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A DECADE OF LOW-GWP REFRIGERANT R1234yf: REVIEW OF MAINLY APPLICATIONS.

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Abstract. *The third generation of fluids, the hydrofluorocarbons (HFC) was created as a main alternative to solve high ozone depletion potential (ODP), which was introduced by the previous generation. Even so, there is still considerable contribution in a high global warming potential (GWP.) For example, R134a is the most significant HFC, but it has a high GWP (1430). For this reason, it is necessary to transition to the fourth generation of refrigerants low-GWP. This article is intended to show a review of R1234yf as one of the ways to get the last family of fluids to replace HFC., The subjects discussed in this article are its application in the vapor compression refrigeration systems and thermal heating as refrigerators, air conditioning systems, heat pump, as well as Organic Rankine Cycle for energy generation. In these areas are most of the theoretical and experimental studies about this fluid. The greatest impact of R1234yf was reflected in the implementation of automotive air conditioning systems as a result of restrictions imposed by The European Union over refrigerants with high GWP.*

Keywords: *Review, refrigerants, R1234yf, low GWP, refrigeration systems.*

1. INTRODUCTION

In the refrigeration industry, proposals are frequently made to reduce environmental damages, this last being reflected mainly in the ozone layer depletion and global warming, These two factors have become the main development conditions for new refrigerants, compounding a large area of research to minimize the negative impact of these substances (Belman. F y Ledesma, 2015). At the same time these new fluids should contribute to the reduction of energy consumption, which has increased by the growth energy demand in developing countries such as China and others with a large territorial extension, as India (Subiantoro y Ooi, 2013).

The European Union has established new guidelines in its legislation to gradually replace R134a and instead of using refrigerants with a GWP of less than 150 in new car models from 2011 and in all new vehicles for 2017, it shows the need for the fourth generation of refrigerants with low global warming potential. The most studied alternatives to replace R134a (the most representative of HFCs) are natural refrigerants such as ammonia, carbon dioxide or mixtures of hydrocarbons (HC); Hydrofluorocarbons (HFC) with low GWP, highlighting R32 and R152a; HFO, specifically

R1234yf (Janković *et al.* 2015). Due to the fact that the thermophysical properties of R1234yf are similar to those of R134a, it becomes the first option to replace the R134A in automotive air conditioning systems.

R1234yf is a HFC (hydrofluorocarbons), the analyzes that have been performed show a low GWP (4), it also has zero ODP, low toxicity, a relatively low limit of flammability, a high minimum ignition energy, a very low combustion rate and it has a high autoignition temperature (Higashi *et al.* 2017). This article presented a review of this fluid quoting the main studies carried out in the last ten years, and in this way, showing the results when R1234yf is used in different thermal and refrigeration systems.

2. VAPOR COMPRESSION SYSTEMS

In the vapor compression systems, different analyzes have been carried out to use the R1234yf as a working fluid, which has the advantage of having a low GWP and thermodynamic properties similar to R134a. For this reason, it is important to emphasize the studies about compressors and ejectors presented comparing both refrigerants operating in different systems.

2.1 Compressor

The Tab. 1 shows the investigations made to analyze the behavior of R1234yf in compressors and compared with other refrigerants.

Table 1. Researches carried out in compressors using R1234yf.

Author	Type of Compressor	Refrigerants Analyzed	Type of Study
Navarro E <i>et al.</i> (2013)	Open piston compressor.	R-1234yf, R-134a and R-290.	Experimental / Comparative
Belman-Flores <i>et al.</i> (2015)	Reciprocating compressor.	R1234yf and R134a.	Model / Comparative
Mendoza-Miranda <i>et al.</i> (2016)	Variable speed reciprocating compressor.	R1234yf, R1234ze(E), R450A and R134a.	Comparative
Ortega Sotomayor and Reis Parise (2016)	Open piston compressor.	R134a, R1234yf and R290.	Model
Xu <i>et al.</i> (2017)	Gas-Injected scroll compressor.	R32 and R1234yf.	Experimental
Schmidt <i>et al.</i> (2019)	Light-commercial compressor.	R134a, R1234yf, R410A, R32 and R1234ze(E)	Comparative

These studies show that R1234yf has great results and performance replacing R134a in compressors. Based on Navarro E *et al.* (2013) analysis in an open piston compressor, R1234yf improved its efficiency compared to R134a for high pressure ratio. It presents less heat losses than R134a, but 20 % more than propane, and also considering this refrigerant as a direct “drop-in” for R134a will lead to a reduction of 10-15 % in the system’s cooling capacity.

R1234yf was still tested in reciprocating compressors by Mendoza-Miranda *et al.* (2016). The results of this developed model showed that the COP difference obtained were between 8 % and 13 % lower than those obtained with R134a. The average cooling capacity using R1234yf was 9 % higher compared with R134a. The differences between these refrigerants decreases when the condensation temperature increases.

2.2 Ejector

The Tab. 2 shows the results obtained from the studies made in the ejectors, in this way a comparison of the refrigerants is made for each case of study.

Table 2. Comparison studies of different refrigerants with the R1234yf in the ejectors.

Author	Refrigerants Analyzed	Results
Lawrence and Elbel (2014)	R134a and R1234yf.	With a cycle of two evaporation temperature expansion valves, the ejector cycle showed COP of 12 % with R1234yf and 8 % with R134a. For a one-valve cycle, the COP of 6 % with R1234yf and 5 % with R134a.

Boumaraf <i>et al.</i> (2014)	R134a and R1234yf.	A better COP for R1234yf is recorded, specifically at high condensing temperatures.
Li <i>et al.</i> (2014)	R134a and R1234yf.	At condensing temperatures of 40 °C and evaporation of 5 °C, the COP and VCC are 5.91 and 2590.76 kJ / for R1234yf.
Milazzo and Rocchetti (2015)	Water, R600a, R134a, R152a, R236ea, R245fa, R365mfc, R1234yf, R1234ze and R1233zd.	For low generator temperatures the R600a, R1234ze, R152a, R134a and R1234yf have a maximum condenser temperature of 35 °C. The other 4 synthetic fluids reach Tcs = 40 °C.
Fiaschi <i>et al.</i> (2015)	R134a, R1234yf, R236fa, R245fa, cyclohexano and N-pentano.	Those with the best performance are R236fa and R245fa, followed by R134a and R1234yf.
Zhang and Cheng (2017)	R1234yf, R134a, R161, R1234ze(E), R1234ze(Z), R1233zd(E), R365mfc and R141b.	R1234ze (Z), R1233zd (E) and R365mfc are suitable for existing ejector cooling systems with thermal pumping effect and with double evacuation chambers in parallel. R1234yf, R161 and R1234ze (E) are suitable only in cooling systems with double evacuation chambers in parallel.
Atmaca <i>et al.</i> (2017)	R1234yf, R1234ze(E) and R134a.	The best operating conditions that produce the maximum COP are closer to R134a and R1234yf in terms of the current pressure range
Zhang <i>et al.</i> (2017)	R1234yf, R290, R134a, R161 and R1234ze(E).	The best setting generation temperatures were 78.4 °C (R1234yf), 80.6 °C (R290), 82.7 °C (R134a), 84.1 °C (R161) and 86.2 °C (R1234ze (E)); deteriorations of COP of 6.51 % / °C (R1234yf), 5.73 % / °C (R290), 2.83 % / °C (R134a), 2.26 % / °C (R161) and 0.89 % / °C (R1234ze (E)).
Marion and Louahlia (2017)	R134a, R601a, R1270, R290, R600, R718, R365mfc, R227ea, Methanol, R245fa, R1234yf and R125.	The most compact system is obtained with R1270, R1234yf, R134a and R290. Fluids such as R601a, R365mfc, methanol and water require much more larger systems.
Fang <i>et al.</i> (2017)	R134a, R1234yf and R1234ze(E).	The R1234yf causes a decrease of 9.6 % for the COP and 19.8 % for the cooling power.
Li <i>et al.</i> (2018)	R134a, R1234yf and R141b.	The cycle studied improves the thermodynamic performance of the heat pump, especially when the ejector sub-cycle uses R141b.

These comparisons between these fourth generation's fluids have shown that in most of the cases, the refrigerants analyzed can achieve comparable results and efficiencies working in ejectors. Lawrence and Elbel (2014) presented experimental results between R1234yf and R134a, which the ejector cycle showed COP of 12 % and 6 % with R1234yf, to two evaporation temperature expansion valves and one valve cycle, respectively, R134a presented 8 % and 5 % under the same conditions. On the other hand Fang *et al.* (2017) considered HFO-HFC mixtures inside the ejectors. Furthermore, the improvements obtained were: 4.1 % for R134a-R1234yf mixture and 11 % for R134a-R1234ze(E) mixture. In this context R1234yf can be considered as a good substitute of HFC. However, the results' values in the ejectors are very closer analyzing R1234yf as replacement for HFCs, but it is possible to establish this fluid as a good alternative with low GWP.

3. AUTOMOBILES AIR CONDITIONERS

The R1234yf is frequently used to replace R134a in automobiles air conditioners in Europe, because it is the best option for automotive refrigeration systems, Cho *et al.*, (2013) have performed out a comparison between R134a and R1234yf applying it in the same automotive cooling systems to compare the features of the refrigeration cycle of both fluids. The R1234yf had a compressor power consumption of 4 % and a refrigeration capacity of 7 % in comparison to R134a, an internal heat exchanger was installed to improve the cooling performance of R1234yf, obtaining a cooling capacity of 1.8 % and a system COP of 2.9 %. Another comparative study about the performance of R1234yf as a substitute for R134a in automobiles air conditioners was carried out by Daviran *et al.* (2017) where simulated a flat plate and multiple plate evaporator, a wobbie-plate compressor, a parallel flow condenser and a thermostatic expansion valve show that the overall heat transfer coefficient of the R1234yf is between 18-21 % lower than that of R134a and the pressure drop with values of 24 % and 20 % smaller than R134a during the condensation and evaporation processes.

Devecioğlu and Oruç (2017) in their investigations have used R1234yf, R444A and R445A because these fluids have low global warming potential (GWP). Analysis to use these fluids in mobile air conditioner systems were made the calculations showed lower COP values for R444A and R445A in comparison to R1234yf, the research also showed that the cooling capacity of R444A and R445A is greater than the one of R1234yf. Di Battista and Cipollone (2016) presented a model of a high efficiency air conditioning for the automotive sector, showing that when R1234yf is used as a working fluid there is a reduction of approximately 22 % of the compression work, in record to the air cooled condenser, this energy represents 8 % of the propulsion power of the middle class cars.

Dimitrova and Maréchal (2015) have studied an energy integration in a hybrid energy system of an electric vehicle using process integration techniques. They selected the refrigerants R1234yf and ammonia for their low GWP and low critical temperature. The results showed that the vehicle is a system with excess of heat and for the energy integration it is necessary to apply a cooler. In addition, based on Golzari' *et al.* (2017) investigations over the second law of an air conditioning system for automobiles that uses R1234yf, they concluded that the use of the latter in air conditioners leads to a greater exergy efficiency compared to R134a.

4. RESIDENTIAL AIR CONDITIONERS

Nowadays residential air conditioners have been designed to operate with high GWP refrigerants, due to the restrictions imposed by the Montreal Protocol in 2007 it is necessary to consider other types of fluids. The Tab. 3 is a investigations' compilation of refrigerants studied to replace the conventional fluids in residential air conditioners.

Table 3. Comparative studies of different refrigerants with the R1234yf in residential air conditioners.

Author	Application	Refrigerants to replace	Analyzed Refrigerants	Results
Subiantoro and Ooi (2013)	Medium scale air-conditioners	-	R22, CO ₂ , R134a, NH ₃ , R32, R404A, R1234yf, R410A, R407C and R438A.	For an increase in expander efficiency from 30 % to 60 %, using R1234yf reduces the recovery period from 5.3 to 3.4 years.
Bansal and Shen (2015)	Window air conditioners.	R410A.	R32, R32 / R125, R600a, R290, R1234yf, R1234ze and R134a.	R1234yf requires higher displacement volumes of the compressor to achieve the same cooling capacity of the other fluids.
Pottker and Hrnjak (2015)	Air conditioners (with and without internal heat exchanger)	-	R134a and R1234yf.	Under established operating conditions, the system COP increased 18 % for R1234yf, this produces a more efficient air conditioning system.
Devotta et al. (2016)	Room air conditioners.	HCFC-22.	HC-290, HC-1270, HFC-161, HFC-32, HFC-1234yf, HC-290, HFC-161, HFC-32, HC-290 and HFC-32.	HFC-1234yf was not considered for the experimental evaluation because it was found to be inappropriate.

5. HEAT PUMP

The studies carried out in the last ten years on thermodynamic properties of R1234yf have had a great impact, reflected in heat pumps with residential applications. Botticella and Viscito (2015) modeled and simulated through the IMST-ART software an air-water residential heat pump operating with R290 and R1234yf. The results of the simulations show the need for a new design of the evaporator to minimize pressure losses with R1234yf. Abas *et al.* (2015) they performed a parametric quantification to select optimal refrigerants applied to solar water heaters operated by thermosyphon, 29 fluids were simulated with REFPROP, it could be deduced that R1234yf presented flaws for commercial water heating applications, while presenting the best results.

On the other hand there are studies focused on the efficiency of heat pumps, Fukuda *et al.* (2016) studied the irreversibilities in heat pumps using mixtures of R744 / R32 / R1234yf and R744 / R32 / R1234ze (E), according to the results they could deduce that YF300 (R744 / R32 / R1234yf; 4/44/52 % by mass) and ZE300 (R744 / R32 / R1234ze (E); 4/43/53 % by mass) are the most suitable to replace R410A and R32. Bellos and Tzivanidis (2019) carried out an investigation of an electricity production system and solar heating ideal for residential applications, the system is

composed of hybrid photovoltaic collectors and a heat pump, seven refrigerants (R404A, R32, R1234yf, R290, R600a, R245fa and R152a) were evaluated in optimization under steady state conditions for heat pumps, R32 was chosen as the best option and secondly R1234yf.

In the Tab. 4 there are works in which various refrigerants (one of them R1234yf) are analyzed when applied to heat pumps.

Table 4. Works on the applicability of various refrigerants in heat pumps.

Author	Application	Refrigerants Analyzed
Guo et al. (2011)	Novel cogeneration system (ORC subsystem, exchanger subsystem and a heat pump subsystem).	R1270, R143a, R290, R22, R115, R218, R717, R12, R1234yf, R134a, E170, R152a, R227ea, R124, R600a, R142b, RC318, R236fa, R600, R114, R236ea, R245fa, R11, R245ca, R123, R141b and R113.
Ghoubali et al. (2014)	Heat pump for simultaneous heating and cooling coupled.	R407C, R290 and HFO1234yf.
In et al. (2014)	Residential heat pump.	R-32 and L-41b.
Wang (2014)	Air conditioners system and heat pump systems.	R1234yf and R134a.
Zhao et al. (2014)	Auto-cascade heat pump cycle.	Butene, R32, R125, R3110, R1270, R143a, R1234ze, R290, R161, R227ea, R600, R218, R-C318, R600a, R1234yf, R236fa, Isobutene, R134a, R236ea, Neopentane, R152a and R245fa.
Yan et al. (2016)	Ejector-compressor heat pump cycle. (ejector and heat pump air source).	R134a and R1234yf.
Nawaz et al. (2017)	Residential heat pump water heaters.	R1234yf, R1234ze (E) and R134a.
Pitarch et al. (2017)	Heat Pump (Evaluation of optimal subcooling).	R290, R134a, R1234yf and R32.

6. DOMESTIC APPLICATIONS

Domestic refrigeration has been greatly affected by international regulations to reduce greenhouse gases, for this reason it is sought to phase out HFCs. Aprea *et al.*, (2016), Belman-Flores *et al.* (2017a) and Belman-Flores *et al.* (2017b) In their studies with domestic refrigerators they have used HFO1234yf to replace HFC134a, they analyzed energy efficiency, in the second case the exergy and in the third investigation they made an experimental study with three identical refrigerators.

Some recent studies in domestic refrigerators, where it is proposed to replace R134a with R1234yf, show that in some cases the first refrigerant shows a better performance. This is the case of Rangel-Hernández *et al.* (2019) they applied an exergoeconomic cost analysis to an experimental installation of refrigerators, their results showed that R134a performs better than R1234yf in different operating conditions, the optimization allows to reduce the cost of cold produced in a 9.8 % when using R134a and in a 6.5 % when using R1234yf. On the other hand Belman F *et al.* (2015) made a review of the different fields of research on domestic refrigeration based on vapor compression, where they cited R1234yf and R1234ze as alternative refrigerants for their low GWP and low levels of toxicity, concluded that these fluids required a more efficient long suction line to start higher speeds compared to systems that use R134a.

7. ORGANIC RANKINE CYCLE (ORC)

The energy systems that use Organic Rankine Cycle (ORC) are also evaluating the use of the fourth generation of refrigerants with low GWP, specifically the R1234yf, Al Jubori *et al.* (2016) developed axial and radial microscale turbines for ORC with R141b, R1234yf, R245fa, n-butane and n-pentane, it was determined that R1234yf has a minimum efficiency of the second law compared to other refrigerants, this is due to the lower performance of turbine and as a consequence it has lower efficiency of the second law. Likewise Heberle *et al.*, (2016) carried out a life cycle assessment to generate geothermal energy by means of binary power plants, for this research the subcritical and two-stage ORC systems were considered, as well as the supercritical cycles, the replacement of R245fa was proposed and

R134a for refrigerants such as R1233zd and R1234yf or natural hydrocarbons, the results in the supercritical cycle with R1234yf showed an increased in efficiency of 37 %.

Wang et al., (2017) studied a double-loop regenerative ORC system using two refrigerants (R1234yf and R1233zd) of low GWP (4 and 1 respectively) as work fluids, to recover energy from a compressed natural gas (CNG) engine, taking into account the environmental impact and the thermodynamic performance, it is considered that R1234yf is one of the most favorable refrigerants for the systems that operate with ORC of double supercritical-subcritical regenerative circuit. Boyaghchi et al. (2018) they made a multi-generation system consisting of a double ORC and a proton exchange membrane electrolyze (PEM) to produce synthesis gas, energy, cooling effect, heating load, hydrogen and oxygen, three mixtures were made with the refrigerants used for ORC R245fa-R134a, R236fa-R1234yf and R600-R290, the greatest increase in the environmental impact rate was recorded for R236fa-R1234yf at 34.69 %.

The Tab. 5 shows other research done on R1234yf with application in energy systems with ORC, when in turn other fluids are considered in the study

Table 5. Research focused on the R1234yf in energy systems with ORC.

Author	Application	Refrigerants Analyzed	Results
Yamada et al. (2012)	ORC (Study on thermal efficiency).	HFO-1234yf, HFC-134a, HFC-245fa, iso-pentane and ethanol.	It was concluded that HFO-1234yf can be used for low to medium temperature ORC applications, considering that its thermal efficiency was not always the best compared with the other simulated refrigerants.
Liu et al. (2012)	Two stage ORC for electric power plants.	R134a, R245fa, R365mfc, R1234yf, R1216, R600, R290, benzene, toluene and R717.	For R1234yf the differences between the temperatures at the turbine outlet and the saturation temperature are very small.
Liu et al. (2014)	ORC for geothermal power generation.	R1225yeZ, R1234yf, R1234zeE, R1234zeZ, R1243zf, R1225yeE, R1225zc and R1234yeE.	R1234yf is suitable for the generation of geothermal ORC energy at low temperature, because the temperature of the geothermal heat source is 120 °C.
Jung et al. (2015)	ORC for heavy-duty series hybrid electric vehicles.	R134a, R245fa, R1234yf, water and ethanol.	R1234yf as it is a dry refrigerant is adopted as working fluid, because it has more gradient in the saturated line, erosion of the turbine is avoided.
Luo et al. (2015)	ORC for power generation.	Butane, isobutane, isopentane, neopentane, pentane, propane, propylene, R1234yf, R1234ZE, R152a and R161.	It was made a mixture of 5 % R365mfc and 95 % R1234yf, managed to drive 10 % more power.
Nasir and Kim (2016)	Vapor compression cycle coupled to ORC for domestic air conditioning.	R245fa, R123, R134a, R1234yf, R1234ze (E), butane and isobutane.	R1234yf was one of the coolants with the best results to be used in ORC.
Invernizzi et al. (2016)	ORC power plants.	HFC-134a, HFO-1234yf and HFO-1234ze (E).	By means of an experimental thermal stability analysis it was established that 200-250 °C can be a viable working temperature limit for HFO-1234yf.
Manente et al. (2016)	ORC subcritical and supercritical.	R1234yf, R1234ze(E), R1234ze(Z), R134a, R245fa and R600a.	The analysis showed that, for a high exergy, recovery efficiencies greater than 40 % are obtained by means of R1234yf.
Da Lio et al. (2016)	ORC systems.	R1234yf, R134a, R1234ze (E), isobutane, R1234ze (Z), R245fa, isopentane and cyclepentane.	When the volumetric flow ratio is 8, the gain in turbine efficiency is 1.5 % when R1234yf is selected instead of cyclepentane.

8. CONCLUSION

A review of the R1234yf was presented by investigating the environmental impact considering the most predominant parameters (ODP and GWP) in the selection of the new refrigerants (fourth generation). The introduction that this fluid has had in steam compression systems, thermal heating and mobile air conditioning systems has been possible because of the results of the theoretical and experimental studies that have been carried out.

On the other hand, it was evidenced that the industry area with the greatest impact of the R1234yf is in the air conditioning systems in automobiles in Europe because of the restrictions imposed by the European Union on conventional refrigerants with a high GWP.

In the studies carried out in the last ten years of R1234yf favorable results of thermodynamic properties were obtained, this did not exclude it from putting it at a disadvantage compared to refrigerants of the third generation, because in some studies of domestic refrigerators it is intended to replace R134a with R1234yf. The results showed that R134a had a better performance, specifically the cost of cold produced was reduced by 9.8 %.

Taking into account the studies mentioned by various authors, in the study of heat pumps R1234yf in some cases its use is not favorable because it demands for better performance new designs of the systems and in commercial water heating applications other fluids such as carbon dioxide present better results. In residential air conditioners (medium-scale and with / without heat exchangers) it is recommended as a working fluid R1234yf because it reduces the recovery periods and also makes the efficiency of the system better. The energy systems with ORC is where it presents better performance of R1234yf compared to the other processes analyzed in this literature review, as it is a dry refrigerant is adapted as working fluid, especially in electric vehicles, in studies on thermal efficiency can be used for applications of ORC from low to medium temperature.

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