GWP limits. Finally, the last established prohibition is GWP of 750 for single split air-conditioning systems (containing less than 3 kg of HFC), scheduled for 2025. For this application, R32 seems an appropriate alternative (only in new equipment due to its low flammability) and some lower or non-flammable alternatives are still under development (Mota-Babiloni et al., 2017b). Moreover, from 2020 there is a general prohibition on using HFCs with a GWP above 2500, to service or maintain refrigeration equipment charged beyond 40 tonnes of CO_2-eq (Mota-Babiloni et al., 2015). However, this does not apply to military equipment or equipment designed to achieve temperatures below −50 °C.

Those equipment delivering temperatures below −50 °C which were mentioned in the Regulation (EU) No 517/2014 can be defined as ultralow-temperature (ULT) refrigeration, according to the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE). It covers the evaporating temperature range down to −100 °C (Figure 1), which for instance includes freeze-drying as well as cooling in pharmaceutical, chemical and petroleum industries (ASHRAE, 2014).

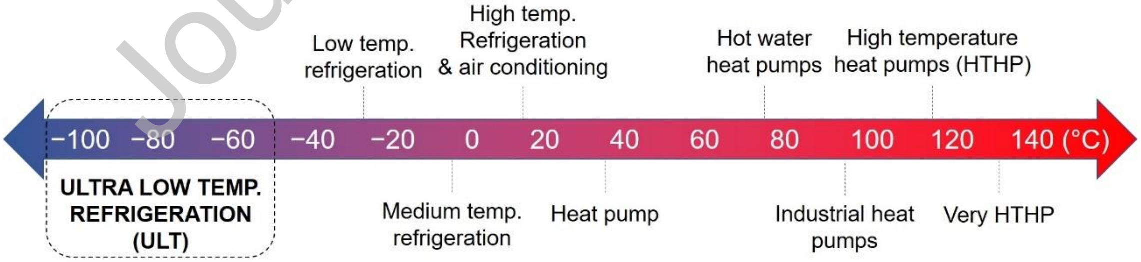


Figure 1. Indicative range of temperatures and applications, highlighting ULT

The decision of not regulating refrigeration below −50 °C can be justified by the small number of units in operation (compared to the other applications) and the lower rate of available research and development (ASHRAE, 2014). In addition, the United States Environmental Protection Agency (US EPA) controls the "very low temperature refrigeration systems" end use only down to −62 °C in its Significant New Alternatives Policy (SNAP) (United States Environmental Protection Agency (US EPA), 2018). Consequently, the Air-Conditioning, Heating and Refrigeration Institute (AHRI), has not considered ULT applications in its low-GWP Alternative Refrigerants Evaluation Program (AREP), whose second phase will be finalized in the near future (AHRI, 2015).

Besides the abovementioned regulations that limit GWP in specific applications and countries, there is another factor promoting the transition towards low GWP refrigerants. Regulation (EU) No 517/2014 established quotas for placing HFCs on the market (starting from 2015) expressed in tonnes of CO_2-eq. and based on the annual average of the period 2009 - 2012 (European Commission and The European Parliament and the Council of the European Union, 2014). Moreover, Kigali Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer (United Nations Environment Programme (UNEP), 2016), has come into force since January 1, 2019, introducing global reduction steps in HFC production and consumption. At the end of 2018 it has been ratified by 60 parties (United Nations, 2018). These HFC quotas are graphically shown in Figure 2.

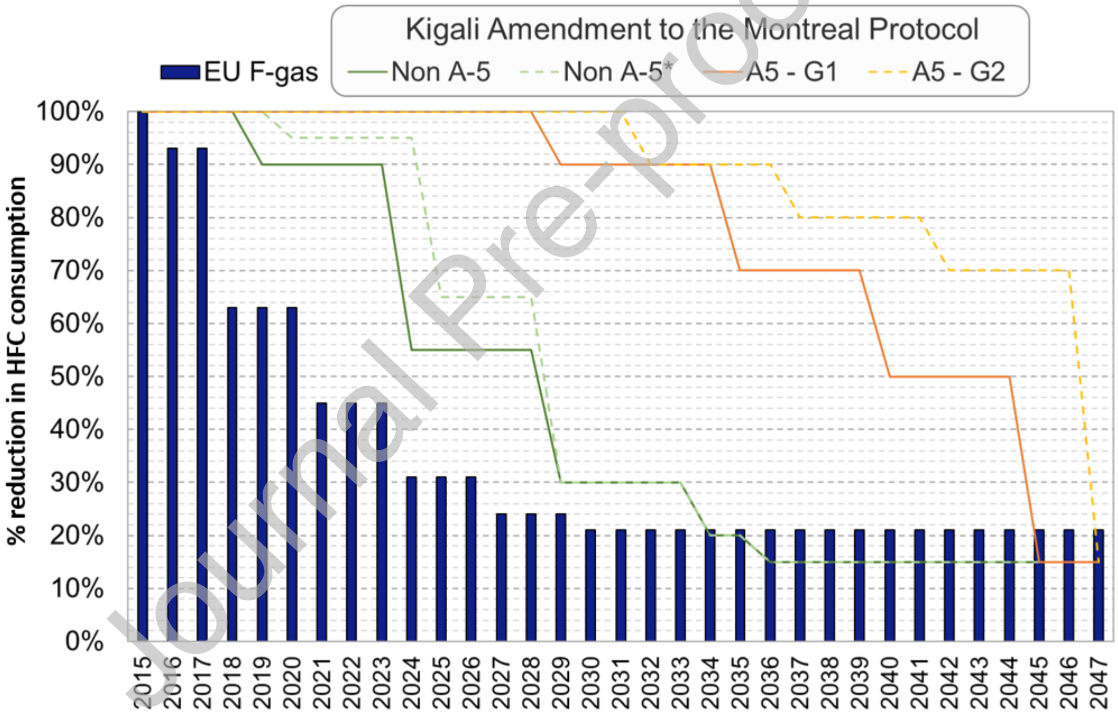
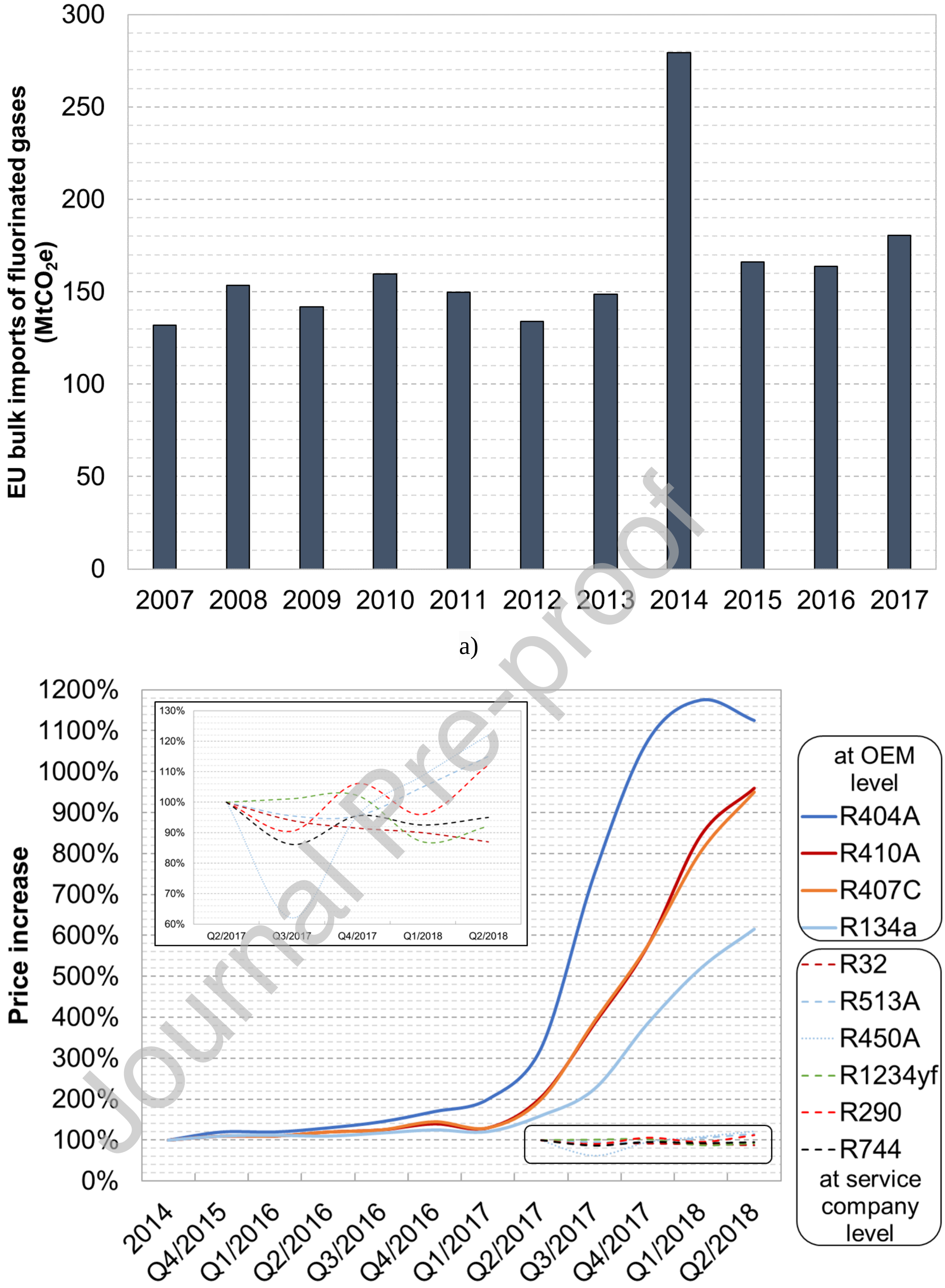


Figure 2. European F-gas and Kigali Amendment HFCs quotas

The consequence of HFC quotas, already started in Europe, has been a substantial increase in the acquisition of these products, increasing with the GWP value (see Figure 3a). For typically used HFCs, the increase at mid-2018 compared to the beginning of 2014 been approximately 600% for R134a or even 1100% for R404A (see Figure 3b) (Öko-Recherche, 2018). R23 and R508B are commonly used in ULT refrigeration, with a GWP around four times that of R404A, and a higher price hike is expected. Note that a complete list of all refrigerants presented in this study and their properties are tabulated in Appendix I.



a)

b)

Figure 3. F-gas in EU: a) bulk imports (European Environment Agency, 2018), and b) price of the most relevant refrigerants (Öko-Recherche, 2018)

Scientific articles published during the past few years that review the environmentally friendly alternatives to HFCs (Abas et al., 2018; Bolaji and Huan, 2013; Ciconkov, 2018; Mota-Babiloni et al., 2017a) do not include the analysis of options for ULT refrigeration and that can be a consequence of excluding ULT refrigerants from the HFC transition policies, regulations and environmental research programs. It is worth pointing out that although alternative (not-in-kind) refrigeration technologies could be used for this range of temperatures (McLinden et al., 2014; Qian et al., 2016), they are currently in the earlier stage of commercial development and research is more focused on increasing their energy efficiency, cooling capacity and temperature span (Aprea et al., 2015; Benedict et al., 2017). Therefore, this paper is only focused on vapor compression systems. It aims to review the current status of ULT refrigeration systems and working fluids, and to analyze different available options to reduce its environmental impact. To do so, first, the most commonly used refrigerants and configurations in ULT refrigeration are introduced. Then, recommendations provided by existing studies to improve the energy efficiency of advanced configurations are presented. Finally, the main characteristics of the most promising low GWP alternatives are presented, including the main barriers against their immediate utilization. The analysis of each natural or synthetic candidate has been personalized to provide a detailed description of its current situation. The outcomes of this study are expected to boost the research and initiate the transition towards the new generation of refrigerants for ULT applications.

2. Traditionally used HFCs

Working fluids typically used in ULT refrigeration are those capable of reaching evaporation temperatures below −80 °C while operating above the atmospheric pressure at the suction point. Consequently, the Normal Boiling Point (NBP) establishes the minimum possible dew point evaporating temperature. Most working fluids typically used in common RACHP systems possess NBP values between −20 and −55 °C (Mota-Babiloni et al., 2017a); hence, they are not suitable for ULT refrigeration. For instance, R404A, a refrigerant used in the so-called low-temperature commercial refrigeration, possesses an NBP of −46.2 °C, and that of its natural alternatives, R717 and R290 are −33.3 and −42.1, respectively (in the case of R744 the sublimation temperature at 1 bar is −78.5 °C). Moreover, it is important that the alternative ULT refrigerant possesses an acceptable vapor density at these temperatures to reduce the required compressor size.

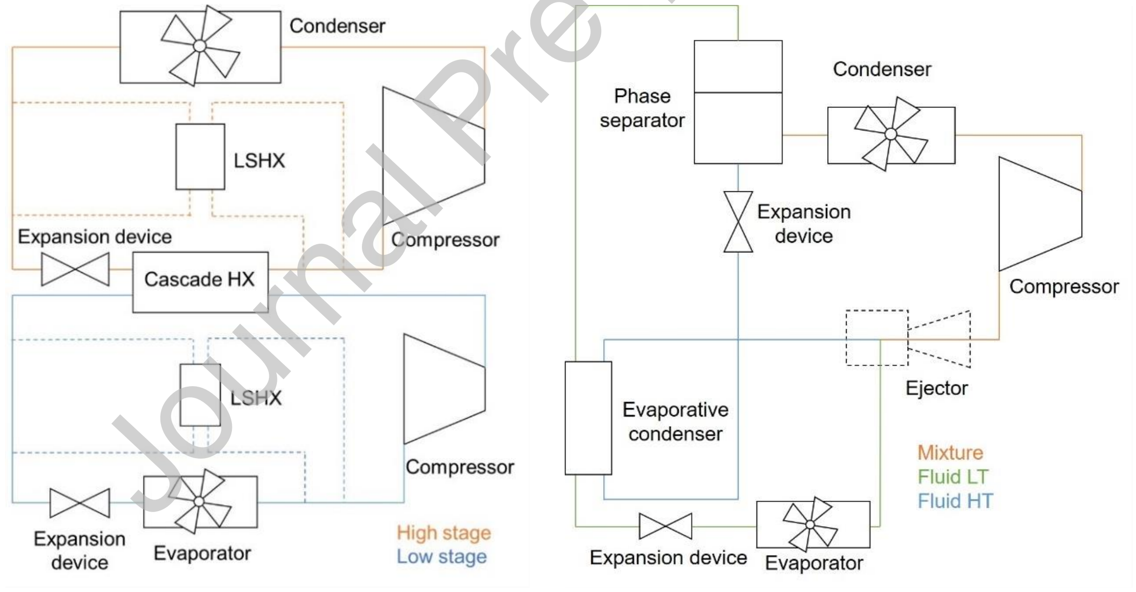
According to the classification of Calm (2008) for general RACHP systems, the ozone-depleting R13 (commercialized since 1945) and R503 (R13/R23, 60/40 wt.%) would be considered as the second generation refrigerants for ULT refrigeration; and R23 and R508B (R23/R116, 46/54 wt.%) (Cook, 1996; Sözen et al., 2007) would be included within the third generation (ASHRAE, 2014). The main emissions of R23 arise as it is an unwanted and potent by-product of R22 production (Velders et al., 2015), which is also included in Annex F, Group II of the Kigali Amendment (Polonara et al., 2017). It should be mentioned that R14, with an NBP of −127.8 °C, could be used for lower temperatures than R13; however, its GWP value is very high (about 6400).

R23 or R508B can be retrofitted in R13 systems considering the resulting suitable discharge temperatures. Note that R23 and R508B are still present in commercialized applications, and even the US EPA SNAP includes them as possible candidates for ULT refrigeration. However, due to their very high GWP values, the expected price increase and availability reduction for environmental protection, they must be soon replaced from the ULT refrigeration industry if candidates or technologies are developed and available.

3. System configurations

3.1. Multi-stage cascade systems

The most common architecture for ULT refrigeration is the two-stage cascade cycle (see Figure 4a), using two different refrigerants thermally coupled by a heat exchanger (denoted by cascade HX in the figure) that acts as an evaporator for the high stage (HS) refrigerant and condenser for the low stage (LS) one (Stegmann, 2000). Cascade systems are effective in those applications where high pressure ratios must be covered; therefore, they can be found in commercial refrigeration for food freezing (Llopis et al., 2015) or high-temperature heat pumps (Mota-Babiloni et al., 2018). Overall, in multi-stage cascade refrigeration, the refrigerant at each stage should be selected according to its NBP (Luyben, 2017).



a) b)

Figure 4. Configurations for ULT refrigeration: a) cascade (dashed with LSHX), and b) auto-cascade (dashed with ejector).

Several studies have been conducted on cascade refrigeration systems including control, performance evaluation, etc. However, they have not been necessarily focused on ULT refrigeration. In this section, those studies on ULT refrigeration or whose outcomes can be extended to ULT refrigeration are briefly presented.

The dynamic control of a three-stage cascade ULT refrigeration system indicates that it can be effective against secondary fluid flowrate disturbances (Johnson et al., 2017). Moreover, energetic and exergetic investigation of an evaporation temperature down to −60 °C revealed that an optimal LS condenser temperature exists (Sun et al., 2016). The exergetic performance coefficient (EPC) criterion applied to a cascade cycle with R23 in the LS showed that the best refrigerant for HS is R717, compared to R290, R404A and R507 (Ust and Karakurt, 2014). Simulating different refrigerants for −40 °C refrigeration using R23 in the LS indicated that R717 was efficient in the HS at limited ranges of polytropic efficiency and temperature difference, and the utilization of R152a and R134a resulted in intermediate performance (Kilicarslan and Hosoz, 2010). An improper pressure adjustment in the compressor suction can cause fluctuation in temperatures and pressures and that vacuum operation must be avoided to prevent lubrication oil evaporation. Note that these results were concluded experimenting an R22/R23 cascade (Chung et al., 2005). Moreover, better performance of R717 and R508B has been reported instead of R12 and R13 (Agnew and Ameli, 2004). Theoretical and experimental investigation of a dual running mode cascade refrigeration cycle (LS can be operated alone or with the HS) was conducted by Liu et al. (2012). They observed a lower system COP under LS independent operation. Therefore, methods to increase COP were proposed, including a bypass between the inlet and outlet of the condenser-evaporator.

Recent studies on cascade systems for different vapor compression applications have been reviewed by Boahen and Choi (2017). They highlighted that the optimization of design parameters is essential for maximum performance. In this way, the lowest possible temperature difference in the cascade heat exchanger is recommended if the cost is assumable in commercial refrigeration (Llopis et al., 2015). Note that refrigerant charge for both stages play a key role in COP and cooling capacity, being worse when undercharged than overcharged (Chae and Choi, 2015). Although cascade architecture can be commonly found in commercial applications of ULT refrigeration, the recently published papers that study this configuration focus more on higher evaporation temperatures. However, conclusions reached can also be extended to ULT refrigeration which are presented in this section.

A multi-objective optimization considering economic, exergetic and environmental aspects besides evaluation of the inherent safety level of a cascade refrigeration system has been conducted by Eini et al. (2016). The utilization of HCs was detrimental for safer operation compared to the toxic R717. Therefore, most cascade refrigeration systems for low-temperature refrigeration usually use R744/R717 (Gupta et al., 2016). Consequently, regression analysis was conducted for setting optimum thermodynamic parameters of the R744/R717 cascade system (Getu and Bansal, 2008). Mumanachit et al. (2012) selected second law efficiency and total annual cost as design objectives. They observed that HS subcooling and LS superheating degrees have a negligible influence on cycle equipment cost and that condenser temperature and temperature difference in the cascade heat exchanger require a trade-off between problem objectives. Finally, multi-objective optimization results indicated that using R1234yf instead of

R717 reduces the operating cost while increasing the second law efficiency (Turgut and Turgut, 2018).

3.2. Auto-cascade systems

Another less common architecture in small capacity packaged ULT refrigeration systems is known as (internal) auto-cascade (ASHRAE, 2014) (see Figure 4b). In this configuration, a mixture composed of two refrigerants with very different boiling points is used, so that these fluids condense and evaporate in different components. A system originally designed for conventional refrigeration using a pure refrigerant was retrofitted to use mixed refrigerants to reach an evaporation temperature of −95 °C (Oh et al., 2016). About 4% reduction was achieved for the electrical power consumption. An auto-cascade refrigeration system using R23/R134a (33.4/66.6 wt.%) was modeled to reach the target evaporator inlet temperature of −87 °C (Hugh et al., 2013). A new optimization approach has been developed for cascade and auto-cascade refrigeration cycles using centrifugal compressors (Montanez-Morantes et al., 2016), which eliminate the lubricating oil problems. It was concluded that the achievable savings depend on the complexity of the cycle but around 3% savings can be achieved in shaft work demand by just changing the operating conditions. As of today, the lowest evaporating temperature has been experimented by the auto-cascade prototype of Aprea and Maiorino (2009).

The auto-cascade refrigeration cycles have recently been modified to use an ejector to reduce the thermodynamic losses in the throttling process. The optimum composition of the mixture and vapor quality at the condenser outlet must be considered to maximize the COP (Yan et al., 2015). Notable improvements were reported in the COP, exergetic efficiency and especially volumetric cooling capacity in a theoretical study considering R290/R170 (Liu et al., 2018). Further experimental work confirmed COP and volumetric refrigeration capacity enhancement up to 80.0 and 78.5%, respectively. Utilization of R134a/R23 (70/30 wt.%) reached COP and exergy efficiency improvements up to 9.6% and 25.1%, respectively (Bai et al., 2018).

3.3. Sublimation cycles

It is worth mentioning that ULT refrigeration can be reached in solid-gas sublimation cycles for instance using R744, a low toxicity, nonflammable and very low GWP refrigerant. In this configuration, the low pressure phase change takes place below the triple point of R744, at 420 kPa and −56.6 °C; therefore, the phase change is from solid to gas. Huang et al. (2008) described the working principle and design requirements of this cycle, and theoretically proved that the system COP can be enhanced by 50%. Chen and Zhang (2014) analyzed the available state-of-the-art regarding the status of this type of systems, including the existing problems in theoretical, numerical and experimental methods, multi-scale problems, new applications and recommendations for future work.

4. Low-GWP alternative fluids

4.1. Introducing remarks about ULT alternative refrigerants

Figure 5 (Calm, 2008) shows generations of refrigerants indicating that the next generation is going to be based on low GWP refrigerants such as R41, R1132a, R170 and R1150. A chronological summary of the refrigerants used in ULT studies presented in this paper are shown in Table 1 and the Ph diagram with the saturation lines is shown in Figure 6. The table clearly shows the trend away from old generation refrigerants (for instance R13) towards more environmentally friendly ones. Moreover, the alternatives chosen before to cover ULT refrigeration were nontoxic and no flame propagation refrigerants; hence, classified as A1 by the ANSI/ASHRAE Standard 34 (ASHRAE, 2016). A graphical summary of different parameters of interest compared to traditionally used refrigerants is shown in Figure 7. Note that the alternative fluids discussed in this study for ULT refrigeration are shown in bold in Appendix I.

Table 1: Chronological summary of studies on ULT refrigeration

Year	Study		System	Refrigerant *									Reference
	Experimental	Theoretical	(maximum cooling capacity, minimum evaporation temperature)	CFC	HCFC	HFC	HC	HO	HFO	Other natural	Other	Mixture $^{\%}$	
1996		✓	Two-stage cascade system (N.A., −73 °C)		R503	R508B						R23/R116/R744	(Cook, 1996)
2000		✓	Two-stage cascade system (708 kW, −65 °C)		R22	R23 R134a R507 R508B				R717			(Stegmann, 2000)
2004		✓	Three-stage cascade system (N.A., −73 °C)	R12 R12 R13		R508B				R717 R717			(Agnew and Ameli, 2004)
2005	✓		Two-stage cascade system (N.A., −85 °C)		R22	R23							(Chung et al., 2005)
2007	✓		Two-stage cascade system (0.7 kW, −68 °C)	R13			R290					R290/R744	(Niu and Zhang, 2007)
2008		✓	Two-stage cascade system (N.A., −50 °C)							R717 R774			(Getu and Bansal, 2008)
2008		✓	Two-stage cascade system (N.A., −80 °C)		R22	R23	R290 R170						(Xie et al., 2008)
2009	✓		Two-stage cascade system (0.45 kW, −85 °C)			R404A						R23/R170 R116/R170 R23/R116/R170	(Gong et al., 2009)
2009	✓		Auto-cascade system (N.A., −150 °C)			NA						R507/R245fa/R116/R23/R14/ R740/R290/R50/R740	(Aprea and Maiorino, 2009)
2010		✓	Two-stage cascade system (1 kW, −65 °C)			R23 R134a R152a R404A R507	R290			R717			(Kilicarslan and Hosoz, 2010)
2011		✓	Two-stage cascade system (N.A., −60 °C)							R717		R170/R744 RE170/R744 R290/R744 R1150/R744 R1270/R744	(Di Nicola et al., 2011)
2012	✓		Two-stage cascade system (0.4 kW, −65 °C)		R22	R23							(Liu et al., 2012)

2013	✓	✓	Two-stage cascade system (1.4 kW, −75 °C)	R134a R23						(Hugh et al., 2013)
2013		✓	Two-stage cascade system (337 kW, −70 °C)		R170	R1150	R717	R744A		(Sarkar et al., 2013)
2015	✓		Two-stage cascade system (N.A., N.A.)	R134a R152a R410A						(Chae and Choi, 2015)
2016		✓	Two-stage cascade system (10 kW, −60 °C)	R23 R41 R404A						(Sun et al., 2016)
2016		✓	Two-stage cascade system (N.A., −56 °C)		R290		R717 R774			(Eini et al., 2016)
2018		✓	Two-stage cascade system (10 kW, −60 °C)	R41 R161 R404A	R170					(Roy and Mandal, 2018)
2018	✓		Cascade system with ejector (N.A., −96 °C)		R170 R290					(Li et al., 2018)
2018		✓	Auto-cascade system (N.A., −71 °C)		R170/R290					(Yan et al., 2015)
2018	✓		Auto-cascade system with ejector (N.A., −50 °C)	R134a/R23						(Bai et al., 2018)
2018		✓	Auto-cascade system with ejector (N.A., −69 °C)		R290/R170					(Liu and Yu, 2018)
2018		✓	Auto-cascade system with ejector (N.A., −73 °C)		R290/R170					(Liu et al., 2018)
2018	✓	✓	Two-stage cascade system (N.A., −85 °C)						Blends including R1132a	(Low, 2018)

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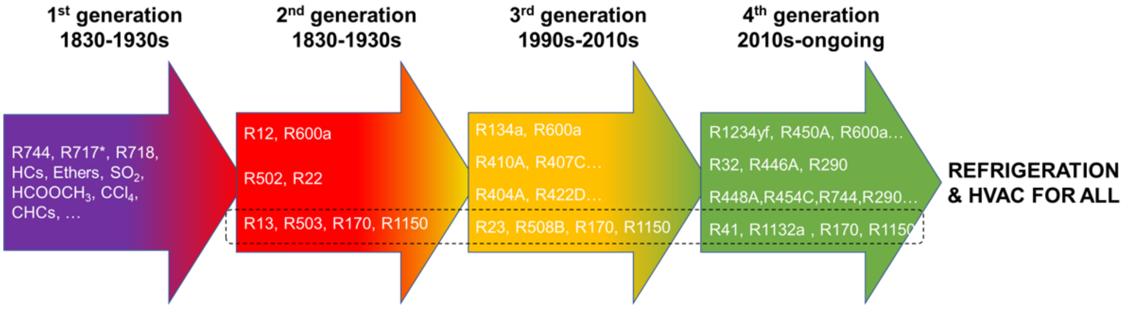
[*] The base refrigerants are shown in bold. The color code is red, green and blue for HS, IS and LS, respectively.

[%] Mixture refers to refrigerants with different types. In other words, for instance, a mixture of two HC refrigerants is presented as HC.



*R717 always dominated large capacity industrial refrigeration

Figure 5. Generation of refrigerants, highlighting ULT refrigeration. Adopted from (Calm, 2008)

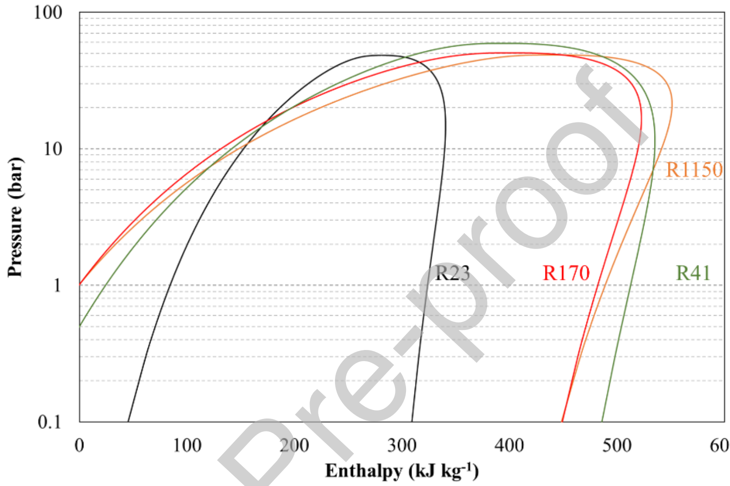
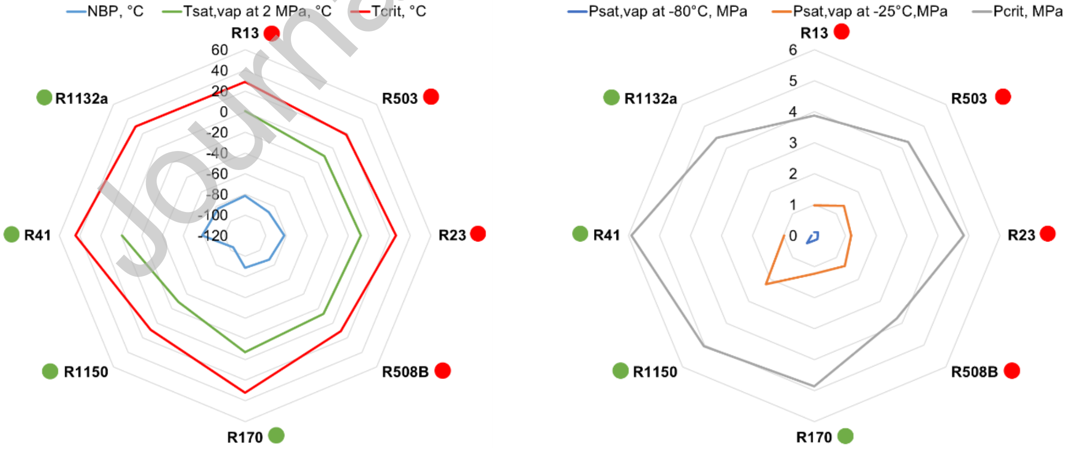


Figure 6. Pressure-enthalpy (Ph) diagram of the low GWP refrigerants for ULT refrigeration



a)

b)

Figure 7. Representative a) temperatures and b) pressures of ULT refrigerants (red and green symbols represent higher and lower GWP refrigerants, respectively).

The transition for high GWP refrigerants in ULT systems will depend on the application and the possibility of utilizing refrigerants with some degree of flammability (classified by ASHRAE). If the application allows highly flammable refrigerants, the transition will face less difficulties as HCs are immediately available. They merely require proper adaptation of the system to this type of refrigerants. However, ULT refrigeration applications which do not allow highly flammable refrigerants are going to be disadvantaged. The situation is even worse if a refrigerant with no flame propagation is required. Under these circumstances, no conventional or direct solution could be used. In this section, natural and synthetic alternative refrigerants are discussed.

4.2. Natural refrigerants

Natural refrigerants are environmentally friendly alternatives to HFCs because of their lower GWP values. They have been considered from the beginning of the development of modern refrigeration (Abas et al., 2018). Among the most extensively used natural refrigerants for common RACHP applications, typical HC refrigerants of R600a, R290 and R1270 can be highlighted. However, their NBPs are not suitable for ULT refrigeration (see Appendix I).

Nevertheless, NBP values of R170 and R1150 are −88.6 and −103.8 °C, respectively. Therefore, they can be utilized in the LS of cascade ULT refrigeration, or as a component in mixed refrigerants for auto-cascade system. Note that, R170 has fewer direct uses and is less readily available, but R1150 is widely used (Adamson, 2006).

R170 and R1150 were typically not included in previous studies that cover several HCs in most extended refrigeration applications. In a general review for natural and synthetic refrigerants, R170 is classified as a flammable cryogenic fluid because of its NBP (together with R50 with an NBP of −161.5 °C), recommending it to be used for sealed hermetic low-temperature applications (Abas et al., 2018). It was also mentioned that R170 presents optimal lower pressure ratio and higher isentropic as well as volumetric efficiency over other refrigerants. Moreover, it was stated that R1150 has not been deeply studied due to its very low critical temperature (see Appendix I), making it inappropriate for normal refrigeration cycles. In another study, only typical HCs of R600a, R290 and R1270 were included in the review of sustainable solutions (Ciconkov, 2018). It highlights that systems which use CFCs can work with HCs without significant modifications because they are compatible with copper and they are miscible with mineral oils (Joybari et al., 2013). In the review of ecological alternatives, R170 was only mentioned in a general properties table and then reporting its use in two mixtures, with R717 and with R290 (Sarbu, 2014). In a specific review for HCs, R170 was only included in three general tables (Harby, 2017), and it was reported suitable for low temperature commercial equipment (sealed hermetic units, accessible semi-hermetic and reciprocating open drive compressor types) and large commercial and industrial (both in reciprocating open drive and screw compressor types) sectors.

A generally named drawback of HCs is their high flammability, which nonetheless, has been exhaustively researched but not for ULT refrigeration. European LIFE FRONT (Flammable Refrigerants Options for Natural Technologies) project (Skačanová et al., 2018) investigated the current and potential use of HCs and the impact of standards on the charge limits. However, this study was limited to typical HCs of R290, R600a and R1270, used at different conditions. An overview of the current situation and evolution of the available international and European standards for the use of HCs as refrigerants in typical RACHP applications has been provided by Corberán et al. (2008). According to this work, the real risk of using higher HC charges is lower than that of fire for many other appliances. The performance of typical HCs (R290, R1270 and R600a) was compared to R22, R134a and R717 in small heat pumps (Palm, 2008). Some methods were recommended to reduce the flammability risk including minimum charge systems, leak detection during production, hermetic design with a minimum number of connections, use of spark-proof electric components and ventilation of confined spaces. The only scientific article that specifically studied the flammability of these non-typical HCs was carried out by Palm (2008). The lower flammability limit (LFL) and upper flammability limit (UFL) of R1150 were experimentally investigated. The results showed that the flammability range shrank 3.42% from 55 to −5 °C. Moreover, LFL increased less than 0.1 and UFL reduced 0.87 in volume fraction when humidifying the air to 42.4%.

A well-known method to reduce the flammability risk of HCs and extend their use is to improve their heat transfer performance in condenser and evaporator. The pool boiling heat transfer of low GWP alternatives on enhanced surfaces was reviewed by Lin and Kedzierski (2019), but neither R1150 nor R170 was included. However, their overview of the predictive methods can be useful to size compact heat exchangers with small refrigerant charge and a large heat exchange area. The refrigerant charge optimization for R290 (Ghoubali et al., 2017) through different types of condensers can be also profitable in ULT refrigeration. Condensers with high thermal efficiency and low internal volume can reduce the charge to extremely low levels, for example by reducing the diameter of distributors (which penalize microchannels heat exchangers) and liquid lines, compressors with POE oil and modifying the layout of the condenser heat exchange surface.

In recent years, the heat transfer phenomena of R170 were covered in a few studies. For instance, the effects of mass flux and saturation pressure on the two-phase flow pattern transitions in a horizontal smooth tube was investigated (Zhuang et al., 2016b). Nucleate pool boiling heat transfer characteristics (including bubble departure diameter and frequency, and available correlations) of R170, R600a and their binary mixtures were experimentally studied on a horizontal flat surface under various pressures and heat fluxes (Gong et al., 2013). As in other mixtures, the heat transfer coefficient is penalized. Then, a flow boiling heat transfer correlation shows very good agreement with 733 data points for the R50/R170 mixture (Zou et al., 2015). Finally, condensation characteristics of R170 were studied experimentally in a 4 mm horizontal tube and compared with several correlations (Zhuang et al., 2016a).

There are few studies available on the performance of non-typical HCs in the abovementioned typical architectures. Adamson (2006) exposed the details of two systems used for different applications of cascade ULT refrigeration using R1150 in the LS, one for a small direct expansion system using scroll compressors (ISO VG32 POE oil), and another one for a large system with flooded evaporators and oil-flooded screw compressors with VG68 synthetic HC oil (to control discharge temperature caused by high specific heat ratio). Application of R1150 at the −100 °C level is recommended in multi-stage cascade system (Luyben, 2017). R290/R170 cascade was proposed to replace R22/R23 (Xie et al., 2008), due to the comparable COP especially at lower condensing and evaporating temperature conditions and that their lower mass flow ratio allows a reduction in flammability risk. Theoretical analysis and intermediate temperature optimization of a cascade system was conducted using R170 and R1150 in the LS (Sarkar et al., 2013). Compared to other selected refrigerants, R170 had superior performance in terms of COP but not regarding volumetric cooling capacity compared to R744A, but its very low GWP favors it. It is worth mentioning that the internal heat exchanger considerably favors R170. An R290/R170 cascade refrigeration system with ejector as the expansion device was theoretically investigated (Liu and Yu, 2018). The system with ejector was found to have superior performance in terms of COP and cooling capacity compared to the one without ejector. Moreover, a similar system with ejector was experimentally studied by Li et al. (2018). It was found that the electric energy consumption of the new system was 4.77% lower than that of the original freezer at the ambient temperature of 25 °C.

Motivated by the high flammability of these fluids, some mixtures have been proposed. An advantage of HC mixtures is that they can be used without replacing the lubricant in the existing HFC or HCFC systems (Sarbu, 2014). The azeotropic mixtures of R170/R23, R170/R116 and R170/R23/R116 were investigated in the LS of a cascade system and compared to R508B while using R404A at the HS (Gong et al., 2009). COP of the R170/R116 mixture was up to 10% higher than that of R508B, but R170/R23/R116 mixture had the highest cooling capacity. Besides, using pure R744 in the HS, pure as well as mixtures of R170/R744 were used in the LS (Jemni et al., 2015). It was found that R170 could achieve COP values close to R744. In addition, R170/R23 mixture showed azeotropic behavior. R170, R1150 and other HCs were mixed with R744 in the LS of a cascade refrigeration system using R717 at the HS with and without internal heat exchanger (Di Nicola et al., 2011). When mixed, the COP was reduced especially in the case of R170, and when using internal heat exchanger. To prevent solidification (operation near triple point), the maximum content of R744 in the mixtures should be 50 wt.%.

These refrigerants can be also mixed to be used in auto-cascade or mixed refrigerant systems. For instance R290/R170 azeotropic mixture has been proposed for ULT applications (Liu et al., 2018). A complementary theoretical analysis concluded that for a given condition an appropriate mixture quality exists having the highest COP and refrigerating capacity (Yan et al., 2018). Moreover, it has been proposed to replace the pure R1150 refrigeration cycle by an auto-cascade using R50, R170, R290 or R728 (Mafi et al., 2009). Two refrigerant mixtures of R50/R1150/R290 and R170/R1150/R1270 have also been proposed (Oh et al., 2016).

It should be mentioned that R744A (GWP of approximately 240), previously mentioned in the study of (Sarkar et al., 2013), is a potential refrigerant to substitute R23. In a two-stage system, similar COP to R23/R134a cascade was achieved at low condensation temperatures and with intermediate injection (Kruse and Rüssmann, 2006). Kauffeld and Maurath (2019) recently studied the R744/R744A refrigerant mixture for applications in which R170 and R1150 cannot be used. They designed a prototype with different lubricants and the energy efficiency was found comparable to commercially available HFC systems at evaporation temperatures down to −80 °C. They also proposed measures to avoid R744A decomposition.

4.3. Synthetic refrigerants

Low (2018) presented R1132a as an alternative refrigerant in ULT refrigeration systems. R1132a belongs to the family of recently commercialized HFOs as R1234yf and R1234ze(E) (Barker et al., 2016), being significantly more stable than other fluorinated ethenes. The flammability range of R1132a is between 6 and 23% by volume at 23 °C and 50% relative humidity. The linear burning velocity of R1132a at 20 °C in dry air in a vertical tube apparatus is approximately 20 cm/s; hence, it is included in A2 safety group by ASHRAE Standard 34 (Low, 2018).

The work of Low (2018) was the first to present this fluid as a possible alternative for ULT refrigeration systems. A few studies are available in the literature on R1132a, which mostly focused on its properties, among other refrigerants. Bruno and Caciari (1994) studied the retention characteristics of eleven ethene-based CFC, bromochlorofluorocarbon (BCFC) and fluorocarbon fluids. The next work that considers it was conducted in 2013, when the Design Institute for Physical Properties (DIPPR) database (American Institute of Chemical Engineers AIChE, 2017) was used for 58 refrigerants to prove that ideal gas contribution to the isobaric heat capacity is a temperature dependent property and check the performance and accuracy of a well-known polynomial correlation (Mulero et al., 2013). They later included R1132a to validate an Artificial Neural Network (ANN) model for the calculation and prediction of surface tension along the liquid-vapor interphase (among 76 refrigerants) (Mulero et al., 2017), to propose a new corresponding-states correlation (CSP) model for the surface tension calculation of refrigerants based on the temperature and surface tension values at the triple point (among 83 fluids considered) (Cachadiña et al., 2017) and another model whose inputs include the temperature and surface tension values at the boiling point (among 80 fluids). Besides, R1132a was also considered for a new semi-empirical scaled correlation for the second virial coefficient of refrigerants, based on the CSP model (Di Nicola et al., 2016). 63 refrigerants with different chemical structures were selected. Then, they were included (number of data was 11) in a list of 14 halogenated alkene refrigerants to analyze the available experimental surface tension data with the most reliable semi-empirical correlation models, based on the CSP model (Di Nicola et al., 2018). In these studies, the Absolute Average Deviation (AAD) with R1132a was greater than other commonly used HFOs, highlighting that limited data is available for these fluids.

R1132a is an example of HFOs that were timely permitted to retrofit the widespread systems with low GWP refrigerants (Abas et al., 2018). An initial thermodynamic and environmental screening (Kazakov et al., 2012) looking for suitable low GWP candidates for refrigeration systems was extended (McLinden et al., 2014). From 56203 compounds, R1132a was among the list of 62 qualifying candidates that passed all the screening filters. However, due to its Relative Exposure Limit (REL) of 1 ppm (NIOSH National institute for occupational safety and health, 2017) making it toxic, R1132a was not included in a posterior more extended analysis (McLinden et al., 2017). Then, when studying low-GWP refrigerants for medium and high-pressure applications (Domanski et al., 2017), R1132a was not simulated because it would be in near-critical or supercritical operation in the condenser. R1132a with an exposure limit of 500 ppm (ACGIH, 2008; Domanski et al., 2017) has been classified in A2 safety group according to ASHRAE Standard 34 (ASHRAE, 2016).

R1132a is potentially unstable in contact with certain materials and the addition of a stabilizer makes it unsuitable for use in refrigeration systems as pure substance. Thus, R1132a is proposed for ULT refrigeration as a component of blends with low NBP (Domanski et al., 2017), for instance, the mixture of R1132a with a second component selected from the group consisting of R116, R170 and their mixtures, and optionally R744 (Low and Sharratt, 2016). R1132a/R170 binary mixture exhibits larger cooling capacity and COP (at −85 °C evaporating temperature) than pure R170, R508B or when R1132a is blended with R116 (Low, 2018).

Another refrigerant that has appeared as alternative in ULT refrigeration is R41 with zero ODP and low GWP (i.e. 116). It can be adopted for most common ULT applications. Theoretical analysis of R41 as a substitute for R23 in the LS of a cascade system (with R404A in the HS) proved higher COP values (Sun et al., 2016). However, compared to R170, the COP results were lower, while the power consumption and exergy losses were higher (Roy and Mandal, 2018). It has been considered as an alternative to R22 in marine RACHP systems (Zakrzewski and Łokietek, 2010). However, the total CO_2-eq. emissions were found to be one of the highest of all refrigerants considered because of lower COP values seen under the higher temperature conditions proposed in that study. In a two-stage cascade configuration, R41/R161 pair resulted in higher COP and thermodynamic performance for evaporation temperatures above −60 °C, being more convenient than R170 (Sun et al., 2019b). Then, considering a three-stage cascade system, R41 and R170 were recommended to replace R23 in the intermediate stage, with R1150 in the LS at evaporating temperatures down to −120 °C (Sun et al., 2019a).

R41 flammability is problematic for its utilization in ULT refrigeration. One strategy is to minimize its charge through more compact heat exchangers. R41 possesses the highest condensation heat transfer coefficient and the lowest pressure drop among a set of selected refrigerants (Guo et al., 2018). Besides, R41 can be mixed with other non-flammable refrigerants, as for instance R744, allowing operation in high ambient temperatures and avoid solid formations, excessive pressures and pressure ratios. R41/R744 (50/50 wt.%) is a potentially nonflammable azeotropic mixture that maximizes the critical temperature and matches the saturated pressure-temperature characteristics and refrigerating capacity of existing refrigerants within this range (Cox et al., 2008). This mixture was proposed also in heat pumps substituting pure R744 (Wang et al., 2017). It has to be pointed out that in recent years, flame retardants and fire inhibitors for A2 and A2L refrigerants (e.g. R32 and R1234yf) received attention (Wu et al., 2019; Yang et al., 2012). These investigations could be extended to the both synthetic alternatives (i.e. R41 and R1132a).

5. Conclusions

Regulation (EU) No 517/2014 has not established GWP limits for the working fluids used in refrigeration systems that operate below −50 °C, also known as ULT refrigeration systems. However, the high GWP values of the common refrigerants can significantly increase their price or even limit their availability due to quota enforcement in the European Nations and around the world (according to Kigali Amendment). The aim of this paper is to present the recent developments in ULT refrigeration systems and working fluids, and to guide future research. Overall, the pace of research advancement is slower than other mechanical cooling applications.

The range of proper refrigerants is quite reduced because of the relatively low evaporation temperature requirement, which must be above the normal boiling point of the fluid. Hence, commonly used refrigerants such as R134a, R404A, R410A and their low GWP alternatives are not useful. When HC alternatives are not permitted due to the refrigerant charge restrictions, the chlorine-free synthetic fluids R23 and R508B are typically used in these systems. However, they possess significantly high GWP values, much greater than refrigerants used in other applications.

The significant temperature slope between the evaporating and condensing (above ambient) temperatures causes significantly high compression ratios that must be reduced using more advanced architectures than single stage. While cascade cycles are most commonly used (and the research continues to obtain more efficient ones), auto-cascade cycles also appear as a solution but are mostly considered for lower operating temperatures. Optimization of design and operating parameters, and selection of the refrigerant pair or mixture is critical for reaching the maximum energy efficiency. Conclusions reached from other RACHP applications can be applied for the performance enhancement of ULT cascade refrigeration systems.

Currently, among HC refrigerants, R170 and R1150 are the best solutions when their flammability is not a problem and the required refrigerant charge is not restricted. They have very low direct environmental impact and could be combined with lower or non-flammability refrigerants in the HS of cascade systems. R1132a, an A2 HFO, has been recently considered but the available information is still limited to the characterization of its thermodynamic properties and designing optimized cycles and components. R41 is another refrigerant but presents some limitations. All these alternative refrigerants have presented promising energy results in theoretical simulations in advanced UTL refrigeration configurations, but additional experimental research is needed to characterize their behavior and reliably dominate the market.

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Declaration of interests

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.

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Appendix I. Refrigerant properties [#]

Type	Refrigerant	Chemical name/composition	ODP	$GWP_{100\text{-yr}}$ (CO_2-eq)	ASHRAE safety group	NBP (°C)	Latent heat (kJ/kg) [*]	Molecular weight (kg/mol)	Critical temp. (°C)	Critical press. (MPa)	OEL (ppm)	RCL (ppm)	Oil type
CFC	R12	Dichlorodifluoromethane	0.73	10,200	A1	−29.75	185.38	120.91	111.97	4.14	1,000	18,000	AB, MO
	R13	Chlorotrifluoromethane	1.00	13,900	A1	−81.48	148.63	104.46	28.85	3.88	1,000	N.A.	AB, MO
HCFC	R22	Chlorodifluoromethane	0.03	1,760	A1	−40.81	256.83	86.47	96.15	4.99	1,000	59,000	AB, MO, POE,
HFC	R23	Trifluoromethane	0	12,400	A1	−82.02	237.71	70.01	26.14	4.83	1,000	41,000	POE
	R32	Difluoromethane	0	677	A2L	−51.65	410.70	52.02	78.11	5.78	1,000	36,000	POE
	R41	**Fluoromethane**	**0**	**116**	**A2**	**−78.31**	**490.19**	**34.03**	**44.13**	**5.90**	**N.A.**	**N.A.**	**POE**
	R134a	1,1,1,2-tetrafluoroethane	0	1300	A1	−26.07	249.67	102.03	101.06	4.06	1,000	50,000	PAG, POE, PVE
	R152a	1,1-difluoroethane	0	138	A2	−24.02	375.25	66.05	113.26	4.52	1,000	12,000	POE
	R161	Fluoroethane	0	4	A3	−37.55	467.54	48.06	102.10	5.01	1800	N.A.	AB, POE,
	R245fa	1,1,1,3,3-pentafluoropropane	0	858	B1	15.14	246.36	134.05	154.01	3.65	300	34,000	POE
	R404A	R143a 52%, R125 44%, R134a 4%	0	3800	A1	−46.22	221.35	97.60	72.12	3.73	1,000	130,000	POE
	R503	R13 60%, R23 40%	0.60	13,600	A1	−87.76	173.35	87.25	18.33	4.27	1,000	N.A.	MO, POE
	R507	R125 50%, R143a 50%	0	4,000	A1	−46.74	217.31	98.86	70.62	3.70	N.A.	N.A.	POE
	R508B	R116 54%, R23 46%	0	13,396	A1	−87.60	160.36	95.39	11.20	3.77	1,000	52,000	POE
PFC	R14	Tetrafluoromethane	0	6,630	A1	−128.05	98.17	88.01	−45.64	3.75	1,000	110,000	PAO
	R116	Hexafluoroethane	0	11,100	A1	−78.09	117.80	138.01	19.88	3.05	1,000	97,000	N.A.
HC	R50	Methane	0	28	A3	−161.48	N.A.[$]	16.04	−82.59	4.60	1,000	N.A.	N.A.
	R170	**Ethane**	**0**	**5.5**	**A3**	**−88.58**	**477.76**	**30.07**	**32.17**	**4.87**	**1,000**	**7,000**	**AB, MO, POE**
	R290	Propane	0	<1	A3	−42.11	462.41	44.10	96.74	4.25	1,000	5,300	AB, MO, POE
	R600a	Isobutane	0	<1	A3	−11.75	419.57	58.12	134.66	3.83	1,000	4,000	AB, MO, PAG, PAO, POE
HO	**R1150**	**Ethene (ethylene)**	**0**	**4**	**A3**	**−103.77**	**444.77**	**28.05**	**9.20**	**5.04**	**200**	N.A.	**AB, MO, POE**
	R1270	Propene (propylene)	0	<1	A3	−47.62	472.63	42.08	91.06	4.55	500	1,000	AB, MO, POE
HFO	**R1132a**	**1,1-difluoroethylene**	**0**	**<1**	**A2**	**−82.81**	**N.A.**	**64.00**	**29.66**	**4.46**	**500**	**13,000**	**POE**
	R1234yf	2,3,3,3-tetrafluoropropene	0	<1	A2L	−29.45	N.A.[^]	114.04	94.70	3.38	500	16,000	PAG, POE
	R1234ze(E)	1,3,3,3-tetrafluoropropene	0	<1	A2L	−18.97	228.53	114.04	109.36	3.63	800	16,000	POE
Other natural	R717	Ammonia	0	0	B2L	−33.33	N.A.[^]	17.03	132.25	11.33	25	320	AB, MO, PAG, PAO
	R728	Nitrogen	0	0	A1	−195.80	N.A.[$]	28.01	−146.96	3.40	N.A.	N.A.	N.A.
	R740	Argon	0	0	A1	−185.85	N.A.[$]	39.94	−122.46	4.86	N.A.	NA	N.A.
	R744	Carbon dioxide	0	1	A1	−78.46	N.A.[^]	44.01	30.98	7.38	5,000	30,000	PAG, PAO, POE
	R744A	Nitrous oxide	N.A.	265	N.A.	−88.47	364.56	44.01	36.37	7.25	N.A.	N.A.	N.A.

[#] (ASHRAE, 2016; Lemmon, E.W., Bell, I.H., Huber, M.L., McLinden, 2018; Low, 2018; Myhre et al., 2013; UNEP, 2019)

[*] Evaluated at an evaporating temperature of −80 °C

[$] Temperature greater than critical temperature

[^] Lower than the limit available in REFPROP 10.0