



25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COB-2019-XXXX

HFO ALTERNATIVE REFRIGERANTS FOR SPLIT RESIDENTIAL AIR-CONDITIONERS AND HEAT PUMPS: A REVIEW ON ENERGY EFFICIENCY, ENVIRONMENTAL IMPACT, FLAMMABILITY, PRODUCT AVAILABILITY AND COSTS

V. R. Weaver,
V. Bautista Paganelli,
M. A. I. Fonseca,
M. V. A. B. Pinto,
L. P. Pereira,
B. C. Manhães,

Pontifícia Universidade Católica do Rio de Janeiro, Department of Mechanical Engineering, Rua Marquês de de São Vicente, 225, Gávea, 20453-900 Rio de Janeiro, RJ, Brazil

e-mails: veronicarweaver@gmail.com ; vane.09@gmail.com ; ma.fonseca.puc@gmail.com ; marcus.adorno@gmail.com ; leoppereira3@yahoo.com.br ; brunocm_272@hotmail.com

E. P. Bandarra Filho

Federal University of Uberlândia, School of Mechanical Engineering, Av. João Naves de Avila, 2121 - Santa Monica, 38400-902 Uberlândia, MG, Brazil

e-mail: bandarra@mecanica.ufu.br

P. O. Sotomayor,

J. A. R. Parise

Pontifícia Universidade Católica do Rio de Janeiro, Department of Mechanical Engineering, Rua Marquês de São Vicente, 225 - Gávea, 20453-900 Rio de Janeiro, RJ, Brazil,

e-mails: ortegas.paul@gmail.com ; parise@puc-rio.br

Abstract. *The paper presents a brief review on the utilization of HFO refrigerants on split residential air conditioners and heat pumps. A description of currently available HFO refrigerants and their mixtures is presented. Baseline refrigerants, mostly HFCs and HCFC, find a distinct substitute, depending on application and manufacturer. The overall performance of this class of refrigerants is discussed regarding different criteria, namely: energy efficiency, environmental impact, flammability, manufacturers and costs. In future, the choice of refrigerant for residential air conditioners and heat pumps, from either R32, hydrocarbons or HFOs, will be dictated by cost (both operational and capital), flammability issues and stricter legislation concerning maximum allowable GWP.*

Keywords: HFO, review, R454C, R444B, ARM-20b

1. HFO REFRIGERANTS

Current residential air conditioning and heat pump systems, operating with the vapor compression cycle, utilize HFC refrigerants or HFC mixtures such as R410A and R407C, with GWP (Global Warming Potential) values of 2088 and 1774, respectively. In developing countries residential units are still commercially available running on R22, an HCFC refrigerant with ODP (Ozone Depletion Potential) and GWP of 0.055 and 1810, respectively. However, the growing global concern about greenhouse effect gases has translated into a number of measures, seeking short and long term solutions. Global HFC phasedown year targets for short-term or interim solution (GWP < 750), as they stand in 2019, are 2024, 2030 and 2032, for Europe, United States and developing nations (including China, India, Brazil and Middle East), respectively. Likewise, for long-term phasedown targets (GWP , 350) one has: 2030, 2035 and 2045, for Europe, United States and developing nations, respectively (Pham and Monnier, 2016).

The EU fluorinated gas regulations, in conjunction with the Montreal Protocol guidelines, have determined a phasedown process for HFC refrigerants. By the year 2030, only 20% of the amount of HFCs sold in 2015 will be

available. The Environmental Protection Agency (EPA) in the United States has developed the Significant New Alternative Policy (SNAP) program that limits to 750 GWP the greenhouse gas effect of refrigerants for use in air conditioners. An interim low-GWP replacement for R410A, will emerge, according to Pham and Monnier (2016), from R32 and HFO blends with best cost tradeoff between energy efficiency, GWP, flammability and high-ambient performance for hot climates.

Due to growing global concern about the use of fluids with a relatively high global warming potential, new low-GWP refrigerants such as HFO-1234yf or HFO-1234ze (E) (hydrofluoroolefins) have been proposed as substitutes for the above mentioned fluids.

Pham and Monnier (2016) reviewed the low-GWP alternative refrigerants for short and long term in air conditioning. They pointed out that, given the global regulation and the current industry status, near drop-in solutions are sought in order to reduce costs. Therefore, current solutions for air-conditioning can make use of alternative refrigerants such as R32 and HFO-based mixtures, which have properties and performance similar to the original refrigerants, and have GWP around 750. New low-GWP refrigerants such as HFO-1234yf or HFO-1234ze (E) (hydrofluoroolefins) have been proposed as substitutes.

However, Pham and Monnier (2016) cite the difficulties associated with the long-term phase-down process when, they estimate, based on AR5, that a GWP limit between 300 and 400 may be imposed by the year 2030-plus, in order to reach the 15-20% quota of HFC production, as predicted by regulation. In addition, it can be argued that the mandate to raise minimum system efficiency standards by 2023, issued by the US Department of Energy (DOE), will exert even greater pressure for sustainable refrigeration practices. Pham and Monnier (2016) also point out that, in Japan and China, low-load mini-split air conditioners operating with R32 have been commercialized due to their low cost and wide availability. Notwithstanding the fact that Europe and the United States have been studying HFO-based mixtures, Pham and Monnier (2016) say their commercialization is unlikely to start until building regulations include A2L refrigerants. They estimate that probable incorporation of A2L class refrigerants into the United States building regulations by 202. The authors conclude that long-term alternatives with GWP in the range of 300-400 (HFO blends), or less than 150 (HFO blends), will likely result in reduced efficiency and changes in system architecture, such as larger heat exchangers and altered compressors, with a resulting impact on cost.

HFO is short for hydrofluoride oleophins, carbon, fluorine and hydrogen chemical compounds with at least one carbon - carbon double bond. HFOs are included in the fourth generation of refrigerants (Calm, 2008), i.e., those with zero ozone depletion (ODP), no chlorine atoms, and low GWP, which may be in some cases, even smaller than that of CO₂. HFOs are relatively stable compounds, but more reactive than HFCs (Makhnatch et al, 2015). This higher reactivity reduces the potential for global warming, mainly due to the relatively short lifetime of these substances in the atmosphere. See Table 1 with a few examples of HFO refrigerants.

Table 1 – Chemical formula, lifetime and GWP from a number of HFOs (IPCC, 2013)

Refrigerant	Chemical formula	Lifetime, days	GWP (100yr)
HFO-1234yf	CF ₃ CF=CH ₂	10.5	<1
HFO-1234ze(E)	CF ₃ Trans- CF ₃ CH=CHF	16.4	<1
HFO-1234ze(Z)	CF ₃ CH=CHF(Z)	10.0	<1

Barve and Cremashi (2012) concluded, from experiments, that pure HFO refrigerants cannot replace R410A because of their different cooling capacities. For this reason, refrigerant manufacturers such as Honeywell, Chemours and Arkema developed substitutes for domestic R410A and R22 using mixtures with HFOs and HFCs. The goal was to obtain a low GWP refrigerant that meets the characteristics required for each application.

Table 2 shows some potential substitutes - and their manufacturers - for R22 and R410A refrigerants. It can be noted that all these new refrigerants have the R32 refrigerant in their mix. This comes from the fact that, to replace R410A, early research proposed to study R32 as its direct replacement. These studies were justifiable because: (i) R410A already has R32 in its composition; (ii) both refrigerants have similar critical point characteristics (Barve and Cremashi, 2012); (iii) R32 has GWP within the allowable (750) by EU Regulation No. 517/2014 (F-gas regulation). R32 is already a known refrigerant and, compared to R410A, it has lower GWP, lower refrigerant charge and higher efficiency. Its major limitation, however, is flammability and for this reason a mixture (50% by weight of each) with R125 (GWP 3500) is used, called R410A (Mota-Babiloni et al, 2017). Barve and Cremashi (2012) also found that R32, when used as pure substance, results in a relatively high compressor discharge temperature. Such a feature may affect system reliability because of metal fatigue.

Table 2 compiled from manufacturers data and (Wang and Karim, 2016), point to the future with a wider range of refrigerants for use in residential air conditioners. Chemours (2019) finds three new refrigerants to replace R410A and another to replace R22, three of them already registered with ASHRAE. Honeywell (2019) offers a replacement for the R410A and another for the R22, both, in turn, distinct from Arkema's new refrigerants.

Table 2 - HFO Refrigerants – Manufacturers and characteristics (Honeywell, 2019; Wang et al, 2016)

Baseline Refrigerant	Manufacturer	Alternative Refrigerant	ASHRAE Number	Composition	Mass (%)	ASHRAE Class	GWP
R-410A				R-32 + R125	50 + 50	A1	1924
	CHEMOURS	XL41	R-454B	R-32 + R125	68.9 + 31.1	A2L	467
	CHEMOURS	XL55	R-452B	R-32 + R125 + R1234yf	67 + 7 + 26	A2L	676
	HONEYWELL	L41	R-447A	R-32 + R-125 + R1234ze	68 + 3.5 + 28.5	A2L	572
	ARKEMA	ARM-71a		R-32 + R1234yf + R1234ze(E)	68 + 26 + 6	A2L	460
R-22				R-22	100	A1	1810
	CHEMOURS	XL20	R-454C	R-32 + R1234yf	21.5 + 78.5	A2L	146
	HONEYWELL	L20	R-444B	R-32 + R1234ze + R-152a	41.5 + 48.5 + 10	A2L	295
	ARKEMA	ARM-20b		R-32 + R1234yf + R152a	35 + 55 + 10	A2L	251

It is noted that the new mixtures of HFCs and HFOs are designated by ASHRAE with numbers starting with 4, which indicates, of course, a non-azeotropic mixture, i.e., there is a temperature glide (TG) at both evaporation and condensation processes. Therefore, the numerical modeling of vapor compression systems running on R22 (TG equal to zero) and R410A (TG <1K) substitutes will not function without modification. It is also noteworthy that these new refrigerants are rated by ASHRAE as A2L, which means they are slightly flammable.

2. ENERGY EFFICIENCY AND ENVIRONMENTAL IMPACT

A number of experimental tests and simulation studies on residential split air conditioners utilizing HFO as refrigerants were carried out, most of them on a drop-in basis. They are presented next. Residential heat pumps were also included.

3. Heat pumps

Uselton (2013) tested a 3.5 TR split-type heat pump designed to operate with R410A refrigerant in two modes, both heating and cooling. Refrigerant R1234yf was used as an alternative in the experiment. Results showed that the HFO refrigerant operated satisfactorily on the heat pump, but only after a series of modifications to the system. It was observed that for R1234yf, the capacity and energy efficiency of the system were lower than the reference refrigerant in both operating modes, heating and cooling. Uselton (2013) points out that, for operation with the R1234yf, the refrigerant mass flow rate was higher and the system reached much lower pressures than for the reference fluid. Additionally it was observed that the discharge temperature was significantly lower than that obtained for R410A. Additionally, it is noteworthy that the thermostatic expansion valve was observed to work very well, according to Uselton (2013), for R1234yf. Also, the Life Cycle Climate Performance (LCCP) revealed a small reduction in the direct contribution to global warming, which was 0.5% compared to R410A. This analysis took into account the required charge of HFO fluid (102% compared to R410A) and consumption around 82% relative to the reference refrigerant. According to the author, this last analysis was performed by the AHRI LCCP HP 1.0 program.

At the Oklahoma State University, experiments were conducted to compare the performance and capacity of a commercial 5 ton heat pump system (R410A) for home applications operating on HFO-1234yf and R32 fluids. Experiments were conducted in a large-scale psychrometric chamber in cooling and heating modes, where the external temperature ranged from 17 ° F (-8 ° C) to 115 ° F (46 ° C). Operating conditions in cooling mode are based on AHRI standards. Two additional conditions were considered with high external temperatures of 110 ° F (43°C) and 115 ° F (46 ° C) to analyze condenser pressure and refrigerant discharge temperature when the unit operates in extremely high external environmental conditions. As a result, the performance with R1234yf provided COPs similar to the R410A, but this refrigerant had quite lower capacities compared to those of the R410A. As the expansion valve opening varied, it improved the capacity of R1234yf by up to 10% by the authors as an alternative only for cooling mode air conditioning for tropical climates, since it presented a 58% lower SCOP than heating R410A, but obtained a higher value of SEER in cooling mode, due to its low electrical consumption.

4. Split air-conditioners

Spatz and Motta (2012) and Spatz et al. 2014, from Honeywell, studied new fluids with potential for use in existing residential air conditioning systems operating with R410A and R22. These were the slightly flammable L, L-20 (GWP <350) and L41 (GWP <500) Series fluids intended for use in new equipment designed to handle any flammability problem. To evaluate proposed fluids, tests were carried out at laboratories in Buffalo, NY. According to the authors the proposed mixtures can provide better energetic performance and GWP reduction from 75% to 95%.

Sethi et al (2015), also from Honeywell, evaluated the use of two HFO refrigerants as replacements for R22 operating in a mini split air conditioner in regions with high temperature conditions. In this work theoretical and experimental analyzes were conducted. A thermodynamic analysis was performed to verify the impact of the use of each refrigerant on operating pressures, refrigerant flow rate, cooling capacity and fluid efficiency. HFO fluids, R444B and R447A, for medium and higher pressures, respectively, were evaluated. The study aimed to verify the effect of ambient temperature on the efficiency of different refrigerants. It has been observed that high pressure refrigerants have greater efficiency losses with increasing temperatures. The thermodynamic analysis showed that both fluids had similar cooling capacity.

In a second step of the theoretical analysis, the R444B fluid was evaluated using a simulation program (Genesym™) which represents a vapor compression refrigeration cycle. In this model, the indoor temperature was set at 27 °C and the external ambient temperature ranged from 35 °C to 52 °C. First, the analysis was performed under the standard condition of the heat exchanger designed for the R22. Refrigerant R444B showed a cooling capacity of 94.5% compared to R22 and 94% of the reference fluid COP value, for an external temperature of 35 °C. Capacity dropped to 92.5% and COP to 92.5% with an external temperature of 52 °C. Simulation was then performed with the same gases and same ambient conditions, but now, with modifications in the design of the heat exchanger, varying the circuit without changing the heat transfer area. According to Sethi et al (2015), both refrigerants performed quite similarly. Also in the same work, Sethi et al (2015) carried out an experimental study with a mini split refrigeration system designed for the R22 fluid, using the optimizations defined in the heat exchanger simulation, as well as optimizing the capillaries for each refrigerant. The environmental conditions were the same as the simulation performed. Refrigerant R444B achieved cooling capacity and efficiency 2% below R22. Suction and discharge pressures and discharge temperature were similar in both tests, suggesting that there is no need to change the compressor design. The authors also revealed that the R444B charge was 15% lower than that of R22. This effect combined with the lower GWP of the HFO fluid corroborates for a lower environmental impact.

Oruç and Devecioğlu (2018) investigated the behavior of R1234yf and R1234ze (E) refrigerants in split conditioners with moderate and high evaporation temperatures. The experiment was carried out under four different ambient conditions (ambient temperatures on the condenser side maintained at 25, 30, 35 and 40 °C), with no equipment modifications except oil change. For R22 mineral oil was used as lubricant whereas, for fluids R1234yf and R1234ze (E), POE oil. The reference fluid cooling capacity of the analyzed equipment was 2.05 kW. The system consisted of a capillary tube, an evaporator, a rotary compressor and a condenser. In each of the tests performed, the loads of the HFO refrigerators were 670g for R1234ze (E) and 700g for R1234yf, while for the reference refrigerant R22, 800g were used. Oruç and Devecioğlu (2018) arrived at the following results: i) The experimental data obtained in the test showed a lower cooling capacity of HFO gases in relation to R22; b) R1234yf obtained 41% of the capacity of R22 while R1234ze (E) obtained 49%; c) Comparatively, the capacity of R1234ze (E) was 13% lower than that of R134yf. On the other hand, the variation in consumption at ambient temperatures used in the test showed that R134yf consumed 14% more electric power than R1234ze (E). The consumption of R22 was 70% higher compared to R1324ze (E) and 48% compared to R1234yf, when the ambient temperature of 30 °C was used.

The mass flow rate found for R1234yf was about 35% higher compared to R1234ze (E). Moreover, the results showed that the mass flow decreases with the increase of the ambient temperature. Both HFO refrigerants had lower mass flow values than R22. Regarding COP, R1234ze (E) obtained values between 5 and 9% higher than R1234yf. However the COP obtained by R22 was higher than the previous ones. Finally, Oruç and Devecioğlu (2018) concluded that, despite the better cooling capacity and consumption achieved by R1234yf based on the tested fluid COPs, R1234ze (E) should be considered as a replacement for R22.

The Air Conditioning, Heating and Refrigeration Institute (AHRI) conducted experimental tests in partnership with the Oak Ridge National Laboratory (ORNL) to evaluate the performance of low GWP refrigerants in two air conditioning mini splits units for high ambient temperature. Both units had a capacity of ~ 5.25 kWth (~ 1.5 TR). One unit was designed to operate with R22 refrigerant, and the other with R410A refrigerant. Six low GWP refrigerants were evaluated as an alternative to R22, namely mixtures N-20B, DR-3, ARM-20B, R-444B, DR-93 and natural refrigerant R290. Likewise, five alternatives to R410A were tested, namely: R-32, DR-55, R-447A, ARM-71a, and HPR-2a. In total, 84 soft-optimized tests were performed, which consisted of an adjustment to the capillary tube length and optimized refrigerant charge. Both units were tested with base refrigerants and their alternatives under six different environmental conditions, where the dry bulb external temperature ranged from 27.8 to 55 °C. As expected, for all refrigerants, efficiency decreased with increasing outdoor temperature, with COP degraded by around 40% for the projected unit for R22 and 45% for R410A when compared between temperatures 27.8 and 55 °C (Abdelaziz and Shrestha, 2016).

Refrigerant mixtures R-452B and R-454B (containing HFO-1234yf), which have low GWP and flammability, are considered as possible substitutes for R410A refrigerant, as they have properties and cooling capacity close to the original refrigerant. In this respect, Hughes and Shah (2016), from Chemours, conducted experimental tests evaluating the performance, thermal stability, lubricant miscibility, and material compatibility of alternative refrigerants, applied to a residential air conditioning system designed for the R410A, operating under standard conditions and also, of high temperatures. The tests were carried out with minor changes to the original system (“soft optimization”) such as replacing the non-adjustable TXV OEM valve with an electronic expansion valve, making it possible to equalize the amount of system overheating operating with R410A. In addition, refrigerant charges have also been optimized to ensure energy efficiency. Results showed similar performance of both R-452-B and R-454-B with R410A in all tests, confirming that they are good options for replacing R410A in small and medium sized air conditioning systems.

A study of Hashimoto et al. (2019), from AGC Chemicals, on HFO-1123 and mixtures HFO-1123 / HFC-32 (40 / 60 wt%) and HFO-1123 / HFC-32 / HFO-1234yf (40/44 /16 wt%) was carried out to evaluate its potentials as possible substitutes for R410A in air conditioners. The authors provided analyses of: physical properties, theoretical thermodynamic cycle, lubricating oil compatibility, drop-in tests on a 4kW air conditioner and self-decomposition of HFO-1123 refrigerant after forced ignition. The results showed performance similar to current HFC refrigerants. Self-decomposition occurred for HFO-1123, but results showed that it does not occur for HFO-1123 / HFC-32 mixtures with at least 40% by mass of HFC-32. Therefore, the authors concluded that mixtures HFO-1123 / HFC-32 and HFO-1123 / HFC-32 / HFO-1234yf are good alternatives to R410A.

5. FLAMMABILITY

Given the pros and cons of HFOs, the importance of studying their flammability is undeniable. Many experiments on the flammability of HFOs have been reported in the literature, but still in insufficient numbers, in view of their future use in industry, commerce and homes. In spite of all the benefits, HFOs have been questioned about their safety, an issue that is due to the flammability of some fluids of this class. (Wu, 2019; Kondo et al., 2012).

Fluorinated hydrocarbons, which contain more fluorine atoms and fewer hydrogen atoms, are considered to be low flammability substances, since fluorine is an inert element in combustion, while hydrogen is an aggravating element. Some fluids of this class are flammable, such as HFO-1234ze and HFO-1234yf, while others are not, such as HFO 1336mzz-Z. Some HFOs are considered toxic, in as much as, when submitted to high temperatures, they decompose into hydrogen fluoride and, when solubilized with water vapor, they form acid that can cause eye, skin and throat irritation and may even lead to death (Kondo et al., 2011).

The prerequisites for combustion of a substance are: fuel, ignition source and oxidizer. The sources of ignition used to test the flammability of refrigerants are usually heaters or electronic devices (capacitors) that discharge electricity, even though the presence of a hot surface may be another source of potential ignition (Tsai et al., 2018).

In order to take the correct safety measures, the basic characteristics of flammability must be known. The most relevant indicators are: lower flammability limit, upper flammability limit, firing rate, minimum ignition energy, surface ignition temperature, self-ignition temperature, ignition temperature, thermal decomposition, heat of combustion, combustion products. Flammability is also influenced by environmental conditions such as pressure, temperature and humidity (Wu, et a., 2019). Given their flammability characteristics, refrigerants are rated for safety (ASHRAE 34, 2016) as: Class 3: Highly flammable fluids; Class 2: Low flammable fluids; Subclass 2L: Slightly flammable fluids (ASHRAE 34, 2016; ISO 817, 2014); Class 1: Fluids without flame propagation.

Refrigerants can be classified for safety from the lower and upper flammability limits, (LFL) and (UFL), respectively. These data are measured under specified test conditions of ambient temperature and pressure - 23 °C and 101.3 kPa (ISO 817, 2014). They indicate the range within which the minimum and maximum concentration, respectively, of a flame-capable refrigerant in a homogeneous mixture with air. If the refrigerant concentration is higher than UFL the flame will not be observed due to lack of oxidizer in the mixture.

For comparison purposes, Table 3 presents flammability characteristics of a number of refrigerants, including HFO1234yf.

Table 3. Flammability characteristics of a few refrigerants (Spatz and Minor, 2008).

Refrigerant	Lower Flammability Limit (%vol)	Upper Flammability Limit (%vol)	Minimum Energy Limit (mJ)	Burning Velocity (cm/s)	Class
Propane	2.2	10.0	0.25	46	3
R152a	3.9	16.9	0.38	23	2
R32	14.4	29.3	30-100	6.7	2L
Ammonia	15	28	100-300	7.2	2L
HFO1234yf	6.5	12.3	>1000	1.5	2L

When it comes to HFCs the relationship between flammability and temperature can be made by White's law (White, 1925). Several class 2L refrigerants had their LFL to UFL ranges measured at different temperatures. The range between HFC limits and HFOs has been shown to increase with increasing temperature, but White's rule has not been valid for HF's (Kondo et al., 2011).

Although the flammability limits of HF's are not related to air humidity, Kondo et al. (2011) hypothesized that air humidity was related to the flammability limits of HFOs. Results have showed that this dependence is real (Kondo et al., 2011). All of these flammability limits are tested by traditional methods such as ASTM E 681, ASHRAE 34, ISO 10156, DIN 51649-1, EN 1839, etc. It is noteworthy that these limits may vary greatly depending on the method under which measurements are carried out.

A number of articles show LFL and UFL values for R1234yf that have been measured by varying ambient temperature and humidity. Some results can be seen according to ASTM method E681 - 04 by Minor and Spatz (2008) or, according to ASHRAE 34-7, by Kondo et. al (2009), who republished the results in 2012, following the same methodology as Takizawa et al. (2009). Each of these published results showed a different flammability limit range, leading to the assumption that R1234yf refrigerant is sensitive to variations in ambient air humidity and temperature. The higher the ambient temperature the lower is LFL value and the greater is UFL, i.e., the flame propagation interval becomes wider, which increases the risk of refrigerant combustion.

Another factor that directly affects the R1234yf LFL-to-UFL interval is ambient pressure (Tsai et al., 2018). Experiments have showed that UFL increases by a much larger proportion than LFL decreases. For example, the value of LFL decreases by 5% at 1000 kPa whereas, for 2000 kPa, the UFL value has an increase of 20% (NEDO, 2011).

Refrigerant R1234ze (E) showed no flame propagation at room temperature, according to EC Standard Testing Method A11 and US Department of Transportation (Knopeck and Rittinger, 2014; Zakel et al, 2019; Honeywell, 2018), the latter according to ASTM E681-04 at 21 ° C. However, tests were performed at higher temperatures of 60 °C and 100 °C according to ASTM E 681 standard (Honeywell 2018) and a range of 5.7% to 11.3% and 7% to 12%, respectively, was found. Humidity on the other hand directly affects R1234ze (E) flammability even when ambient temperature is below 30 °C (Yang et al., 2015a).

Kondo et al (2009) performed tests according to standard ASHRAE 34-07 method on humid air at 35°C and the values obtained in the flammability range were 5.86% to 12.8%. Three years later this same experiment was repeated under the same humidity conditions (Kondo et al., 2012) and results were different, once again suggesting the influence of moisture on the flammability range.

From the research data collected so far, it may not be possible to fully assess the safety level of R1234yf and R1234ze operation in refrigeration systems. Even though they are of a low flammability class, literature shows that limits to combustion may be altered due to variations in parameters such as ambient condition (temperature, pressure and relative humidity).

6. MANUFACTURERS

A brief survey was carried out on the websites of national (Brazilian) and international manufacturers of residential air conditioners and heat pumps, and related compressors, in order to predict any trend towards the adoption of HFOs for such systems. Brazil, as a matter of fact, is concluding officially the transition from HCFCs to HFCs. The moment is still for the replacement of R22 with R410A. Appliances with R22 can still be found for sale. Products advertised on the manufacturers' websites are for R410A, nonetheless.

The present situation in Europe and the United States is the use of R410A as well as R32 for air conditioners. Regarding the choice between the two fluids there seems to be no clear direction, as both can be found in equipment of more than one manufacturer and in different capacities.

In December 2018, after extensive tests and evaluations with low-GWP fluids to replace R410A, Carrier, in partnership with Chemours, announced the adoption of R454B as the primary solution for all its ducted residential and light commercial packaged solutions sold in the United States (Carrier, 2018).

In April 2019, Mitsubishi Heavy Industries, Thermal Systems Division, developed a demo unit for a small-capacity residential air conditioner operating on R454C refrigerant, with a GWP of 146. The announcement regards this as the first worldwide initiative to adopt an HFO fluid in a small residential air conditioning unit. The original fluid was refrigerant R410A and the manufacturer alleged that no major modifications were required beyond refrigerant replacement. The change of fluids represented a 91.3% reduction in system GWP. Model SRK25ZSX-S was used for tests, with a standard 5-meter tubing. The manufacturer cites that the typical shortcomings of refrigerant R454C, namely poor heat exchanger performance, attributed to heat transfer with refrigerant mixtures, was counterbalanced with refrigerant circuiting optimization.

With regard to larger air conditioners, such as devices called VRF (Variable Refrigerant Flow), there are reports on the interest of replacing R410A with R466A, as in the case reported by Toshiba Carrier in January 2019.

7. COSTS

Cost stands out among the major disadvantages of HFOs. It is noteworthy that the cost of R1234ze is a fraction of the cost of R1234yf and therefore mixtures of R1234ze may potentially be closer in price to R410 (Pham and Rajendran, 2012). Table 4 shows the average costs of residential air conditioners. It is seen that the cost of R1234yf is higher compared to other alternatives (Mota-Babiloni et al, 2017). This is mainly due to the higher mass flow rate at the compressor inlet. It is also noteworthy that HFO refrigerants require a larger heat exchanger which, therefore, increases its costs (Botticella et al, 2018). For sizing an HFO-operated domestic heat pump, condenser calculations point to relatively larger pipes, resulting in a higher cost due to the larger pipe diameter and, consequently, an increased refrigerant charge (Nawaz et al, 2017).

Table 4. Alternatives to R22 e R410A in residential air conditioners

Alternative	GWP	Flammability	Equipment cost	Refrigerant cost	Efficiency
R290	3	High (A3)	Low	Low	High
R32	677	Low (A2L)	Low	Medium	High
R441A*	1	Medium (A2L)	Low	Medium	High
R1234yf	<1	Low (A2L)	Medium	High	Low

* Mixture R170/290/600a/600.

According to a report (Goetzler et al. 2016) prepared for the US Department of Energy (2016), alternatives that include refrigerant mixtures (HFC / HFO) are likely to be cheaper than HFO refrigerants, since many low GWP HFOs can result in high costs due to their complex production process. The authors state that there are no studies that estimate costs of implementing HFOS in air conditioners, but point out that experts have estimated an initial cost of up to 10 times the cost of the current R134a to replace it with R-1234yf in an automotive air conditioning system, which may decrease to 4 times or less after the market matures.

A report (Park et al. 2019) produced by Lawrence Berkeley National Laboratory describes the challenges and recommendations for global scale implementation of low GWP refrigerants and with high efficiency in air conditioners. The study was conducted by means of interviews with experts and a recent literature review. On costs associated with the transition to low GWP refrigerants, the report cites initial costs to the manufacturer that include research and development to redesign the system, retrofit production lines and to conduct tests to address safety issues associated with flammable refrigerants. Although the material cost of alternative refrigerant is higher, as in the case of the implementation of HFOs, the report points out that the impact of refrigerants on cost will depend in the short term on the relationship between supply and demand and, in the long run, on the cost savings. Adopting the implementation of flammable refrigerants, regulations may consider requiring training and technical certification, as well as installing additional system components such as refrigerant leak detectors and implementing electronic components so as to prevent sparks. These guidelines may result in additional costs to manufacturers.

8. CONCLUDING REMARKS

Based on experimental tests proposed by researchers and industry using pure HFO fluids (HFO-1234yf, HFO-1234ze (E)) as possible replacements for R410A or R22 fluid for residential applications have shown that achieving the same cooling or heating capacity as with the baseline refrigerant would be difficult. Some components such as the expansion valve would need to be modified or other components added to the system, such as an intermediate heat exchanger or ejector. On the other hand, a more successful alternative has been the creation of pure HFO-based refrigerant mixtures, with which laboratories were able to achieve close values of capacity (95%) and efficiencies (between 95% and 100%) compared to systems operating with the original fluids (R410A and R22).

The commercial availability of residential air conditioners or heat pumps already adopting HFOs or their mixtures has also been addressed. A survey among manufacturers has shown that the number of such models is still scarce. The relatively low interest in adopting HFOs in small systems, currently observed, can be explained by the higher cost of these fluids and the modifications required in system components to operate with them (Park et al., 2019). These modifications include suitability for refrigerant flammability and optimization of the refrigerant coil (Mitsubishi, 2019). Other needs are reported by Hughes and Shah (2016).

From the literature review, it is concluded that there are still few works of HFOs specifically applied to residential air conditioners. Still, one notes that the trend among researchers from academia and development engineers from industry is to seek near drop-in solutions for existing systems to lower costs while meeting low GWP regulations. This explains why substitutes such as R32 and HFC / HFO-based mixtures have been touted as good alternatives. However, for residential applications, the A2L flammability of HFOs and HFO mixtures is still an obstacle, and further studies

need to be done. It can also be concluded that, in the long run, more significant changes in system architecture will have to be adopted as a result of a likely stricter policy, which will force industry to adopt even lower (<400) GWP refrigerants by discarding, therefore R-32 and many HFC / HFO mixtures. HFOs are the new fourth generation refrigerants. They have low GWP, sometimes even less than 1. For sustainability, well-known companies are investing on HFO-related research, but price and flammability remain obstacles on the widespread use of these refrigerants.

Residential air conditioning equipment running on HFO refrigerants are bound to be more expensive because of the high capital and operational cost.

Finally, it should be noted that, in spite of the title of the present article, related work was also sought for residential air conditioners and heat pumps of the window type. However, to the authors' knowledge and until the date of submission, nothing was found about window-type air conditioners or heat pumps operating with an HFO refrigerant.

9. ACKNOWLEDGEMENTS

The authors appreciate the financial support from CAPES, CNPq, FAPEMIG and FAPERJ. This paper is based on a lecture given by one of the authors ("HFO as a technological alternative", by José A. R. Parise) at the Meeting on Technologies for the Air Conditioning Sector - SP, 28th March 2019, organized by the United Nations Industrial Development Organization.

10. REFERENCES

- AHRI Low Global Warming Potential Alternative Refrigerants Evaluation Program Conference, Jan. 2016, http://www.ahrinet.org/App_Content/ahri/files/RESEARCH/AREP_II/0_AHR_Low-GWP_AREP_opening-closing.pdf Visited at Sep. 11, 2019.
- Air-Conditioning, Heating, and Refrigeration Institute (AHRI), "System Soft-Optimized Test of Refrigerant HFO-1234yf (R-1234yf) in a Split System Heat Pump", 2013.
- ASHRAE 34, 2016. Designation and safety classification of refrigerants. ANSI/ASHRAE Standard. Atlanta.
- Barve, A., Cremaschi, L., 2012. Drop-in Performance of Low GWP Refrigerants in a Heat Pump System for Residential Applications. International Refrigeration and Air Conditioning Conference at Purdue, USA.
- Botticella, F., F. de Rossi, A. W. Mauro, G. P. Vanoli, and L. Viscito. 2018. "Multi-Criteria (Thermodynamic, Economic and Environmental) Analysis of Possible Design Options for Residential Heating Split Systems Working with Low GWP Refrigerants." International Journal of Refrigeration 87:131–53.
- Calm, J. M., The next generation of refrigerants – Historical review, considerations, and outlook, *International Journal of Refrigeration*, 2008. "Vol. 31, No.7, pp. 1123-1133, <https://doi.org/10.1016/j.ijrefrig.2008.01.013>
- Carrier, 2019. www.carrier.com/carrier/en/us/news/news-article/carrier_introduces_puron_advance_the_next_generation_refrigerant.aspx. Visited at Sep. 10, 2019.
- Chemours, https://www.chemours.com/Opteon_Stationary/en_GB/index.html. Visited at Sep. 11, 2019.
- Hashimoto, M., Otsuka, T., Fukushima, M., Okamoto, H., Hayamizu, H., Ueno, K., Akasaka, R., 2019, Development of New Low-GWP Refrigerants–Refrigerant Mixtures Including HFO-1123, *Science and Technology for the Built Environment*, 25, 776–783.
- Honeywell, 2018. Solstice Refrigerant (HFO-1234ze(E)) traditional refrigerants fourth generation refrigerants for the 21st century hydrofluoroolefins (HFOs). 3274 Ref A4 EU V7, October.
- Honeywell, 2019. <https://www.honeywell-refrigerants.com/europe/wp-content/uploads/2016/04/Honeywell-Refrigerants-Roadmap.pdf>. Visited at Sep. 11, 2019.
- Hughes, J., Shah, Sonali, 2013. "Testing of Low GWP Replacements for R-410A in Stationary Air Conditioning" (2016). International Refrigeration and Air Conditioning Conference. Paper 1805. <http://docs.lib.purdue.edu/iracc/1805>
- IPCC, 2013. "Climate Change 2013: The Physical Science Basis,".
- ISO 817, 2014. Refrigerants - Designation and safety classification. International Organization for Standardization (ISO). Geneva.
- Knopeck, G. Rittinger, H., 2011. Honeywell's HFO-1234ze(E) delivers an environmentally preferable solution for aerosol propellants. *Spray Technology & Marketing*. 21, 22-25.
- Kondo, S., Takizawa, K., Takahashi, A., Tokuhashi, K., Mizukado, J., 2009. Flammability limits of olefinic and saturated fluoro-compounds. *J. Hazard. Mater.* 171, 613-618. doi:10.1016/j.jhazmat.2009.06.042
- Kondo, S., Takizawa, K., Tokuhashi, K., 2012. Effects of temperature and humidity on the flammability limits of several 2L refrigerants, 2012. Effects of temperature and humidity on the flammability limits of several 2L refrigerants.

- Journal of Fluorine Chemistry 144, 130-136. <https://doi.org/10.1016/j.jfluchem.2012.08.00>
- Makhnatch, P., Khodabandeh, R., Palm, B., HFO refrigerants explained, 31st Oct, 2015. <https://www.kth.se/en/itm/inst/energiteknik/forskning/ett/projekt/koldmedier-med-lag-gwp/low-gwp-news/nagot-om-hfo-koldmedier-1.602602> Visited at Sep. 11, 2019.
- Minor, B., Spatz, M., 2008. HFO-1234yf low GWP refrigerant update. 12th International Refrigeration and Air Conditioning Conference at Purdue. July 12-17, Purdue.
- Mitsubishi Heavy Industries Thermal Systems, 2019. www.mhi.com/news/story/190418.html. Visited at Sep. 10, 2019.
- Mota-Babiloni, A., Makhnatch, P., Khodabandeh, R. 2017. Recent Investigations in HFCs substitution with lower GWP synthetic alternatives: Focus on energetic performance and environmental impact. International Journal of Refrigeration 82 (2017) 288-301.
- Mota-Babiloni, Adrián, Joaquín Navarro-Esbri, Pavel Makhnatch, and Francisco Molés. 2017. "Refrigerant R32 as Lower GWP Working Fluid in Residential Air Conditioning Systems in Europe and the USA." Renewable and Sustainable Energy Reviews 80(June):1031–42.
- Nawaz, Kashif, Bo Shen, Ahmed Elatar, Van Baxter, and Omar Abdelaziz. 2017. "R1234yf and R1234ze(E) as Low-GWP Refrigerants for Residential Heat Pump Water Heaters." International Journal of Refrigeration 82:348–65.
- NEDO, 2011. Development of nonflon type energy saving refrigeration air conditioning system. Ex-post evaluation report. New Energy and Industrial Technology Development Organization (NEDO). 1-786.
- Oruç, V., Devecioğlu, A. G., 2018. "Retrofitting an air-conditioning device to utilize R1234yf and R1234ze(E) refrigerants as alternatives to R22." Journal of the Brazilian Society of Mechanical Sciences and Engineering, Vol.40, No.226.
- Pham, H. M., Monnier, K., "Interim And Long-Term Low-GWP Refrigerant Solutions For Air Conditioning" (2016). International Refrigeration and Air Conditioning Conference. Paper 1734. <http://docs.lib.purdue.edu/iracc/1734>
- Pham, H.M., R. Rajendran. R., 2012. "R32 and HFOs As Low-GWP Refrigerants For Air Conditioning." International Refrigeration and Air Conditioning Conference 2262, 1–10.
- Sethi, A., Vera Becerra, E., Yana Motta, S. F., Spatz, M. W. 2015." Low GWP R22 replacement for air conditioning in high ambient conditions." International Journal of Refrigeration, Vol.57, pp 26–34.
- M. Spatz, M., Minor, B., 2008. A low-GWP refrigerant for MAC, SAE World Congress, Detroit, Michigan, April 14-17
- Spatz, M., Motta, S.Y., 2012. "Recent Developments in low GWP Refrigerants for air conditioning application". Set. 2019 <<https://www.honeywell-refrigerants.com/india/?document=recent-developments-in-low-gwp-refrigerants-for-air-conditioning-applications-paper-november-2012&download=1>>.
- Spatz, M., Motta, S.Y., Seeton C., Niu, Y. 2014. "Low global warming refrigerants for residential air conditioning applications". International Journal of Air-Conditioning and Refrigeration. pp. 1-8.
- Tsai, Y.T., Liao, J.Y., Shu, C.M., 2018. Explosion characteristics of chlorodifluoromethane and isobutane at high temperature and pressure using a 20-L apparatus. Int. J. Refrig. 96, 155-160.
- United States Environmental Protection Agency (US EPA), 2015. "Transitioning to Low-GWP Alternatives in Residential & Light Commercial Air Conditioning". Set. 2019 <<https://www.epa.gov/snap/transitioning-low-gwp-alternatives-residential-and-light-commercial-air-conditioning>>.
- United States Environmental Protection Agency (US EPA), 2016. "Transitioning to Low-GWP Alternatives in Residential and Commercial Air Conditioning and Chillers". Set. 2019 <<https://www.epa.gov/ozone-layer-protection/transitioning-low-gwp-alternatives-residential-and-commercial-air>>.
- Uselton, D. (2013). TEST REPORT # 10 System Soft-Optimized Test of Refrigerant HFO-1234yf (R-1234yf) in a Split System Heat Pump (with Addendum) List of Tested Refrigerant ' s Composition (Mass %) R-1234yf
- Wang, X., Amrane, Karim, 2016, "AHRI Low Global Warming Potential Alternative Refrigerants Evaluation Program (Low-GWP AREP) â€“ Summary of Phase II Testing Results", International Refrigeration and Air Conditioning Conference. Paper 1586. <http://docs.lib.purdue.edu/iracc/1586>
- White, A.G., 1925. XCVI.—Limits for the propagation of flame in inflammable gas–air mixtures. Part III. The effects of temperature on the limits, Journal of the Chemical Society 127, 672-684.
- Wu, X., Dang, C., Xu, S., Hihara, E., 2019. State of the art on the flammability of hydrofluoroolefin (HFO) refrigerant, International Journal of Refrigeration, in press, <https://doi.org/10.1016/j.ijrefrig.2019.08.025>.
- Yang, Z., Wu, X., Tian, T., 2015a. Flammability of trans-1,3,3,3-tetrafluoroprop-1-ene and its binary blends. Energy. 91, 386-392.
- Zhai, R., Yang, Z., Feng, B., Sun, S., 2019. Effect of environmental condition on the flammability limits of two isomers of tetrafluoropropene. Combust. Flame 207, 295-301.

11. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.