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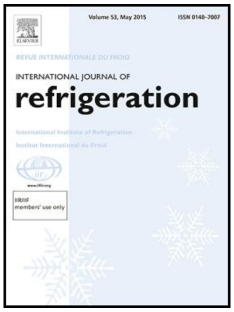

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Recent investigations in HFCs substitution with lower GWP synthetic alternatives: focus on energetic performance and environmental impact

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HIGHLIGHTS

Recent investigations in HFCs substitution with lower GWP synthetic alternatives: focus on energetic performance and environmental impact

- More studies about lower GWP refrigerants are needed to facilitate the phase-out HFCs.
- HFO studies are mostly found in MAC and domestic refrigerators.
- Stationary refrigeration equipment presents the major variety of studies.
- Multipack centralized refrigeration systems studies are being dominated by CO_2 (R744).
- R32 is limited by the discharge temperature and injection cycles are needed.
- Mixtures could help to overcome pure fluids handicaps.

Abstract

Kigali's amendment on Montreal Protocol has recognized the great impact of hydrofluorocarbons (HFCs) on climate change. In the European Union, the Regulation (EU) No 517/2014 (F-gas Regulation) controls the use of HFCs in several applications. This paper reviews the recent investigations performed because of F-gas Regulation, with focus on lower global warming potential (GWP) synthetic alternatives. The GWP limit and the date of prohibition have an influence on the studies found for each application. The major relevance of studies has been observed on mobile air conditioners for pure hydrofluoroolefins (HFOs), possibly caused by the earlier control. Additionally, a great number of studies have been found for stationary refrigeration systems using several mixtures and residential air conditioners using R32. An important number of articles investigate synthetic alternatives for domestic refrigerators given the flammability barriers for hydrocarbons in some countries. Despite higher GWP allowance on cascade supermarket systems, few articles are available on this topic. Given the extent of the current studies and the rate of new refrigerant developments, an increase in studies using the new synthetic mixture is expected in the coming years.

Keywords
Global warming potential; HFO/HFC mixtures; refrigeration; air conditioning; F-gas regulation.

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Abbreviations

AHRI	Air-Conditioning, Heating, and Refrigeration Institute
AREP	Alternative Refrigerants Evaluation Program
ATEL	Acute Toxicity Exposure Limit (kJ m^{-3})
COP	coefficient of performance
CO_2-eq.	carbon dioxide equivalent
DX	direct expansion
F-gas Regulation	Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006
GHG	greenhouse gas
GWP	Global Warming Potential for 100 years
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
IHX	internal heat exchanger
LT	low temperature
MAC	mobile air conditioning
MT	medium temperature
NA	not availableODL Oxygen Deprivation Limit (kJ m^{-3})
ODP	Ozone Depletion Potential
Q_{evap}	Cooling capacity (kW)
Q_{vol}	volumetric refrigerating capacity (kJ m^{-3})

1. Introduction

Once the hydrochlorofluorocarbons (HCFCs) emissions are approaching zero in Europe (Graziosi et al., 2015), the focus shifted to the hydrofluorocarbon (HFCs) emissions reduction. While the share of HFCs in total greenhouse gasses (GHG) emissions to date is approximately 1%, the consumption of HFCs is increasing at a high rate, contained in existing refrigeration and air conditioning equipment, foams, and other products. It is thus important to phase-down HFCs use in order to mitigate climate change. HFCs phase down is also an opportunity to redesign the existing refrigerating and air conditioning equipment to achieve improvements in their energy efficiency, similar to that achieved during HCFC phase out (Zaelke and Borgford-Parnell, 2015).

In February 2017, the European Commission has adopted a proposal to ratify the Kigali's amendment to the Montreal Protocol to gradually limit the HFCs production and use. A drastic reduction of the consumption of these chemicals would potentially help to maintain global temperature rise well below 2 °C by 2100 (European Commission, 2017). At the European Union level, the HFC phase-down has already started (European Commission, 2017).

The Directive 2006/40/EC (The European Parliament and the Council of the European Union, 2006a) placed the first HFCs prohibition and affected mobile air conditioners (fitted to passenger cars and light commercial vehicles) establishing the GWP limit at 150, below that presented by R134a (1430), the HFC refrigerant most commonly used in Europe in this application. Simultaneously, the Regulation (EC) No 842/2006 has been published with the objective to achieve stabilization of GHG concentrations in the atmosphere at a level that prevents dangerous anthropogenic interference with the climate system (The European Parliament and the Council of the European Union, 2006b). Then, the EU Regulation No 517/2014 (The European Parliament and the Council of the European Union, 2014) (F-gas Regulation) repealed the latter regulation and extended the global warming potential (GWP) limits to most of the refrigeration and air conditioning vapor compression systems. In the F-gas regulation, the GWP values considered are those proposed in the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2007).

The recent statistics reported by the European Commission shows, Figure 1, that the level of HFC placed on EU market in 2015 was within the limits set by the F-gas Regulation (European Commission, 2016a). However, there is a noticeable spike in HFCs placed on the European market in 2014 (measured in megatons of CO_2 equivalent, Mt CO_2-eq.), the last year before F-gas Regulation limited this amount. According to the requirements of the regulation, by the beginning of 2018, the maximum quantity of hydrofluorocarbons to be placed on the market has to be reduced to 63% of the baseline 2009-2012 (by 32% from the currently allowed level). Thus, conventional HFCs replacement with low and lower GWP refrigerants will help to achieve further reduction.

Natural fluids have always been considered in refrigeration and air conditioning systems (Riffat et al., 1997). However, because of different reasons (safety, the cost of equipment, etc.), synthetic fluids had imposed in many of these applications. Now, GWP restrictions have brought another opportunity to the natural refrigerants (Bolaji and Huan, 2013). Several authors have reviewed the particularities of the most relevant natural refrigerants used in vapor compression systems in the last few years. For instance, Bansal (2012) focused on CO_2 low evaporation temperature operation and Ma et al. (2013) in the CO_2 transcritical cycle operation. Despite the safety concerns remaining in some European countries (European Commission, 2016b), Pearson (2008) and Palm (2008), have discussed the opportunities of ammonia and hydrocarbons, respectively, as working fluids.

Apart from the possibility of using available natural refrigerants, researchers and manufacturers should consider low GWP synthetic refrigerant alternatives more reliable and closer to the industry than currently available. It was shown, however, that taking into account stability and toxicity characteristics and suitable thermodynamic properties the limits of chemistry result in only 62 low GWP fluids usable in refrigeration and air conditioning equipment (McLinden et al., 2014), most of which are flammable. From these fluids, none is ideal in all regards and tradeoff should be performed. The refrigerant mixtures could address these tradeoffs because of the resulting intermediate properties, especially flammability and GWP.

Some recently developed low GWP refrigerants and their mixtures have been investigated in a number of works. However, the knowledge about the consequences of the utilization of pure and mixed HFOs in vapor compression systems is still at an earlier stage. Devecioğlu and Oruç (2015) highlight that HFO (hydrofluoroolefin)/HFC mixtures present good characteristics to replace high GWP working fluids but they still require additional investigations to be widely used in the market. Moreover, Sarbu (2014) states that along with the reduced atmospheric warming potential of new refrigerants they should be also as energetically efficient as possible.

Mota-Babiloni et al. (2015a) reviewed the applicability of some developmental working fluids to substitute currently used ones in various refrigeration systems. In the last few years, a substantial number of refrigerants have been commercialized and the search for the most appropriate solution in the different refrigeration and air conditioning sectors is a matter of great importance. In this study, the consequences of the approval of the European F-gas Regulation were analyzed and the focus was given to the possibility of HFCs substitution using the available synthetic refrigerant mixtures. The authors focus on advantages and disadvantages of each refrigerant for the different applications. The conclusions of this paper can be also applied to systems not covered by the F-gas Regulation and thus help in the HFCs phase-down.

The paper starts with the review of the papers for mobile air conditioners and then the structure of the paper follows the classification proposed in Annex III of the EU Regulation No 517/2014. The focus is given to applicability of these new refrigerants to replace high GWP refrigerants that are currently in use in each of the discussed categories. The conclusions section includes an analysis of the future developments in HFC/HFO mixtures.

2. Mobile air conditioning (MAC)

About 80% of the total direct MACs CO_2-eq. emissions are due to R134a (GWP of 1430) leakages from service process because the high service rate and no recycle of refrigerant (Su et al., 2015). Then, operational emissions represent 17% of the total emissions, followed by the end-of-life emissions and initial emissions. The same study revealed strong emission reduction potentials, including the usage of the HFO R1234yf (GWP of 4).

Zilio et al. (2011) published the pioneering paper about the usage of R1234yf as R134a drop-in alternative in MAC systems. They noticed the lower system performance using R1234yf so they proposed an enhancement of the condenser and evaporator area by 20 and 10%, and an overridden compressor to match the coefficient of performance (COP). The early technical note of Lee and Jung (2012) quantified the loss in COP using R1234yf between 0.8 and 2.7%, whereas the loss in cooling capacity was up to 4.0%. The rest of previous studies about R1234yf performance in air conditioning systems can be found in Wang (2014).

According to the previous studies, R1234yf seemed to be the most important alternative to R134a in mobile air conditioning as the transition to R1234yf does not require substantial MAC system modifications. However, the observed R1234yf cooling capacity and energy performance drop in comparison to R134a is a barrier to the extension of the use of the HFO in MACs. Therefore, more papers concerning MAC modeling and the influence of its components have been published to have a better understanding of the effect of the replacement in the system performance.

Daviran et al. (2017) simulated drop-in R134a automotive air conditioning substitution by R1234yf. While for a match in cooling capacity the COP of R1234yf was between 1.3 and 5% lower than that of

R134a, for a constant mass flow rate state the COP was 18% higher. Ortega Sotomayor and Reis Parise (2016) developed and validated a semi-empirical model for MAC compressors that uses characterization parameters valid for the simulation using new refrigerants.

Di Battista and Cipollone (2016) used a mathematical model considering R1234yf as working fluid to study the influence of design and off-design conditions of the individual components: proper orifice, evaporator and condenser sizing, or liquid cooled condenser usage. Qi (2015) proved that a microchannel parallel flow evaporator reduces the cooling capacity difference between R1234yf and R134a. Cho et al. (2013) pointed out the performance enhancement using an internal double-pipe heat exchanger with R1234yf refrigeration system (compressor speed between 800 and 2500 rpm). This additional element can reduce the cooling capacity and COP difference with R134a up to 1.8% and 2.9%. Whereas the COP of the R1234yf internal heat exchanger (IHX) system (Figure 2) is lower than that of the R134a basic system for a compressor speed between 800 and 1800 rpm, it is 0.9% higher at a compressor speed of 2500 rpm (Cho and Park, 2016). Pottker and Hrnjak (2015) have quantified that the maximum COP improvement due to condenser subcooling is 18%, against 9% for the system with IHX. R1234yf thermostatic expansion valve (TXV) adjustment can improve the cooling capacity by 11.3% and the COP by 8%, on average (Shi et al., 2016).

Other synthetic refrigerants recently proposed in mobile air conditioners were R152a, R444A, and R445A (GWP of 124, 92, and 134). In a validated model for a four-stage cycle with two-phase refrigerant injection, Lee et al. (2015) obtained the largest COP using R1234yf (compared to R134a, R152a, R444A, and R445A). According to Li et al. (2014), the COP of R152a in an indirect system (instead of the evaporator, an intermediate fluid is used to cool the space concerned) is between 5 and 10% higher than that of R134a in a direct expansion system. The proposed system also offers 35% reduction in refrigerant charge.

These fluids have been studied also in air-conditioning systems of heavy vehicles (not considered in the F-gas Regulation). In the study of Devecioğlu and Oruç (2017), R444A and R445A also show lower COP but the use of these mixtures in R134a systems is recommended if possible highest COP is not the key objective. Schulze et al. (2015) have evaluated R445A as R134a drop-in alternative in bus air conditioning system (not included in the Directive 2006/40/EC). The results were not favorable for the new mixture since the COP and the cooling capacity were lower, the high pressure and the compressor outlet temperature increased, and the there is a higher risk of ice formation.

The future innovations in MAC systems can arise from the active developments in electrical vehicles (Peng and Du, 2016). In such vehicles, due to the significant amount of energy required for heating, the MAC system becomes a significant energy consumer and thus attracts greater attention from vehicle manufacturers to achieve designs that are more efficient.

3. Domestic refrigerators and freezers

Domestic refrigerators and freezers are the home appliances with the second greatest energy consumption (Belman-Flores et al., 2015). Leakages of refrigerant are also important since no periodical leakage controls or end of life refrigerant recovery is clearly established. Belman-Flores et al. (2015) include in their review R152a, R1234yf, and several pure hydrocarbons and hydrocarbons-based mixtures as alternatives to R134a in domestic refrigeration but highlights the lack of research with new synthetic alternatives.

Limitation of GWP 150 has reduced the options to replace HFCs in the domestic refrigerators and freezers to replace R134a. However, in the EU, low GWP alternatives to HFCs are being used in 90% of new domestic refrigerators/freezers (IIFIIR, 2016). All the refrigerant alternatives that can be considered in such equipment in the European market are flammable: the aforementioned pure HFOs and the hydrocarbons.

If security regulation allows hydrocarbons in domestic refrigeration, these fluids can substitute R134a and bring environmental benefits arising from the low GWP value and the generally high energetic performance. In Japan, for example, the use of R600a instead of R134a has shown to be able to reduce the global warming impact from 2022 kt CO_2-eq. in 1998 to 72 kt CO_2-eq. in 2030 (Xue et al., 2017). However, the countries with stronger safety regulations prefer to use less flammable refrigerants to replace R134a. While in the United States the charge of hydrocarbons in domestic refrigeration systems is limited to 57 g (United States Environmental Protection Agency, 2016), in the EU the limit is 150 g.

The research on domestic refrigerators is now focused on new fluorinated options, whereas R152a was investigated prior to that as it presents better performance compared to R134a and R32 (GWP of 675), as depicted by Bolaji (2010). It is worth noting that HFOs used in domestic refrigerators normally performed above the baseline R134a, contrary to other refrigeration and air conditioning systems that present energetic deficiencies.

Thus, in an energetic comparison of R134a with R1234yf (according to UNI-ISO 15502:2005), Aprea et al. (2016a) measured a 3% energy saving despite the higher compression ratio. In the domestic refrigerator used by Belman-Flores et al. (2017), the resulting energy consumption (according to Mexican Norm NOM-015-ENER-2012) was 4% higher than that of R134a. Then, using experimental data from an A+ domestic refrigerator, Aprea et al. (2016b) concluded that R1234ze(E) (GWP of 6) has less contribution to climate change than R134a because of resulting lower 24-h energy consumption and very low GWP value of R1234ze(E). Throughout the performance analysis of a roll-bond evaporator, Righetti et al. (2015) concluded that among different low GWP alternatives (R1234yf, R1234ze(E) and R600a), R1234yf can be considered a direct drop-in alternative to R134a in domestic refrigeration since both exhibit similar vaporization performance. According to the experimental tests carried out by Aprea et al. (2017), the non-flammable refrigerant mixture R134a/R1234yf (10/90% weight) leads to an energy saving equal to 16% and 14% with respect to R134a and R1234yf (Figure 3) and its operating conditions are comparable to that of R134a.

4. Refrigerators and freezers for commercial use (hermetically sealed equipment)

Concerning new synthetic refrigerants alternative for refrigerators and freezers for commercial use to replace R134a, similar conclusions as those observed for the replacements in domestic systems can be drawn (same GWP limitation of 150). R1234yf shows similar cooling capacity (Q_{evap}) and efficiency to

R134a and it is benefited from a slightly larger suction line diameter and employing a suction line to liquid line heat exchanger in new systems. R1234ze(E) needs a larger compressor to match the capacity of R134a that reduces significantly the COP (Sethi et al., 2016a) (Figure 4).

The available pure HFOs present significant thermodynamic differences to R404A and R507A (GWP of 3922 and 3985) and cannot be considered as retrofit alternatives to these refrigerants. The substitution of these refrigerants with pure HFOs is problematic due to the resulting large volumetric capacity drop and the flammability of such fluids (Pigani et al., 2016). Then, only flammable mixtures can be considered as synthetic refrigerant alternatives to replace R404A. Sethi et al. (2016b) tested R448A and R455A (GWP of 1387 and 148) in a self-contained freezer and compared the results to R404A. Both alternatives showed about 9 and 6% lower 24-h compressor energy consumption than R404A. Despite the better energy results of R448A, only R455A will be allowable in European systems due to the GWP limitation.

5. Stationary refrigeration equipment

From 2020, the refrigerants with GWP≥2500 are banned from use in stationary refrigeration equipment (apart from the equipment designed to cool products to temperatures below – 50 °C). In addition, these refrigerants will be prohibited from being used to service or maintain refrigeration equipment with a charge size of 40 tons of CO_2-eq. or more (also called “service ban”). Only recycled refrigerant will be allowed for this purpose until 2030.

According to the recent survey study (Öko-Recherche, 2017), the majority of commercial refrigeration systems installed or used today in Europe still are based on HFCs as well as certain amount of natural refrigerants, Figure 5. The most used synthetic refrigerants indicated by the survey are R134a, R404A, the R407 series, R410A and R507A; whereas the most used natural refrigerants are CO_2, ammonia and propane.

As seen from the data presented in Figure 5, R134a is a widely-used refrigerant in the stationary refrigeration systems. Jarall (2012) and Navarro-Esbrí et al. (2013a) performed the earlier R1234yf comparison with R134a in refrigeration systems. The conclusion of the first study mentioned, based on the observation of a small refrigeration unit, was that R1234yf gives less refrigerating capacity, COP, and compressor efficiency between 3.4 and 13.7%, and between 0.35 and 11.88%, respectively. In the second one, in addition to operating temperatures, the effect of superheating degree and compressor speed was also analyzed. Then, Belman-Flores and Ledesma (2015) used these data to confirm that the temperatures of the secondary fluids are the most important parameters to define the energy performance. Using the same refrigeration test bench, Navarro-Esbrí et al. (2013b) confirmed the major influence of IHX on R1234yf. The R1234yf COP increase is benefited from higher compression ratios (Figure 6).

As for domestic and commercial refrigerators and freezers, R1234ze(E) was also considered in these systems (Mota-Babiloni et al., 2016). Janković et al.’s (2015) conclusion about the performance of R1234ze(E) in a small capacity refrigeration unit was that it shows around 25% lower cooling capacity but between 4 and 7% higher COP than R134a. If an overridden compressor is used to match the HFOs cooling capacity to that of R134a, R1234ze(E) presents a lesser drop in COP than R1234yf. Mota-Babiloni et al. (2017a) suggest the introduction of an IHX and a 43% higher displacement compressor to reach an R1234ze(E) match in cooling capacity with R134a. Finally, Kabeel et al. (2016), using a commercial vapor compression system used to refrigerate a walk-in cold room, obtained similar energetic parameters deviation between R134a and R1234ze(E) to that predicted by the model of Leighton et al. (2012).

Mixtures composed by HFOs and HFCs have also been proposed to replace R134a in stationary refrigeration systems as a trade-off solution. In a small unit, R513A (GWP of 631) (Mota-Babiloni et al., 2017b) presented better energetic values than R134a at low evaporating and condensing temperatures. In a larger unit, R450A (GWP of 605) (Mota-Babiloni et al., 2015b) has comparable COP but lower cooling capacity than R134a. In both studies, similar or higher COP and lower GWP can lead to a reduction of CO_2-eq. emissions with minor system modifications.

Among the refrigerants used for low evaporating temperatures, the F-gas Regulation is going to affect mostly R404A and R507A. The alternatives to them are non-flammable refrigerant mixtures with GWP under 2500. Two synthetic options can be differenced: the HFC and the HFC/HFO mixtures.

HFC mixtures were the first group developed and R407F and R410A (GWP of 1825 and 2088) were the refrigerants found in the literature review. Bortolini et al. (2015) concluded that the most suitable refrigerant to replace R404A in medium evaporating temperature conditions is R410A and in freezing cooling loads, R407F (Figure 7). Then, Cascini et al. (2016) use the results of two commercial walk-in refrigeration systems to emphasize that the operating conditions and the refrigerant leakage are the most critical parameters to reduce climate change contribution from R404A systems using lower GWP mixtures. Pigani et al. (2016) highlight R407F as the best option in refrigeration systems for passenger ships compared to low GWP refrigerants as ammonia, CO_2 and pure HFOs.

R448A and R449A (GWP of 1397) are A1 mixture refrigerants with very similar composition proposed in commercial units with higher performance at high condensing (ambient) temperatures and lower GWP than HFC mixtures (Mota-Babiloni et al., 2015c). R449A offers comparable energy performance without operating problems if retrofitted in R404A real supermarket system (Makhnatch et al., 2017).

Despite the promising results of these mixtures, more research is necessary to promote these fluids in stationary refrigeration equipment. Recently published studies based on supermarket refrigeration system analysis still use R404A (Braun et al., 2016) despite near phase out.

6. Multipack centralized refrigeration systems for commercial use with a rated capacity of 40 kW or more

Supermarket refrigeration systems have raised considerable interest because of its high leakage rate, mostly because of pipe or joint failure and valves leaking (Francis et al., 2017), and refrigerant charge compared to other vapor compression systems, Table 1. Given the relevance of leakages of R404A, R134a and R410A HFCs in European supermarkets (Francis et al., 2017), the introduction of low and lower GWP refrigerants in this type of systems should be prioritized.

However, the number of investigations using low GWP refrigerants is limited. The GWP threshold of 150 makes all drop-in synthetic solutions impossible since it is very low for all nonflammable synthetic refrigerants. Hence, the most feasible solution is to completely replace the system and use CO_2 refrigerant in new optimized stores. Systems using CO_2 are more recommendable in colder climates where the energy performance is still acceptable because is far enough from the low critical temperature of this fluid (32 °C). On the contrary, in warmer locations, transcritical refrigeration systems are continuously improved through technology improvements and their performance is becoming comparable to systems using common HFCs (Sawalha et al., 2017).

Despite the GWP limitation, a few refrigerants have been tested in centralized refrigeration systems that can be applied in the transition process or in countries still not regulated. Llopis et al. (2017) tested R407H (GWP of 1495) in a low temperature DX system at different condensing conditions. Compared to R404A, the energy consumption reduction was up to 7.7% in the compressor and 4.0% in the whole system and the maximum increment of compressor discharge temperature was 13.8 K.

Sethi et al. (2016b) presented R448A in a supermarket refrigeration system connected to 14 low and medium-temperature display cases. Compared to the R404A operation in a direct expansion (DX) configuration, R448A provided similar capacity and a between 9% and 20% lower energy consumption (condenser fans and scroll compressors) than R404A, varying the ambient temperatures between −9 and 35°C. In addition, the case temperatures were very similar between R448A and R404A.

Beshr et al. (2015) performed a Life Cycle Climate Performance analysis considering several refrigerants and systems combinations and locations. R448A can produce a great reduction of total emissions through the substitution of R404A in DX systems (Figure 8). However, under the common scenario in supermarket refrigeration systems of leakage rates higher than 2%, the transcritical CO_2 option is the most environmentally friendly option. To consider lower GWP refrigerants (or more charge conservative systems) increases the influence of the hourly emission rate for electricity production on the total CO_2-eq. emissions and reduces the impact of the uncertainty in the inputs related to the direct CO_2-eq. emissions.

7. Cascade supermarket systems

The possibility of using refrigerants up to 1500 GWP in cascade refrigeration systems of supermarkets have resurged the research of these configurations. The advantages of cascade systems are lower pressure ratios and refrigerant charge. Besides, among the drawbacks, higher initial cost or additional heat exchanger.

The refrigerant typically considered in the high temperature stage of this application is R134a and it can be maintained because the limit established by the F-gas Regulation does not ban its use. Through the combination of R134a and then CO_2 in the low stage, low evaporating temperature cooling loads can be covered and CO_2 subcritical operation settled.

In the recent years, some studies have assessed modifications to reduce the CO_2-eq. emissions of R134a/CO_2 cascade systems. To reduce the refrigerant amount of charge, Sánchez et al. (2017) studied the conversion of a direct to indirect supermarket system using two different heat transfer fluids. They measured a decrease between 1.9 and 3.5 °C of the evaporation temperature so the energy consumption increased up to 15%. Llopis et al. (2016) used an IHX in the low temperature cycle in a cascade refrigeration plant. The IHX increases the COP of the cascade system up to 3.7% even though it slightly reduces the cooling capacity, Figure 9.

Apart from R134a, other low and lower GWP refrigerants have been studied in the high stage. Gullo and Cortella (2016) simulated several R1234ze(E)/CO_2 combined cascade/indirect configurations. The greatest total equivalent warming impact reduction was obtained in the configuration that includes desuperheating and flooded evaporators, between 28% in Athens and 42% in Rome conditions. Besides, Beshr et al. (2015) obtained a noticeable reduction of CO_2-eq. emissions proposing R448A/CO_2 cascade instead of R448A direct expansion. The life cycle climate performance results obtained with CO_2 in the low stage can be improved considering a low GWP synthetic refrigerant instead (Figure 8). Cabello et al. (2017) have shown that the performance of an R152a cascade test bench with CO_2 at low stage is at a similar level than that using R134a. The selected evaporating temperature was within −40 to −30 °C.

8. Single split air conditioning systems containing less than 3 kg of fluorinated GHGs

The use of lower GWP alternatives in air conditioning and heat pump systems is essential, since these applications are the second sector in number of units in operation, after domestic refrigerators and freezers (IIFIIR, 2015). Single split air conditioning systems mainly use R410A in developed countries and R22 (GWP of 1810 and ozone depleting fluid) in the rest. Hence, this section will focus the replacement of R410A using lower GWP refrigerants.

To replace R410A, the first studies published propose R32, which is just below the GWP limitation of 750 set by the F-gas Regulation. This refrigerant offers a great opportunity to reduce direct emissions in new equipment (or with system modifications) due to three main factors: great GWP reduction compared to R410A (66%), lower refrigerant charges and higher efficiencies in refrigeration and air conditioning systems. Even though R32 is a well-known refrigerant, some limitations as flammability and high discharge temperatures have led to its use in the 50/50 mixture with R125 (GWP of 3500) (denoted as R410A) during the last decades. Pure HFO refrigerants are not applicable to replace R410A because of their very different capacity (Barve and Cremaschi, 2012).

The majority of the studies conclude that R32 presents higher energy performance than R410A but the excessive compressor discharge temperature limits its application. Barve and Cremaschi (2012) obtained greater or comparable COP and cooling capacity than R410A in heating and cooling modes. Zilio et al. (2015) simulated an R410A packaged air-to-water reversible unit and obtained that R32 capacities are approximately 6% higher, being more feasible its use in cooling mode. Both studies alert about excessive R32 discharge temperature and recommend an optimization of the system. In extreme high temperature conditions, R32 discharge temperature (8.3 K higher than the maximum acceptable temperature of the most widely used B- insulation class motor) might be a concern for the compressor lifetime cycle (Wu et al. 2016), Figure 10.

Several basic cycle configuration modifications have been proposed to decrease the discharge temperature and in the same time, increase the energy performance of the air conditioning system using R32. Shuxue et al. (2013) quantified the discharge temperature reduction by the use of enhanced vapor injection between 10 and 20 K but Xu et al. (2013) only measured energy performance improvement using this configuration at non-extreme cooling and heating conditions. Yang et al. (2015) concluded that two-phase injection outperforms liquid injection (Figure 11) and two-phase suction in both cooling capacity and COP by 12% and 5%. Contrary to other synthetic refrigerants, the use of IHX in R32 systems is not recommended because it reduces the COP and increases the discharge temperature (Park et al., 2015). Qv et al. (2017) obtained better economic, energetic and environmental results using an injection-assisted air conditioner using R32 than a conventional R410A air conditioning system.

Another way to decrease the discharge temperature and maintain it under a critical value is to blend R32 with other HFCs, HFOs, and hydrocarbons. Moreover, proposed mixtures and R32 can reduce the amount of optimal charge compared to R410A. In a residential air conditioning system, according to the EN14825 standard, In et al. (2015) obtained better energy efficiency values for R32 than R446A (GWP of 461) in spite of these results were lower than R410A. Furthermore, R446A (a low flammable mixture also developed for these systems) could not solve the high discharge temperature concern.

Some available studies using lower GWP alternatives for air conditioning system use developmental mixtures that have not been yet registered. Lee et al. (2016) perform an energetic and environmental evaluation of R410A, R32, R290 and four lower GWP mixtures considering several configurations and locations. The conclusion is that the CO_2-eq. reduction achieved using the new mixtures is below that obtained with the natural alternative and R32. Then, in a 10.55 kW air conditioning system (Alabdulkarem et al., 2015), a mixture with GWP of 494 was shown to perform better than R410A and R32 in terms of cooling capacity, heating capacity, and energy performance. These tests have also confirmed that the IHX does not provide significant improvement for R32 and the mixture.

9. Future developments

Many refrigerants used to replace conventional HFCs are HFOs or HFO mixtures. Only one HFC, namely R32, is often used as a pure refrigerant in single split air conditioning systems and as a component in various mixtures (primarily those used to replace R404A and R410A). However, its GWP is 675 and cannot be sufficiently low to meet long term environmental targets.

Based on the work results of Kazakov et al. (2012), McLinden et al. (2014) have identified 62 candidate refrigerants with GWP below 200 and suitable thermodynamic properties and their stability and toxicity characteristics. However, the great majority of the identified refrigerants are flammable. Among the identified refrigerants, only a few (namely R152a, R1234yf and R1234ze(E)) are included in this review as substitutions to conventional HFCs. Some others, as for instance R1234ze(Z) (Fukuda et al., 2014), are not yet commercialized despite the research activities that have been held over the years. One possible explanation is that the categories of refrigeration equipment that could utilize these refrigerants are not yet directly regulated.

Even though the number of potential low GWP refrigerants is limited, most of the current refrigeration and air conditioning applications are met with a finite set of synthetic fluids (Table 2) and their blends (Table 3 and 4) (McLinden et al. 2014). There are more than one hundred refrigerant blends identified and the majority of the new blends are based on HFOs being mixed with other synthetic refrigerants (ASHRAE, 2016).

Given the great number of new refrigerants and refrigerant blends and considering the urgent demand for their use, it is important to obtain reliable refrigerant characteristics in a timely manner. For instance, McLinden et al. (2017), using reduced properties of new refrigerants, have presented the theoretical COP and volumetric capacity for new low GWP refrigerants (relative to those for R410A) and several of conventional refrigerants in different refrigeration cycles (Figure 12).

As it can be seen from the Figure 12, all the potential new fluids, except for R32 (which cannot be included in low GWP refrigerant designation as discussed before), introduces the trade-offs regarding the COP and cooling capacity. When modelled in the basic vapor compression cycle, only few fluids as R1141 and R1123 can provide higher capacity results at the expense of lower energy efficiency. Many of the alternatives have a significantly lower capacity (more than a 50% reduction for the majority of the fluids) and thus they will require a significantly larger compressor to meet cooling demands comparable to R410A. In this case, the use of the optimized vapor compression cycles can improve the capacity of some of the alternatives (McLinden et al. 2017).

A great number of new refrigerants have been evaluated within the low global warming potential alternative refrigerants evaluation program (AREP) that is being performed by the Air Conditioning, Heating, and Refrigeration Institute (AHRI) which aims to identify and evaluate the feasibility of several low-GWP alternatives to HFCs and R22 in refrigeration and air conditioning appliances (Wang and Amrane, 2014).

The testing has been performed in 2 periods and during the second phase (started in January 2014), being focused on refrigerants in applications not tested in the first phase or at high ambient conditions. The methods considered are compressor calorimeter, drop-in and soft-optimized tests (Wang and Amrane, 2016). They identified as main barriers for the introduction of the new fluids: temperature glide, better knowledge of heat transfer and transport properties, material compatibility and flammability.

In the coming years a significant amount of papers dealing with the behavior of second phase synthetic mixtures can be expected considering the Wang and Amrane (2016)'s recommendation of additional studies through further soft optimization of the refrigeration and air conditioning systems.

10. Conclusions

To replace HFCs with environmental friendly refrigerants is a matter of great importance in the refrigerating and air conditioning industry since GWP limitations affect most of the applications in Europe and possibly, the rest of the world in the short term. This paper has reviewed some interesting aspects about the use of new pure and mixture synthetic refrigerants in substitution of high environmental impact HFCs using the information available in the open literature.

The number of available refrigerants is increasing to produce a refrigerant for each refrigeration and air conditioning application. The application that allows more synthetic refrigerant options are the stationary refrigeration industry because of the high GWP threshold value established by the F-gas Regulation. However, cascade refrigeration systems are still not widely studied despite the high GWP limit and the interest is given to transcritical CO_2 systems. In MACs, domestic refrigeration and hermetically sealed commercial refrigeration equipment, studies using pure HFOs are the most prevalent. In single split air conditioning systems, mixtures alternatives to R410A dos not offer new advantages compared to pure R32. In the coming years, a relevant increase of the number of available studies using new refrigerants is expected.

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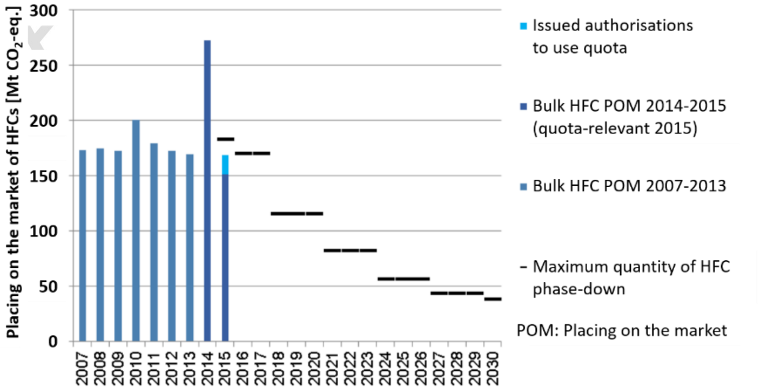


Note: *Values from 2007-2013 are based on the reporting obligations of Regulation (EC) No 842/2006 and are therefore not fully comparable to data from 2014 onwards (based on obligations of Regulation (EU) No 517/2014). Similarly, the maximum quantities of the HFC phase-down will be recalculated in 2018 and are therefore for indicative purposes only.*

Figure 1. Historical values of the amount of HFCs placed on the market in the recent years in Mt of CO_2-eq (Modified from European Commission, 2016a).

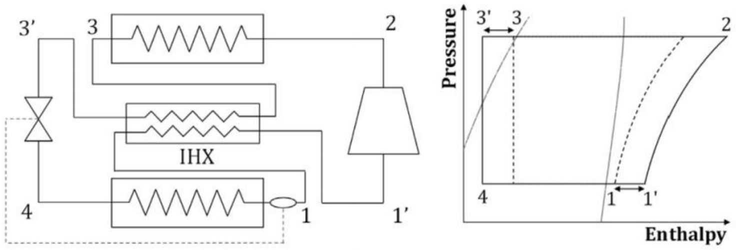


Figure 2. Schematic (left) and P-h diagram (right) of an IHX refrigeration system

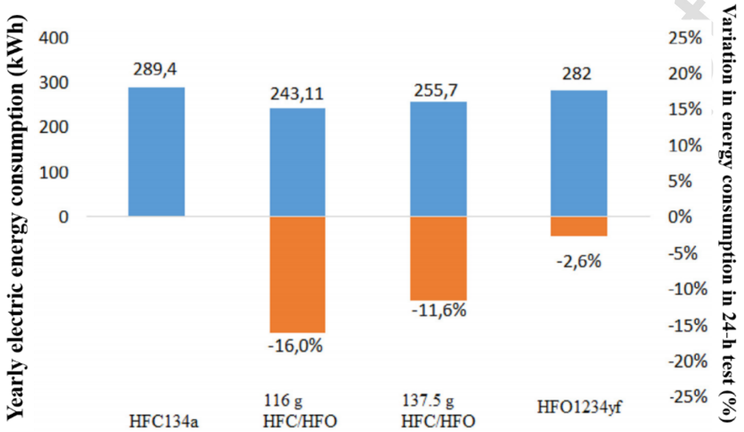


Figure 3. Yearly electric energy consumption and energy saving for the refrigerant fluids in a 24-hour test (Aprea et al., 2017).

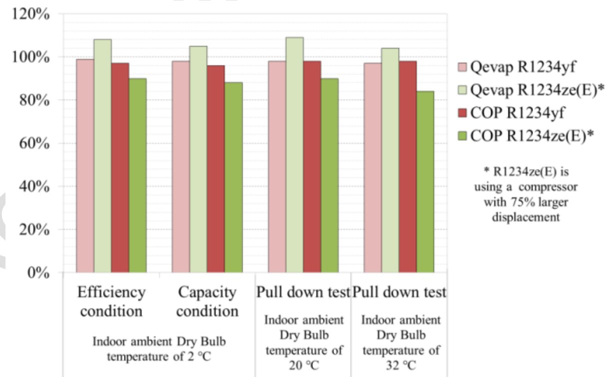
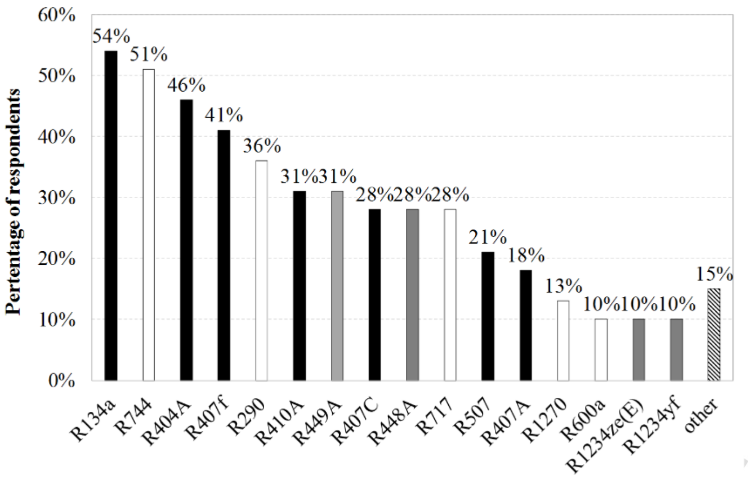


Figure 4. Experimental results in a vending machine compared to R134a (Sethi et al., 2016a)



Note: *Other includes R22, R401A, R401B, R413A, R417A, R422A, R422D, R434A, R442A, R450A, R452A, R453A and R513A*

Figure 5. Percentage of questionnaire respondents indicating a refrigerant as currently installed or used for commercial refrigeration by them (Öko-Recherche, 2017).

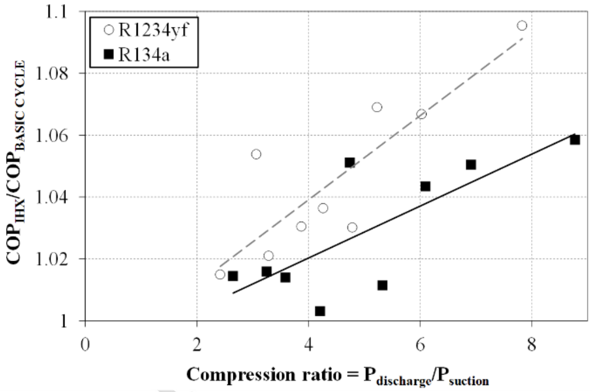


Figure 6. COP variation due to IHX activation versus compression ratio (Navarro-Esbrí et al., 2013b).

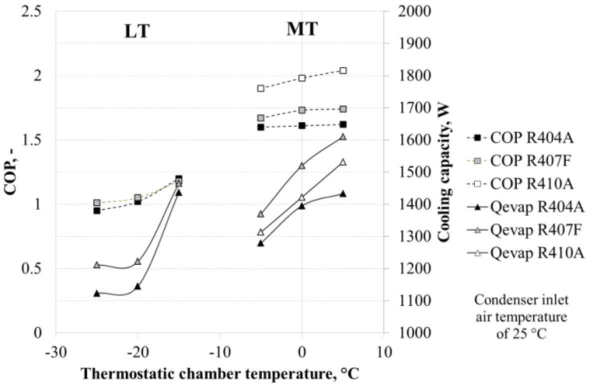


Figure 7. Cooling capacity (Q_{evap}) and COP in a walk-in thermostatic chamber (Bortolini et al., 2015).

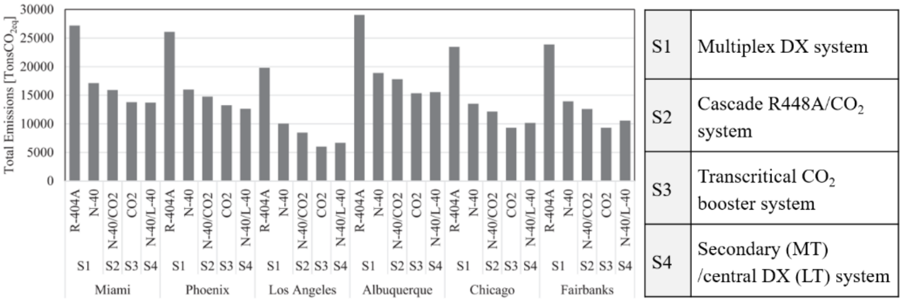
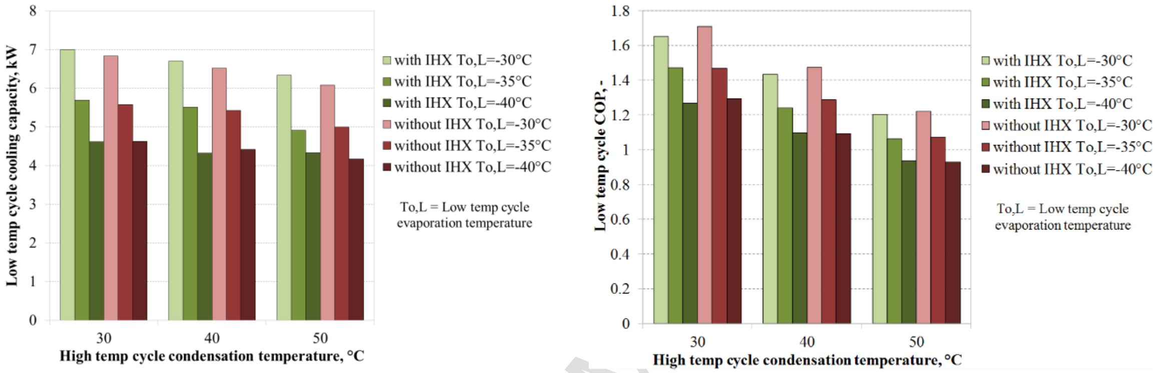


Figure 8. Total emissions of four refrigeration systems using different refrigerants at several US locations (Beshr et al., 2015).



a) b)

Figure 9. a) Cooling capacity and b) COP with and without IHX at the maximum COP condition

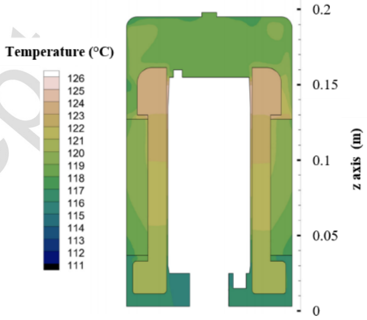
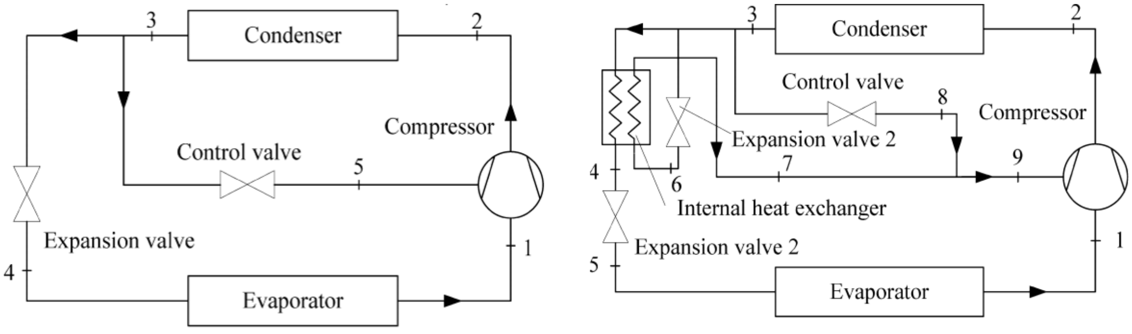


Figure 10. Wu et al. (2016) simulated results of temperature (T) distribution in y = 0 mm plane at different compressor's height (z axis).



a) b)

Figure 11. Schematics of a) liquid and b) two-phase injection systems (Yang et al., 2015).

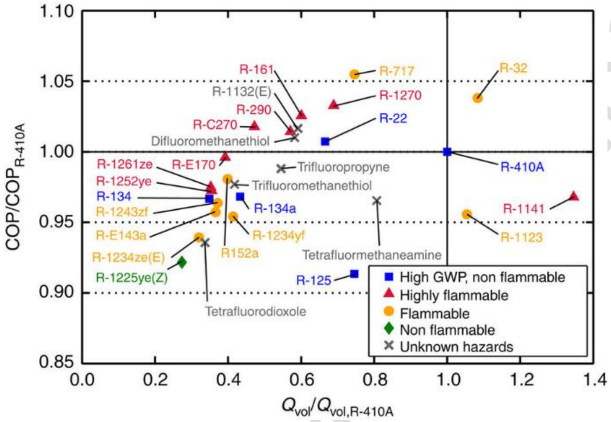


Figure 12. The COP and volumetric refrigerating capacity (Q_{vol}) of selected low global warming potential fluids in the basic vapor compression cycle (McLinden et al., 2017).

Table 1. Annual leakage rate (for UK sector and using the simple screening method) and refrigerant charge (using the simple screening method) (Koronaki et al., 2012).

	Annual leakage rate	**Annual leakage rate**	**Refrigerant charge**
Type of equipment	UK sector	Using the simple screening method	
Domestic refrigeration	0.3%	NA	NA
Stand-alone commercial applications	2.0%	<1%	<30 kg
Medium & large commercial applications	11.0%	20-30%	30-300 kg
Industrial refrigeration	8.0%	15-20%	>300 kg
Chillers	3.0%	NA	NA
Residential and commercial air conditioning	8.5%	15-20%	>30 kg

Table 2. Summary of pure fluids studies

Application in section / max GWP / HFC to replace	**Alternative**	**Studied in reference**
2. Mobile air conditioning / 150 R134a	R1234yf	Cho et al., 2013 Cho and Park, 2016 Daviran et al., 2016

		Di Battista and Cipollone, 2016 Lee et al., 2015 Lee and Jung, 2012 Ortega Sotomayor and Reis Parise, 2016 Pottker and Hrnjak, 2015 Qi, 2015 Shi et al., 2016 Zilio et al., 2011
	R152a	Lee et al., 2015 Li et al., 2014
3. Domestic refrigerators and freezers / 150 / R134a	R1234yf	Aprea et al., 2016a
	R1234ze(E)	Aprea et al., 2016b
	R1234yf and R1234ze(E)	Righetti et al., 2015
	R152a	Bolaji, 2010
4. Refrigerators and freezers for commercial use / 150 / R404A	R1234yf and R1234ze(E)	Pigani et al., 2016 Sethi et al., 2016a
5. Stationary refrigeration equipment / 2500 / R134a	R1234yf	Belman-Flores and Ledesma, 2015 Jarall, 2012 Navarro-Esbrí et al., 2013a Navarro-Esbrí et al., 2013b
	R1234ze(E)	Kabeel et al., 2016 Mota-Babiloni et al., 2017a
	R1234yf and R1234ze(E)	Janković et al., 2015 Leighton et al., 2012
7. Cascade supermarket systems / 1500 / R404A and R134a/CO_2	R1234ze(E)	Gullo and Cortella, 2016
	R152a	Cabello et al., 2017
7. Cascade supermarket systems / 1500 / R404A and R134a/CO_2	R32	Barve and Cremaschi, 2012 Park et al., 2015 Qv et al., 2017 Shuxue et al., 2013 Wu et al., 2016 Xu et al., 2013 Yang et al., 2015 Zilio et al., 2015

Table 3. Summary of reviewed mixtures studies

Application in section / max GWP / HFC to replace	**ASHRAE Number**	**Studied in reference**
2. Mobile air conditioning / 150 R134a	R444A	Devecioğlu and Oruç (2017) Lee et al., 2015
	R445A	Devecioğlu and Oruç (2017) Lee et al., 2015 Schulze et al., 2015
4. Refrigerators and freezers for commercial use / 150 / R404A	R448A	Sethi et al., 2016b
	R455A	Sethi et al., 2016b
5. Stationary refrigeration equipment / 2500 /	R450A	Mota-Babiloni et al., 2015b

R134a	R513A	Mota-Babiloni et al., 2017b
5. Stationary refrigeration equipment / 2500 / R404A	R407F	Bortolini et al., 2015 Cascini et al., 2016 Pigani et al., 2016
	R410A	Bortolini et al., 2015 Cascini et al., 2016
	R448A	Mota-Babiloni et al., 2015c
	R449A	Makhnatch et al., 2017
6. Multipack centralized refrigeration systems / 150 / R404A	R407H	Llopis et al., 2017
	R448A	Sethi et al., 2016b Beshr et al., 2015
7. Cascade supermarket systems / 1500 / R404A and R134a/CO_2	R448A	Beshr et al., 2015
8. Single split air conditioning systems / 750 / R410A	R446A	In et al., 2015

Table 4. Main characteristics of the reviewed mixtures and the HFCs to replace.

Refrigerant	**R134a**	**R444A**	**R445A**	**R450A**	**R513A**	**R404A**	**R407F**	**R407H**	**R448A**	**R449A**	**R455A**	**R410A**	**R446A**
Molecular weight, g mol^{-1}	102	96.7	103.1	108.7	108.4	97.6	97.6	79.1	86.4	87.4	87.5	72.6	62
Critical temperature, °C	101.1	103.2	98.0	104.4	96.5	72.05	82.7	86.5	83.7	81.5	85.6	71.4	84.2
Critical pressure, MPa	4.059	4.278	3.973	3.820	3.766	3.729	4.755	4.850	4.660	4.447	4.660	4.902	5.524
Normal boiling point, °C	-26.1	-35.7	-49.1	-23.4	-29.6	-46.2	-46.1	-44.7	-46.1	-45.7	-52.0	-51.4	-49.7
Temperature glide at 0.1 MPa, K	0.0	11.1	26.0	0.6	0.1	0.8	6.4	7.0	6.2	5.7	12.9	0.1	5.4
AR4 $GWP_{100\text{-}yr}$, CO_2-eq.	1430	92	134	547	573	3922	1824	1495	1387	1397	145	2088	461
ODP	0	0	0	0	0	0	0	0	0	0	0	0	0
ASHRAE Standard 34 Safety Group Classification	A1	A2L	A2L	A1	A1	A1	A1	A1	A1	A1	A2L	A1	A2L
ATEL/ODL, kg m^{-3}	0.21	0.32	0.27	0.33	0.32	0.52	0.32	0.3	0.39	0.36	0.41	0.42	0.07
Liquid density at 0 °C, kg m^{-3}	1294.8	1199.1	1232.3	1259.6	1221.9	1150.0	1218.2	1207.5	1197.7	1197.6	1128.8	1170.0	1093.8
Vapor density at 25 °C, kg m^{-3}	32.35	28.50	28.63	29.55	37.63	65.27	47.52	41.86	48.90	49.32	45.56	65.97	42.28
$Q_{vol}{}^a$, kJ m^{-3}	1442.6	1471.2	1497.0	1250.3	1490.3	2440.8	2601.4	2459.2	2510.5	2477.0	2402.6	3498.0	3176.7
COP^a, -	2.96	2.96	3.14	2.96	2.89	2.71	2.83	2.86	2.82	2.82	2.82	2.76	2.84

$^a T_{cond,x=1/2}$=40 °C, $T_{evap,x=2/3}$=-10 °C, SHD=10 K, SCD=4 K, η_{iso}=0.7