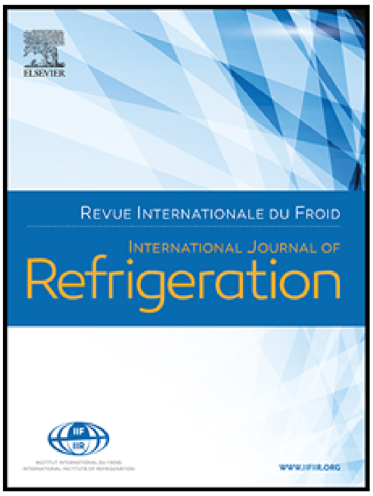

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Overview of low GWP mixtures for the replacement of HFC refrigerants: R134a, R404A and R410A

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Abstract

The current European F-gas regulation establishes restrictions in the use of fluoride refrigerants with a high global warming potential (GWP) in applications of refrigeration and air conditioning (RAC) systems. Moreover, a gradual limitation on the GWP weight of the fluoride refrigerants placed on the market is ong [illegible] C systems operate with refrigerants R134a, R404A, and R410A that have GWP values of 1300, 3943 and 2088, respectively, are being forced to be replaced by environmentally friendly alternatives, like hydrofluoroolefin (HFO) refrigerants and their mixtures with hydrofluorocarbons (HFC), which can be designed to present intermediate characteristics and become the ideal candidate many RAC applications. This work presents the most recent HFC/HFO/HC/R744 refrigerant mixture options for an alternative to the refrigerants mentiond above and compares their energetic and performance with the early developed mixture prototypes.

***Keywords*:** Review; HFC replacement; refrigeration and air conditioning; low GWP mixtures; coefficient of performance; energy.

Nomenclature

CFC	Chlorofluorocarbons
COP	Coefficient of performance
GWP	Global warming potential
h	Enthalpy [$kJ\cdot kg^{-1}$]
HC	Hydrocarbons
HCFC	Hydrochlorofluorocarbons
HFC	Hydrofluorocarbons
HFO	Hydrofluoroolefins
MAC	Mobile air conditioning

ND	
ODP	Ozone depletion potential
P	Pressure [kPa]
Q_v	Volumetric cooling capacity [MJ m^{-3}]
RAC	Refrigeration and air conditioning systems
TEWI	Total equivalent warming impact [kg_{CO2}]
ρ	Density [kg m^{-3}]

1. Introduction

Cold generation systems based on vapor compression technology have operated with a diversity of refrigerants, one the first refrigerants used was ethyl-ether in 1834 (Duarte et al. 2017). After this, other natural refrigerants were used, like carbon dioxide, ammonia, some hydrocarbons (HC), etc. Highly toxic and flammable substances were found among them, which caused the beginning of the evolution in refrigerants, because of the need to find safer substances (Ciconkov, 2018). Calm (2008) described the evolution of the refrigerants and classified them in four generations, which first generation starts with different substances mentioned above. In the 30s, the chlorofluorocarbons (CFC) were developed and this began the second generation, in which synthetic fluids spread all over most of the RAC applications. Around 1950, hydrochlorofluorocarbons (HCFC) were announced and entered into the market because they were able to improve the thermal and energy performance presented by the CFCs in many RAC applications such as commercial refrigeration or stationary air conditioning. Years later, CFC and HCFC substances were widely known for their effect on the degradation of the ozone layer, ODP. Hence, the third generation emerged with a focus on protecting the ozone layer. In the 90s, HFCs emerged in the market as a result of the restrictions in the Montreal Protocol which proposed a gradual reduction of the CFCs and HCFCs production (Brack, 2006). HFCs do not affect the ozone layer and were considered as a replacement for CFCs and HCFCs. These substances still usually maintain the benefit of the low acquisition cost, no flame propagation, chemically stable and good thermodynamic properties (Domanski et al. 2018).

Ho [illegible] 's temperature due to its high global warming potential values and high permanency in the atmosphere. Therefore, at the beginning of the XXI century, the fourth generation of refrigerants appeared to replace HFCs. HFOs are synthetic refrigerants with good thermodynamic properties and great environmental benefits due to their low GWP (<1) and ODP (= 0) (Ciconkov, 2018). These refrigerants are considered as possible substitutes in the vapor compression systems as automotive air conditioning and domestic refrigerator (Aprea et al. 2016; Golzari et al. 2017; Belman-Flores et al. 2017). Also, HCs have been evaluated as possible substitutes for the HFCs. HCs possess a very low GWP and good thermodynamic properties, though their use is limited because of the range of flammability they show (Abas et al. 2018).

In the last decades, different environmental regulations have been proposed with the aim of reducing the problems caused by the direct emissions and its negative effects, all this through the regulation of the production, placing on market and utilization of the different substances responsible for the destruction of the ozone layer and the increase of the global warming (Polonara et al. 2017; Durieux et al. 2019). Another measure taken in the Europe Union to mitigate the impact generated by the refrigerants is established in the Regulation EU No. 517/2014, which aims to limit the emission of fluorinated gases by banning the marketing of RAC equipment using these refrigerants. Through this regulation, the HFCs will be strictly limited for some applications according to their GWP value as observed in Table 1 (Medina, 2014).

Table 1. Ban on the marketing of equipment according to the Regulation EU No. 517/2014.

Systems	**GWP**	**Prohibition Date**
Household refrigerators and freezers	≥ 150	01/01/2015
Commercial refrigerators and freezers	≥ 2500	01/01/2020
	≥ 150	01/01/2022
Fixed refrigeration devices, except applications designed to work at temperatures below -50 °C	≥ 2500	01/01/2020
Compact multi-compressor refrigeration plants (≥40 kW). With the exception of the primary cooling circuits of cascade systems	≥ 150 ≥ 1500	01/01/2022
Portable air conditioners	≥ 150	01/01/2020
Simple split A/C systems containing less than 3 kg of fluorinated gases	≥ 750	01/01/2025

Table 2. Studies based on alternative refrigerants with a low GWP.

Remarks	Mclinden et al. (2014)	Sarbu (2014)	Wang and Amrane (2014)	Mota-Babiloni et al. (2015)	Wang and Amrane (2016)	Mota-Babiloni et al. (2017a)	Harby (2017)	Abas et al. (2018)	Ciconkov (2018)
The low flammability alternatives like R444A, R447A, could be used in primary circuits of secondary systems, cascade systems in high stage or low load applications.				▨		▨			▨
HFC/HFO mixtures (R448A, R450A) developed do not provide a definitive solution due to restrictions such as flammability or GWP values higher than those set by the EU Regulation.				▨					▨
Mixtures of HC and HFC composed of R290, R600a, R32 y R152a improve the environmental and safety characteristics of refrigerants (reduce GWP and flammability).	▨	▨					▨		▨
R32 has good thermophysical characteristics, whereby is presented as an alternative for the elaboration of mixtures like R454B, R446A, R447A, DR-55 for the replacement of the R410A.					▨	▨			
For some alternatives of low GWP (HC, HFC, and its mixtures) is necessary to realize modifications to the system to improving its energy efficiency, mainly those mixtures containing R600a and R290.		▨	▨		▨	▨	▨		
Natural refrigerants such as R717, R744, and HCs are the best alternatives for HFCs, but there are some limitations such as toxicity, flammability and poor compatibility with materials.	▨	▨				▨	▨	▨	▨
Because of the thermophysical characteristics of natural refrigerant (R717) and HCs (R600a, R290), the initial cost of equipment is usually higher compared to HFC-based systems.		▨							▨
In terms of energy efficiency, the refrigerants N40, L40 and DR-7 are good alternatives for R404A and L41 and DR-5 can be suitable replacements for R410A.			▨	▨					

Table 3. Properties of the replacement refrigerants for R134a[1].

Properties	R134a	R445A	R430A	R515A	R436A	R456A	ND[2]	R516A
Composition	---	R134a/R1234ze(E)/R744	R152a/R600a	R1234ze/R227ea	R600a/R290	R32/R134a/R1234ze (E)	R134a/R1234yf/R1234ze (E)	R1234yf/R134a/R152a
Mass percentage	---	(9/85/6)	(76/24)	(88/12)	(46/54)	(6/45/49)	(40/22/38)	(77.5/8.5/14)
Boiling point [K]	247.1	224.0	245.6	254.4	238.9	242.4	251.7	243.8
Critical temperature [K]	374.2	379.2	380.2	381.8	398.0	375.8	391.5	369.8
Critical pressure [kPa]	4059.3	4544.4	4089.1	3555.7	4272.8	4175.2	3968.8	3615.2
Liquid density [kg m^{-3}]	1206.7	1149.0	760.1	1187.2	517.9	1164.4	1182.9	1066.8
Vapor density [kg m^{-3}]	32.35	28.60	19.60	27.18	13.34	30.96	17.71	34.58
Latent heat [kJ kg^{-1}]	216.9	226.5	327.1	187.9	414.1	220.7	219.0	202.83
C_p liquid [kJ $kg^{-1}K^{-1}$]	1.425	1.445	1.971	1.361	2.570	1.434	1.356	1.456
C_p vapor [kJ $kg^{-1}K^{-1}$]	1.032	0.983	1.428	0.966	1.861	1.020	0.942	1.089
Liquid conductivity [mW $m^{-1}K^{-1}$]	81.13	77.98	90.06	72.89	92.49	79.90	78.50	70.09
Vapor conductivity [mW $m^{-1}K^{-1}$]	13.83	14.33	15.55	13.93	18.01	13.99	13.24	14.38
Viscosity of liquid [μPa s^{-1}]	194.9	175.5	142.9	194.1	116.0	179.6	196.9	154.8
Viscosity vapor [μPa s^{-1}]	11.69	12.64	9.47	12.17	7.90	12.01	10.86	11.42
GWP	1300	130[3]	110[4]	387[5]	10[6]	687[7]	522[8]	131[7]
Class (ASHRAE)	A1	A2L[3]	A3[4]	A1[5]	A3[6]	A1[7]	---	A2L[7]

[1] Data obtained through REFPROP v10 (Lemmon et al. 2013) to temperature of 298.15 K.
[2] ND: Not Defined, Kumar (2018).
[3] Devecioğlu and Oruç (2017)
[4] Chen et al. (2014)
[5] Sethi and Motta (2016)
[6] Rasti et al. (2010)
[7] Bitzer (2018)
[8] Kumar (2018)

Table 4. Properties of replacement refrigerants for R404A[1].

Properties	R404A	R454C	R455A	R442A	R454A	R449A	R407H	R459B	R465A
Composition	R-125/143a/134a	R32/R1234yf	R744/R32/R1234yf	R125/R32/R134a/ R227ea/R152a	R32/R1234yf	R32/R125/R134a/ R1234yf	R125/R32/R134a	R32/R1234yf/R1234ze (E)	R32/R290/R1234yf
Mass percentage	(44.0/52.0/4.0)	(21.5/78.5)	(3/21.5/75.5)	(31/31/30/5/3)	(35/65)	(24.3/24.7/25.7/25.3)	(15/32.5/52.5)	(21/69/10)	(21/7.9/71.1)
Boiling point [K]	226.9	227.8	221.1	226.7	225.3	227.4	228.6	228.2	221.7
Critical temperature [K]	345.3	358.8	358.7	355.6	354.9	355.2	359.7	360.6	354.7
Critical pressure [kPa]	3734.9	4318.8	4653.8	4747.7	4627.3	4499.7	4856.7	4360.6	4343.0
Liquid density [kg m^{-3}]	1044.1	1042.4	1033.4	1108.5	1020.9	1097.1	1111.2	1051.1	934.6
Vapor density [kg m^{-3}]	65.27	44.45	45.56	47.40	48.11	49.32	41.86	43.03	45.16
Latent heat [kJ kg^{-1}]	200.9	227.2	239.4	257.4	251.3	238.6	269.9	228.1	245.2
C_p liquid [kJ kg^{-1}K^{-1}]	1.542	1.539	1.567	1.579	1.622	1.550	1.585	1.531	1.662
C_p vapor [kJ kg^{-1}K^{-1}]	1.221	1.135	1.136	1.184	1.215	1.162	1.,176	1.123	1.230
Liquid conductivity [mW m^{-1}K^{-1}]	62.71	75.58	76.94	85.83	83.76	80.00	90.20	76.45	76.22
Vapor conductivity [mW m^{-1}K^{-1}]	17.00	14.35	14.56	14.76	14.60	14.67	14.58	14.31	15.23
Viscosity of liquid [µPa s^{-1}]	128.3	129.4	126.1	141.5	122.2	138.9	148.6	132.2	115.0
Viscosity vapor [µPa s^{-1}]	12.23	12.08	12.24	12.63	12.35	12.42	12.19	12.10	11.86
GWP	3943	146[9]	146[9]	1888[10]	244[11]	1282[11]	1378[11]	143[12]	143[12]
Class (ASHRAE)	A1	A2L[9]	A2L[9]	A1[10]	A2L[11]	A1[11]	A1[11]	A2L[12]	A2[12]

[1] Data obtained through REFPROP v10 (Lemmon et al. 2013) to temperature of 298.15 K.

[9] Zgliczynski and Sedliak (2018)

[10] Oruc et al. (2018)

[11] Llopis et al. (2017)

[12] Bitzer (2018)

Table 5. Properties of the replacement refrigerants for R410A[1].

Properties	**R410A**	**R446A**	**R447B**	**R452B**	**ARM-71A**	**ARM-20A**	**ARM-20B**	**R463A**	**R466A**
Composition	R-32/125	R32/R600a/R1234ze(E)	R32/R125/R1234ze (E)	R32/R125/R1234yf	R32/R1234yf/ 1234ze(E)	R32/R1234yf/152a	R32/R1234yf/152a	R744/R32/R125 /R1234yf/R134a	R32/R125/R13I1
Mass percentage	(50.0/50.0)	(29/3/68)	(68/8/24)	(67/7/26)	(68/26/6)	(18/70/12)	(35/55/10)	(6/36/30/14/14)	(49/11.5/39.5)
Boiling point [K]	221.7	223.4	223.2	222.5	222.9	230.6	226.7	213.3	219.1
Critical temperature [K]	344.5	359.1	356.7	350.2	352.77	363.2	358.4	348.8	346.3
Critical pressure [kPa]	4901.0	5725.2	5644.7	5220.1	5359.7	4308.0	4721.3	5244.0	5282.5
Liquid density [kg m^{-3}]	1058.6	1001.4	1020.9	993.5	991.6	1028.1	1005.8	1051.4	1285.9
Vapor density [kg m^{-3}]	65.97	42.51	45.97	52.39	49.33	38.86	42.45	57.67	77.52
Latent heat [kJ kg^{-1}]	272.9	327.2	320.4	331.8	315.9	238.13	267.4	279.0	239.4
C_p liquid [kJ $kg^{-1}K^{-1}$]	1.708	1.787	1.759	1.789	1.786	1.558	1.649	1.694	1.376
C_p vapor [kJ $kg^{-1}K^{-1}$]	1.445	1.335	1.339	1.439	1.403	1.146	1.222	1.256	1.167
Liquid conductivity [mW $m^{-1}K^{-1}$]	89.19	113.79	109.35	103.57	106.09	78.36	87.77	87.16	104.6
Vapor conductivity [mW $m^{-1}K^{-1}$]	15.73	14.70	14.72	15.16	14.97	14.49	14.63	15,47	14.58
Viscosity of liquid [μPa s^{-1}]	117.9	125.2	121.8	114.7	116.3	134.8	125.4	122.1	139.4
Viscosity vapor [μPa s^{-1}]	13.66	12.73	13.07	12.93	12.81	11.85	12.18	13.15	15.30
GWP	2088	470 [13]	710[13]	677[13]	460[14]	139 [14]	251[14]	1377[15]	143[15]
Class (ASHRAE)	A1	A2L[13]	A2L[13]	A2L[13]	A2L [14]	A2L [14]	A2L[14]	A1[15]	A2[15]

[1] Data obtained through REFPROP v10 (Lemmon et al. 2013) to temperature of 298.15 K.

[13] Pham et al. (2016)

[14] Abdelaziz et al. (2016)

[15] Bitzer (2018)

Thus, the refrigeration industry has been forced to work on changes to find refrigerant substances with a lower environmental impact and higher or similar thermal and energy performances in the equipment. The objective of studying different mixtures of HC, HFC, HFO, and R744 is to reduce the environmental impact by obtaining a substance with a lower GWP to improve the thermophysical characteristics and to reduce the level of risk, especially in HCs (Zhao et al. 2004). According to the above, Table 2 summarizes the main conclusions obtained on applications of some alternative refrigerants in recent years. The conclusions are related to an area shaded to work cited. Although it is not mentioned in the table, the use of natural refrigerant R744 is being increased in supermarkets of developed countries (Zolcer and Battesti, 2019). However, the efficient use of R744 requires advanced technologies and configurations, and including this refrigerant in the thermodynamic configuration would end up in an unfair comparison, because its efficiency would be lower compared to HFC systems.

Since the use of HFCs represents around 2% of the greenhouse gases emissions in 2015, and it could represent a 20% by 2050 (Velders et al. 2009), measures were taken to stop the impact generated for using these substances. In this sense, refrigerants R134a, R404A, and R410A, which are widely used in many types of RAC applications, are the most affected by regulations due to their high GWP levels. Zeiger et al. (2016) presented a study in which they proved that refrigerants R134a, R410A and R404A still prevail in different applications for commercial refrigeration systems installed. By considering these data, it is noteworthy that there is still a dependency on vapor compression systems using HFCs.

Due to the above and the requirements in the regulations that affect the use of these substances, it is necessary to propose solutions for their replacement which must comply with the objectives of improving the energy consumption and above all, of reducing the environmental impact. Therefore, this work analyzes the new refrigerant mixtures (HFC/HFO/HC/R744) alternatives developed and registered since 2015 (Mota-Babiloni et al. (2015)) to date, to substitute R134a, R404A, and R410A in their different RAC applications. For this purpose, a careful review was conducted about the new mixtures which show the main researches in this field by considering their classification and selection criteria concerning their thermodynamic and physical properties; moreover, performance potential is presented between them and the refrigerants they are meant to replace.

2. Alternative mixtures for R134a

R134a is widely used in applications of medium temperature since good efficiencies are generated in the cycle. Its operation conditions are limited in some applications due to its boiling point (-26°C). R134a is widely used in chillers (Sieres and Santos, 2018); in countries like China, the growth in the automotive industry has potentialized the consumption of R134a, and thus increasing from 25.52 thousand tons in 2007 to 75.05 thousand tons in 2015, with an annual growth of 14% (Tianduo and Xunmin, 2017); and in Mexico, R134a is still considered the leader in the market of mobile air conditioning (Posada et al. 2017).

Different experimental studies have been conducted to replace R134a directly. In this sense, Devecioğlu and Oruç (2017) evaluated different alternatives to replace R134a in mobile air conditioning systems (MAC); according to their results, R445A showed a higher cooling capacity but a lower COP concerning R134a. Lee et al. (2015) evaluated R445A in which a higher COP than that of R134a was obtained in MAC systems. By considering both studies, it is noteworthy that the variety of results is due to the different operation conditions, in which the best energy performance is presented in low condensation temperatures. R456A is another mixture that has been evaluated as an alternative for R134a in MAC systems; this refrigerant has GWP values approximately 50% lower than R134a and an A1 safety classification according to ASHRAE (Makhnatch, 2018), which is an important factor in the selection of refrigerants for the automotive sector.

Sethi and Motta (2016) theoretically investigated refrigerants to replace R134a in medium pressure applications like a chiller. Among the evaluated refrigerants was R515A, which represented a capacity loss between 25% and 30%, with a similar COP to R134a and a GWP reduction of almost 70% concerning R134a. R515A has also been evaluated in commercial refrigeration systems for medium temperature applications (Petersen et al. 2018). These authors concluded that R515A caused a low environmental impact and its efficiency was greater than R134a.

Although there are limitations due to the safety classification for HCs, they have presented adequate results in replacing R134a; moreover, HCs present a reduction in the refrigerant mass charge of approximately 50% with respect to R134a. For example, Rasti et al. (2013) analyzed the behavior of a domestic refrigerator with R436A and R600a, in which they had to change the compressor to work with R600a. They obtained a reduction in energy consumption in comparison with R134a, between 14.6% and 18.7% for R436A and R600a, respectively. It also had a reduction in the TEWI of 16% and 21% for each refrigerant. R436A was also evaluated by Hastak and Kshirsagar (2018) in a domestic refrigerator; they obtained a reduction in the energy consumption of 41.6% and an increase in the COP of 60% compared with R134a.

Other mixtures have also been studied with small variations in the mass percentage of R436A. Mohanraj (2013) studied mixture R600a/R290 (45.2%/54.8%) and obtained a lower energy consumption of approximately 11% and a COP of around 3.5% higher concerning R134a. Agrawal et al. (2017) evaluated the performance of a domestic refrigerator with R600a/R290 (50%/50%) versus R134a, obtaining an increase in the cooling capacity and minor energy consumption using R600a/R290. It must be considered that the evaluation of HCs do not use the compressor designed for HFC since HCs have a density approximately 55% lower than HFCs; therefore, a compressor with a higher displacement is required to avoid affecting its performance (Zhang et al. 2019), and a special safety provision, so the system works with flammable refrigerants (Uddin et al. 2019). Therefore, these operational aspects and characteristics of HCs promotes the continuous search for new mixtures of HCs.

Other HFC/HC mixtures have also been presented as replacement options for R134a; for example, Abraham and Mohanraj (2019) experimentally analyzed the performed on the behavior of R430A in a MAC obtaining, an increase between 9 and 20% in the COP and a reduction between 6% and 11% in the energy consumption with respect to R134a for the different analyzed conditions. Mohanraj (2019) conducted an experimental study on the energy performance of a domestic refrigerator using R430A, which presented an energy consumption of 3.9% lower with a COP from 3.8% to 6.4% higher in comparison with R134a.

Additional works have considered mixtures from refrigerants R134a, R1234yf and R1234ze. One work evaluated the mixture of R134a/R1234yf in different mass compositions, which proved that in compositions higher than 10% for R134a, the mixture became non-flammable and showed similar performances to R134a (Meng et al. 2018). Kumar (2018) analyzed many parameters like the mass flow, COP, cooling capacity and exergy efficiency for thirty mixtures of R134a, R1234yf and R1234ze. The author concluded that the most efficient mixture (ND) for the direct replacement of R134a was composed of 40% R134a /22% R1234yf /38% R1234ze. Refrigerant R516A, which is considered for its analysis in the present work, is one of the most recent proposed mixtures to replace R134a (Bitzer, 2018).

Mixtures based on HFOs, HFCs and HCs are evaluated as feasible options to reduce the environmental impact and to try to obtain better performances in comparison with pure refrigerants. The GWP value obtained from the mixtures is significantly lower; and is proportional to the mass percentage in each mixture component. Though the GWP reduction for some mixtures can be approximately 50% in comparison with R134a, their values still surpass the ones contemplated in the European regulation; therefore, these mixtures are considered as a temporal alternative in the replacement of HFCs, which means that the development and research must continue in order to find a reduction on the environmental impact in the refrigeration sector.

2.1 Properties of the replacement refrigerants for R134a

Table 3 presents the new refrigerant mixtures recently developed and previously commented as replacements for R134a, indicating their composition in mass (ASHRAE, 2019) and the main properties. The table shows that the density of the liquid mixtures ranges from 2.5% to 6% lower than R134a, except for R436A and R430A, which present a decrease between 57% and 37% respectively, in comparison with R134a. The direct consequence of these changes is the reduction of the refrigerant mass used in the equipment and a direct decrease in the volumetric efficiency of the compressor. The liquid viscosity presents a reduction of 40% for R436A, 26% for R430A and 21% for R516A. The latent heat of R430A and R436A presents an increase of 50 and 90%, respectively, which allows for a major heat extraction per unit of mass. Another of the properties that favor the absorption and rejection of heat is the thermal conductivity of vapor and specific heat, which are found in the same magnitude range for all the refrigerants discussed in this work as alternatives for R134a.

2.2 Energy comparison for the R134a replacement refrigerants

Considering that R134a is widely used in medium temperature applications and based on the range of operation conditions (Mohanraj, 2013; Saravanakumar and Selladurai, 2014; Mota-Babiloni et al. 2019), an evaluation of the energy performance for each mixture is presented in this work according to the following considerations: the isenthalpic process is considered at the expansion device, pressure drops are neglected in the heat exchangers and there is no heat transfer to the surroundings. Through the representation of the vapor compression cycle and in a *P-h* diagram, Figure 1 shows the different mixtures. The comparison was performed by considering the following operation conditions: condensation temperature of 318K, evaporation temperature of 313K, subcooling, and superheating of 5K and a process of isentropic compression. Figure 1 depicts the behavior of each refrigerant under the same operation conditions; most of the saturation curves present very similar values to R134a, excepting refrigerant R436A and R430A, which present a higher refrigeration capacity and higher energy consumption per mass unit of refrigerant in the process of compression due to their great variation in thermophysical properties with respect to R134a.

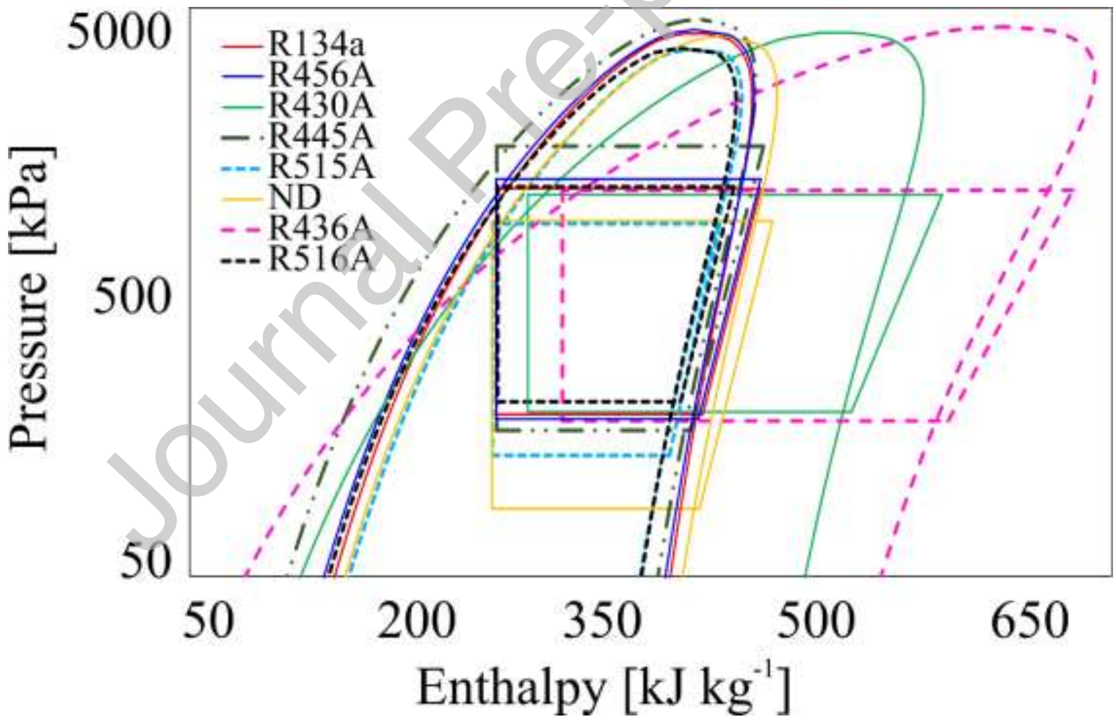

Figure 1. *P-h* diagram of the alternative refrigerant mixtures for R134a.

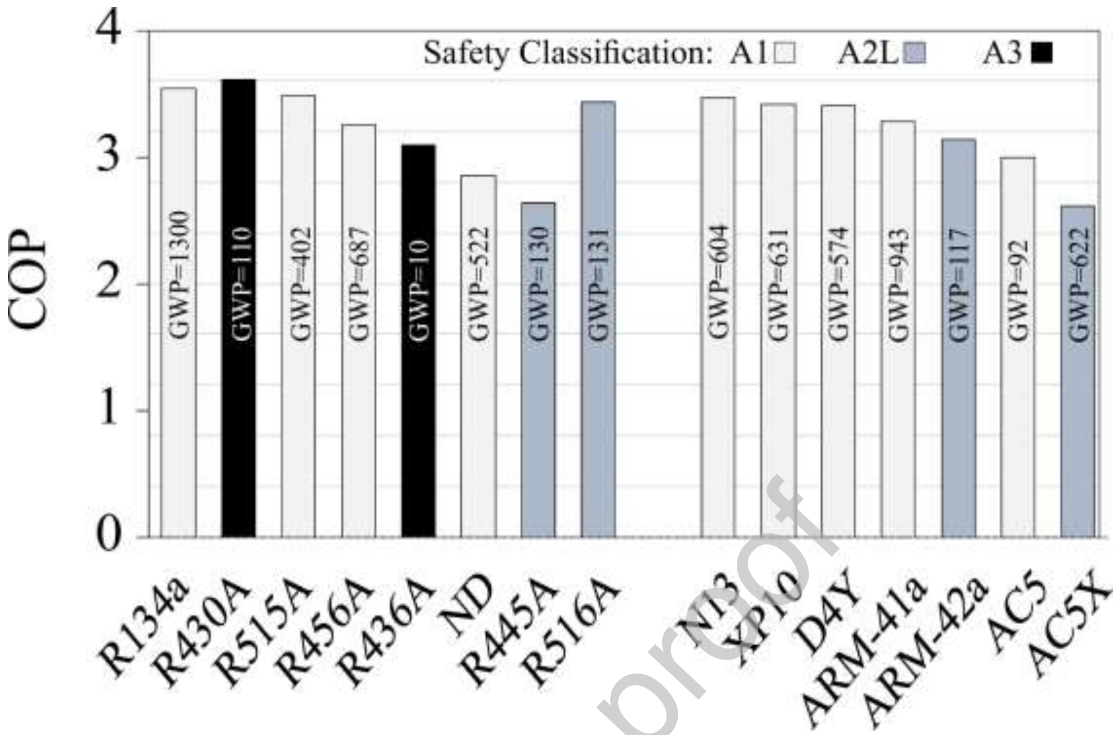

Figure 2. COP comparative between the alternative refrigerants for R134a.

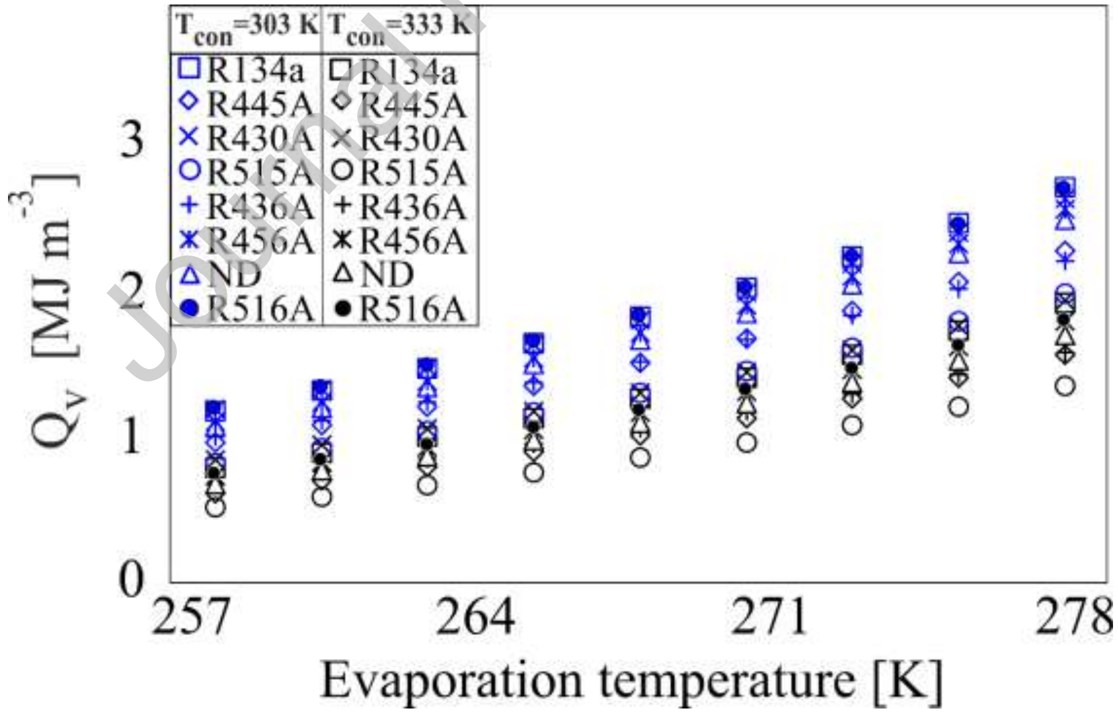

Figure 3. Volumetric cooling capacity *vs* evaporation temperature for R134a alternatives.

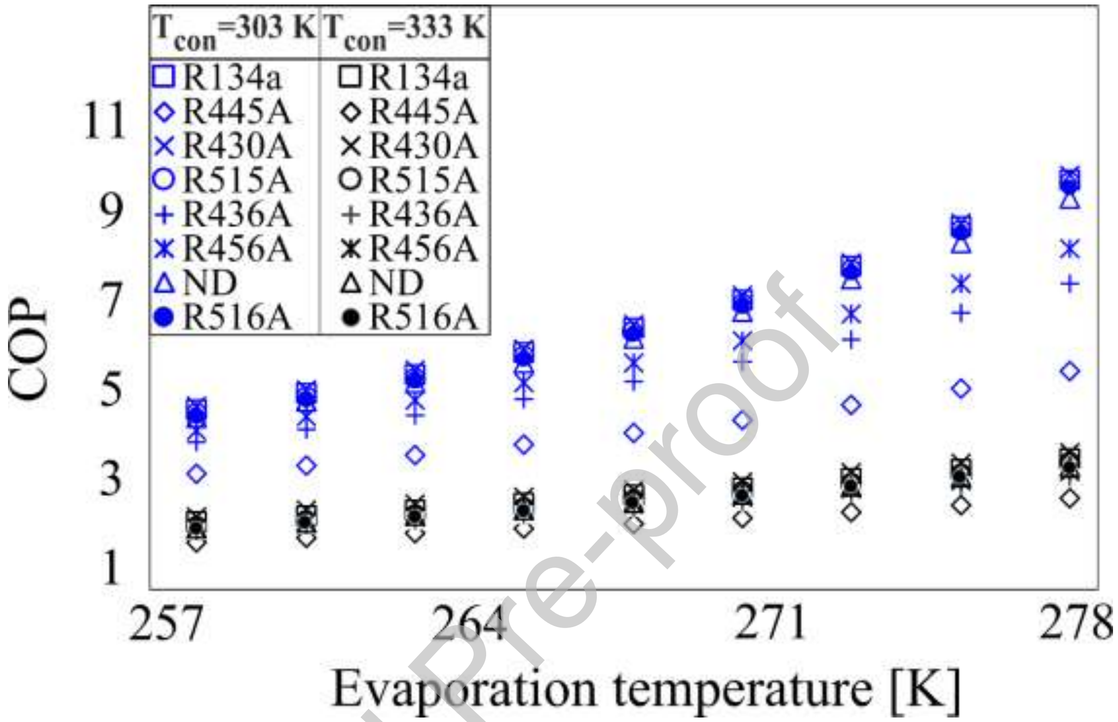

Figure 4. COP *vs* evaporation temperature for R134a alternatives.

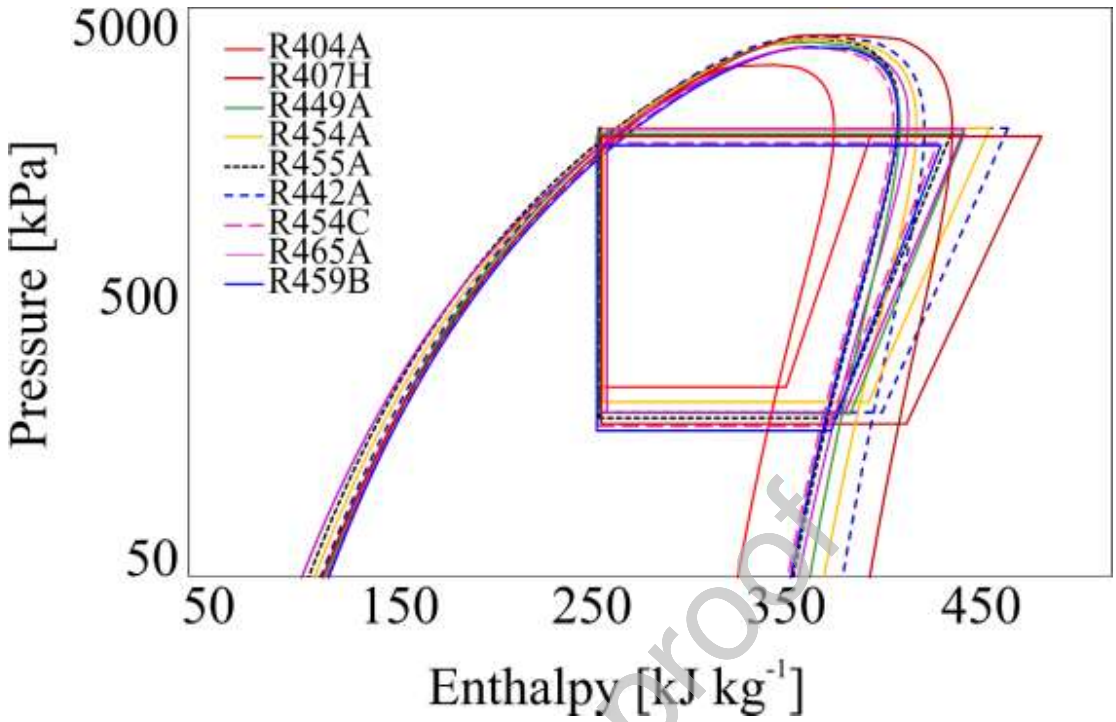

Figure 5. *P-h* diagram of the alternative refrigerant mixtures for R404A.

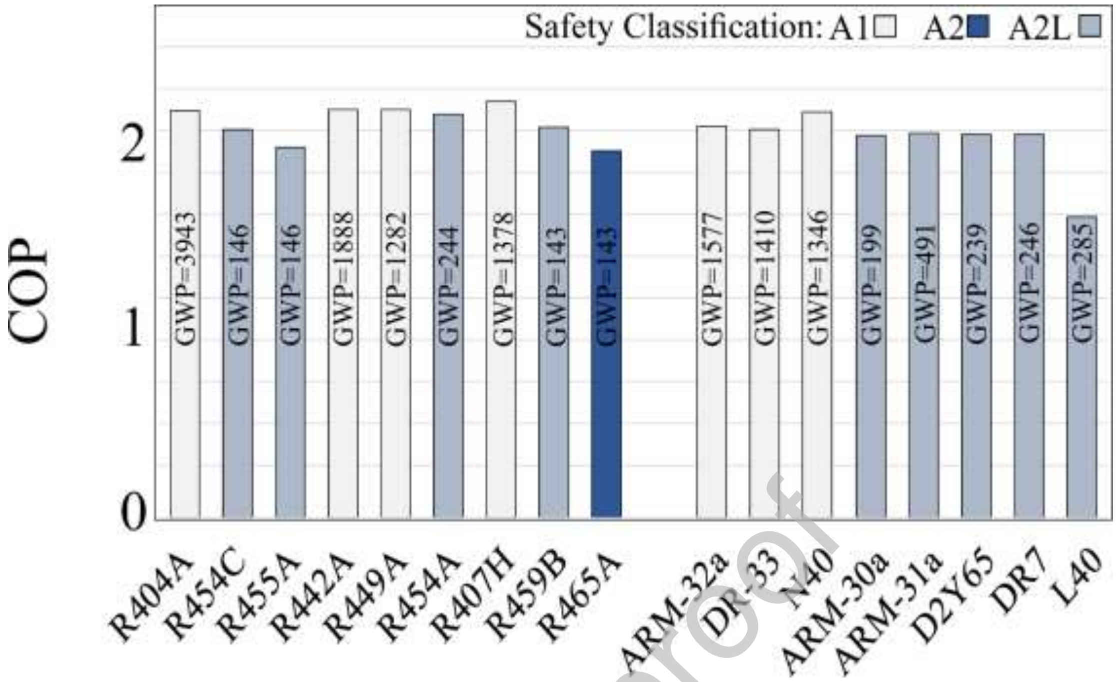

Figure 6. COP comparative between the alternative refrigerants for R404A.

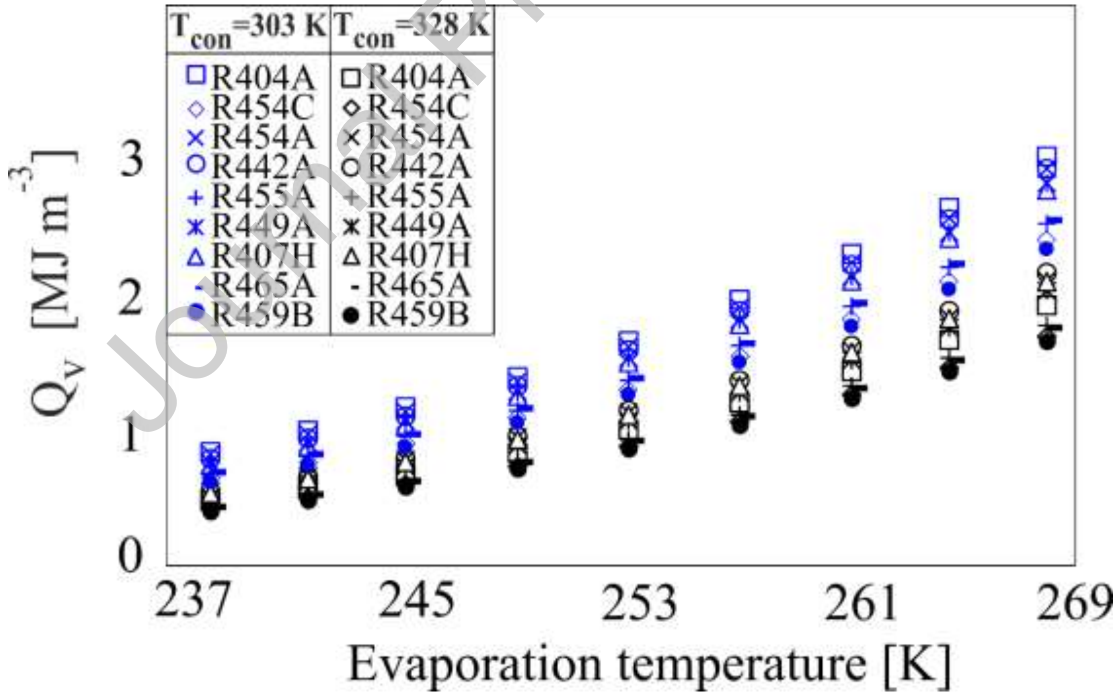

Figure 7. Volumetric cooling capacity *vs* evaporation temperature for R404A alternatives.

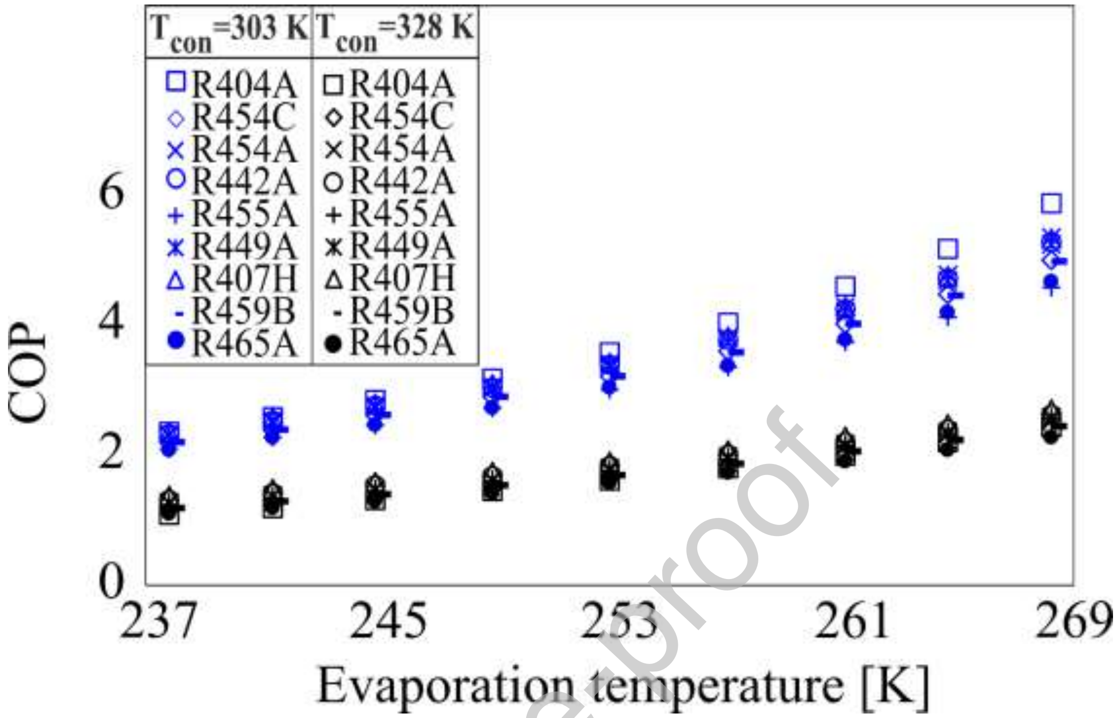

Figure 8. COP *vs* evaporation temperature for R404A alternatives.

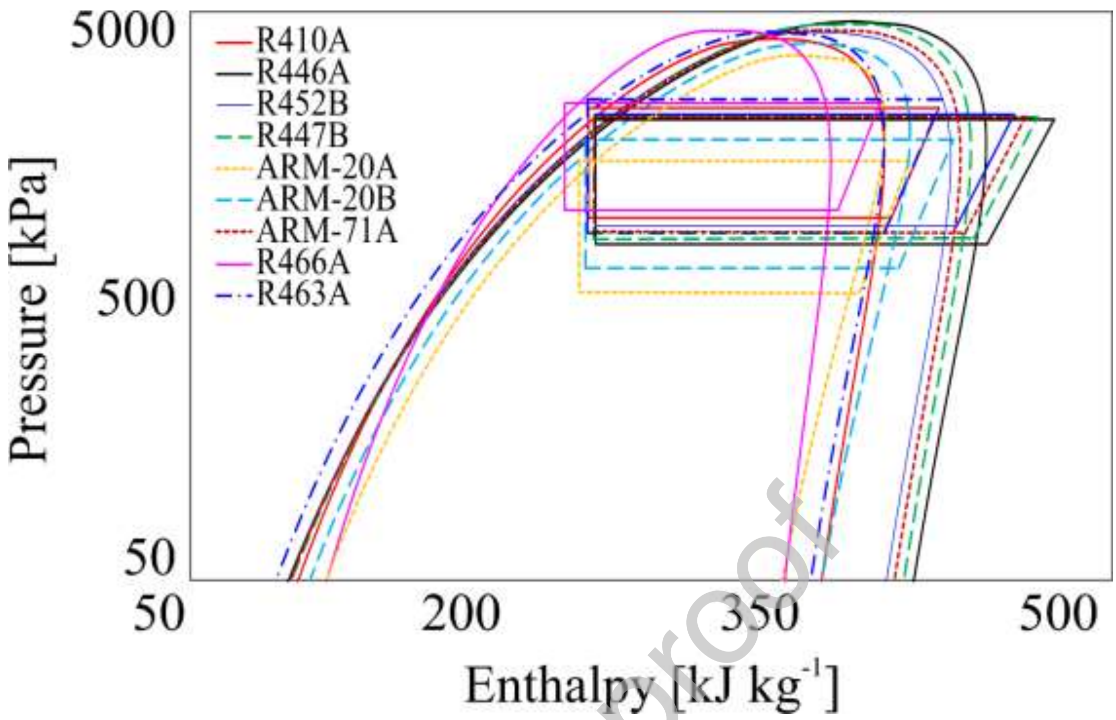

Figure 9. *P-h* diagram for the alternative refrigerant mixtures for R410A.

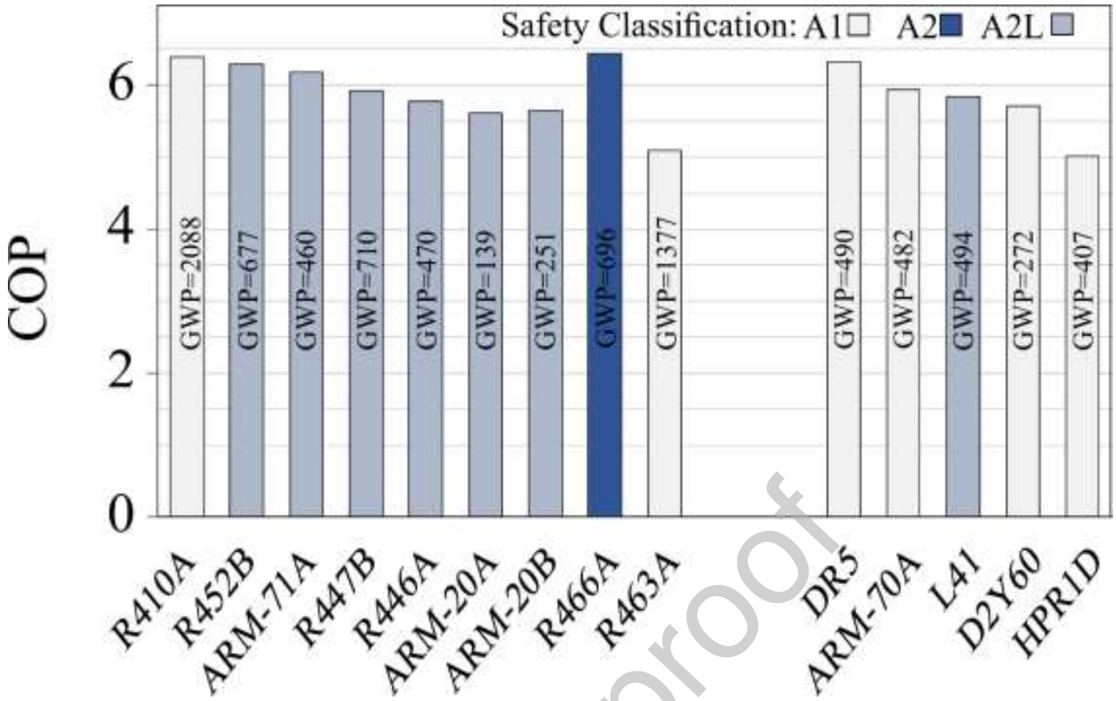

Figure 10. COP comparative between the alternative refrigerants for R410A.

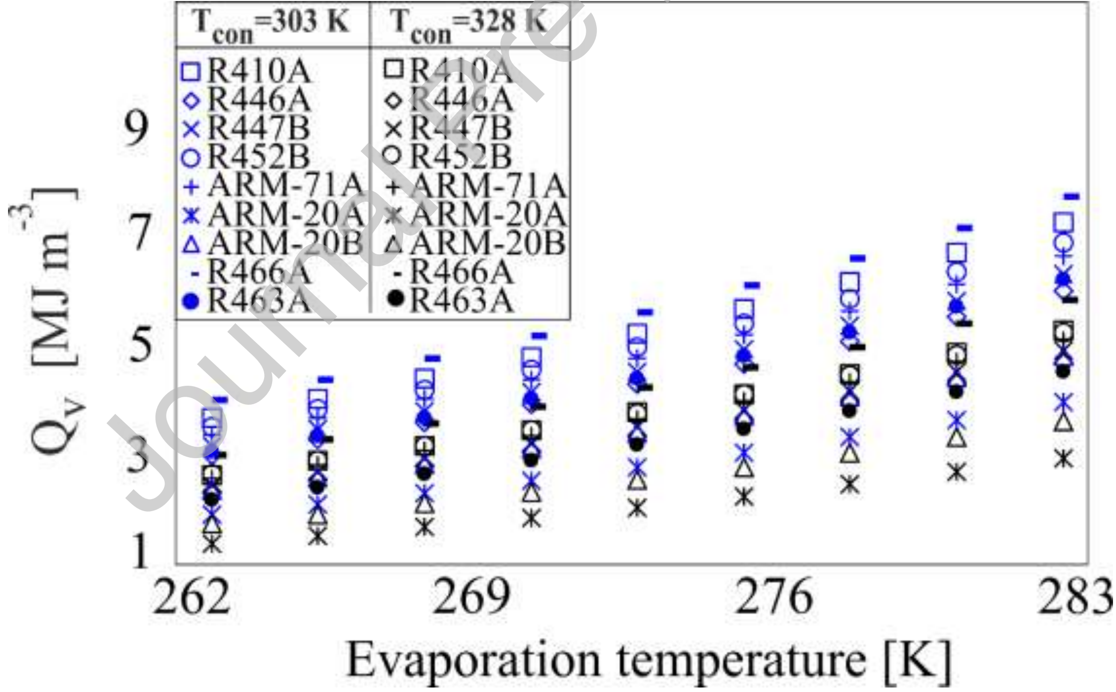

Figure 11. Volumetric cooling capacity *vs* evaporation temperature for 410A alternatives.

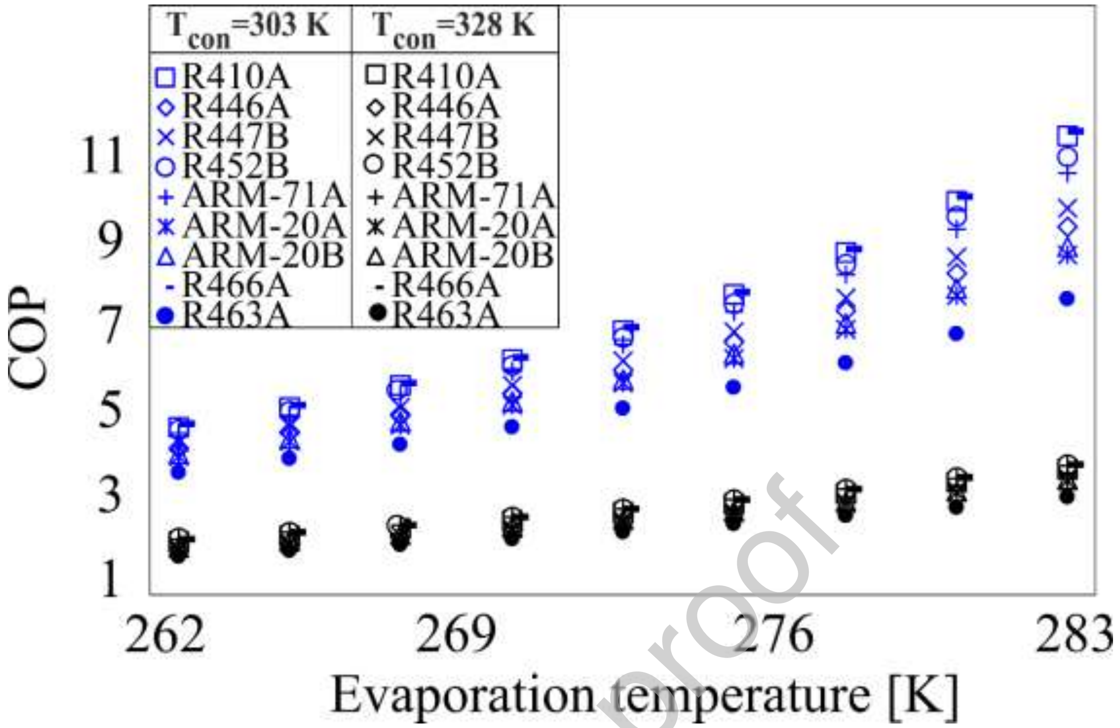

Figure 12. COP *vs* evaporation temperature for R410A alternatives.

Taking as a reference the mixtures presented in the work of Mota-Babiloni et al. (2015) and under the same aforementioned operation conditions, Figure 2 illustrates a comparison of the COP between the different mixtures in addition to illustrating their safety classification. In the figure, it is noted that a minimum of 2.6 of COP is obtained for the mixture R445A and AC5X. Among the new mixtures, a higher COP is achieved with R430A than using R134a. It is also observed that R515A and R516A present a very similar behavior to R134a. In practical terms, adequate energy performances are noted when seeking a replacement for R134a. However, the tendency in recent mixtures is aimed to lower GWP values in comparison with the cited mixtures in Mota-Babiloni et al. (2015).

2.3 Influence of evaporation temperature for R134a alternatives

The volumetric cooling capacity (Q_v) of the refrigerants is a factor that influences both the efficiency as well as the size of the compression unit since a higher refrigeration effect is obtained with the same volume of compressor-displaced refrigerant for higher values of Q_v. The next equation is used to estimate Q_v:

$$Q_v = \rho \cdot \Delta h \tag{1}$$

Figure 3 illustrates the behavior of the Q_v for each mixture. This behavior is reflected in two conditions of condensation temperature, 303K and 333K. In the figure, it is noted that as the evaporation temperature increases a greater Q_v is presented; this is due to the proportional change in the density of the refrigerant, which grows when the evaporation temperature increases. For a lower condensation temperature, a major Q_v is obtained for each mixture.

On the other hand, the COP for each mixture is shown in Figure 4. The figure shows a higher COP as the evaporation temperature rises because of the refrigerant effect increases, and the compression work decreases. Naturally, the evaporation temperature is limited by the temperature needed to sustain the required load. Regarding the condensation temperature effect over the COP, it is noted that when the condensation temperature is lower, the best COPs are obtained. The increase in the condensation temperature causes a higher compression rate along with a lower cooling production which results in a reduction in the COP, as observed in the figure. At a temperature of 333K, the COP for most of the mixtures is very close to R134a, excepting R445A.

R430A presents the closest values to R134a exceeding the COP values for all the working conditions and a minimal reduction in the Q_v for evaporation temperatures lower than 268K and a condensation temperature of 303K. Though the refrigerant R515A presents a COP close to R134a, its Q_v is much lower. Because the operating pressures of R515A are very low for the other refrigerants, and due to the evaluated operation conditions, this refrigerant requires higher superheating to obtain better energy performances.

3. Alternative mixtures for R404A

R404A is a zeotropic mixture composed of R125/R143a/R134a (44%/52%/4%) that presents a low temperature glide (0.8°C), and because of this, it is considered a near-azeotropic mixture. It is only compatible with POE oils; it has low toxicity, and it is not flammable; its boiling point allows it to work in low temperature refrigeration applications. R404A presents the lowest critical point; hence, it is the most suitable for low and medium temperature refrigeration applications (retail stores and supermarkets, among others). R404A, with a composition and properties very similar to those from R507, emerged as a replacement for R22 in commercial applications of medium and low temperatures. This refrigerant must be excluded from all applications as of 2020 according to the regulation EU No. 517/2014; therein lies the necessity to develop new alternatives for its replacement.

Alternative studies have been conducted with HC and mixtures of HFC/HFO as possible replacements for R404A in eutectic refrigeration systems. In this sense, the refrigerant R449A has been analyzed as an alternative for R404A, in which the result showed a reduction in the cooling capacity of 13%, and a decrease in the energy consumption of 4% (Vaitkus and Dagilis, 2017). Mota-Babiloni et al. (2018) presented the feasibility of using refrigerants R454C and R455A. Their experimental results were beneficial for the direct replacement of R404A; these refrigerants presented a similar cooling capacity and an increase of the COP of 10% and 15% for R455A and R454C, respectively. Azzolin et al. (2019) through numerical simulations, it was found that R455A provided a similar value in the cooling capacity and higher efficiency when compared with R404A. One of the disadvantages presented with R455A was the major level of glide to R404A. Zgliczynski and Sedliak (2018) analyzed an alternative hermetic compressor following its thermal profile; in this study, R455A presented a significant increase in the discharge temperature of the compressor. This effect can reduce the useful life of the compressor due to the increase of the coil temperature and a decrease in the performance of the lubricant.

R442A was analyzed through an experimental comparison as a direct substitute of R404A in the refrigeration systems without performing changes to the compression cycle. Among the results, R442A obtained lower energy consumption, an increase in the cooling capacity of 8% and an increase in the COP of 12% (Oruc et al. 2018). Makhnatch et al. 2017 proved that a slight adjustment in the expansion device and an increase of 4% in the refrigerant charge in a supermarket refrigeration system could achieve a similar COP between R404A and R449A.

Cardoso et al. (2017) modelled different alternatives to replace R404A to reduce the environmental impact generated by fluorinated gases and to improve the energy efficiency in the refrigeration systems. They found that R407H and R454A offered better alternatives in the long term, with an increase in the COP of 15% and 9%, respectively. Rydkin et al. (2018) evaluated refrigerant R407H in commercial applications, showed a significant improvement of the COP over R404A in low temperature applications and a moderated improvement in medium temperature applications. Llopis et al. (2017) experimentally studied R407H as a replacement of R404A in a central direct expansion refrigeration system at low temperatures. The authors obtained a reduction in the energy consumption of 7.7% and an increase in the discharge temperature using R407H, which can cause a reduction in its performance over time.

R452A is among the other alternatives that have also been presented in addition to the referred mixtures in Table 4. In the refrigeration systems used for food transportation, the emissions of CO_2 equivalent were reduced between 5% and 15% with this refrigerant since it has a GWP of approximately 50% which corresponds to R404A (Li, 2017). Fluids like R1234ze(E) (Gullo and Cortella, 2016) and R290 (Mastrullo et al. 2014; Kruger et al. 2016) have been evaluated as replacements for R404A; they have shown good ecological and thermodynamic characteristics. However, they are limited because of their flammability level. Other fluids considered for this analysis are R459B and R465A. They were selected from Bitzer's report (2018), and they do not have any studies so far.

3.1 Properties of replacement refrigerants for R404A

The alternatives presented in this work as possible replacements for R404A show very similar thermophysical properties with a lower GWP when considering the reduction on the greenhouse gas emissions and the permitted limits in the environmental regulation EU No. 517/2014. Refrigerants 454C, R455A, R459B, and R465A are represented as the best options from an environmental point of view since their GWP value is reduced up to 96% concerning R404A. The other options present a reduction between 50% and 70% in this parameter; therefore, they can be considered as an option in the short term.

With respect to the heat transfer properties, these refrigerants present considerable changes, like the latent heat which shows an increase from 13 to 34%, the liquid conductivity between 20 and 44%, this favors the heat absorption in the evaporator; and a reduction in the vapor thermal conductivity from 13% to 15%. The critical temperature presents maximum variations of 4% concerning R404A. R407H and R442A have an increase in the critical pressure of 30 and 27%, respectively, which favors the vapor compression cycles to work in a wider range of pressures.

The liquid viscosity is another parameter that shows major increases with respect to R404A for the refrigerants R449A, R442A and R407H of 8, 10 and 15%, respectively, which increases the charge losses in the system; the refrigerant R454A is the only alternative that shows a reduction with respect to this value, close to 5%. The liquid density of the refrigerants R454C and R455A has similar values to R404A; the rest of the replacements have an increase from 5 to 7%, which can minimally affect the volumetric compressor efficiency. This group of low GWP mixtures can be classified as alternatives in the reduction of the environmental impact generated by using R404A, considering the possibility to make improvements in the energy performances of vapor compression systems.

3.2 Energy comparison for replacement refrigerants for R404A

R404A is mainly used in low-temperature applications and considering the operation conditions ranges in which this refrigerant is evaluated (Vaitkus and Dagilis, 2017; Makhnatch et al. 2017). Through the representation of the vapor compression cycle in the *P-h* diagram, the alternative refrigerants for R404A are shown in Figure 5. The performances are evaluated under the following typical operation conditions: condensation temperature of 318K, evaporation temperature of 248K, subcooling, and superheating of 5K and a process of isentropic compression.

As observed in Figure 5, the saturation curves present a minimum variation for R404A, the diagram shows that the mixtures possess a higher cooling capacity, between 20 and 50%. Likewise, the energy consumption per unit of mass in the compression process also increases in the same proportion; therefore, the COP values present minimum variations, between 1 and 5%, and maximum reduction of 10% for R455A and R465A (see Figure 6). The variations in the operating pressures are minimal; because of this, the considerations for the modifications to the compression cycle are minimal, which favors the investment costs in the refrigerant change.

Figure 6 shows the COP for the new mixtures presented in this work and those cited in Mota-Babiloni et al. (2015), for the same operating conditions. It can be seen that the development of new mixtures in the last years has promoted obtaining increases in the COP, inclusively, higher than R404A just as refrigerants R442A, R449A, and R407H demonstrate it. The low GWP they present allows them to be considered as transitioning or in the short term in systems operating with R404A.

3.3 Influence of evaporation temperature for R404A alternatives

Figures 7 and 8 present the Q_v and the COP for each of the mixtures discussed in this work. As observed in Figure 7, at low evaporation temperatures, the mixtures present a very similar Q_v, this is even reflected in the COP of the system, as showed in Figure 8. It is noted that the refrigerant R407H overcomes the COP of R404A at low evaporation and condensation temperatures, but when the evaporation temperature is increased the COP is reduced although it is higher than that presented by R404A for high condensation temperatures. For the refrigerant R455A a higher COP is obtained at low evaporation temperature and high condensation temperatures, though its Q_v presents reductions between 7 and 19% with respect to R404A. For the refrigerant R442A concerning R404A, it presents minimal reductions of 2% in the COP at low condensation and evaporation temperatures, and approximately 10% for high evaporation temperatures and low condensation temperatures although a lower Q_v is obtained as observed in Figure 8 for R404A. All the refrigerants, excepting R455A and R465A present better behaviors at high condensation temperatures concerning R404A.

4. Alternative mixtures for R410A

R410A is widely used in air conditioning systems, in which, for example, the global consumption of HFC for this equipment in 2010 was 91 million metric tons of CO_2 equivalent (Mota-Babiloni et al. 2017b). R410A is a mixture composed of R125/R32 (50%/50%) with a temperature glide of 0.1°C at atmospheric pressure (Elefsen et al. 2002); it is also considered as a near-azeotropic mixture; it is chemically stable and has low toxicity; and it is mainly used in air conditioning equipment. R410A presents a higher operating pressure and higher heat removal capacity than R22. Refrigerant R410A was developed as an R22 replacement for air conditioning systems. R410A has a high cooling capacity, and as a result, it has been used in more compact refrigeration systems, but its high GWP does not agree with the objectives of the regulations. Some of the evaluated replacement mixtures for R410A in air conditioning equipment have shown positive results in the reduction of energy consumption and CO_2 equivalent emissions.

For example, Devecioğlu (2017) theoretically compared the energy aspects of some refrigerants, among them, are R446A and R452B as possible replacements for R410A in air conditioning systems. The results showed a better energy performance for the alternative mixtures, in which R446A was outstanding with lower energy consumption in refrigeration mode. Also, the GWP of these refrigerants presents values between 22% and 33% lower than R410A. Other refrigerants like ARM-71A, ARM-20A, and ARM-20B were analyzed on air conditioning equipment. These refrigerants presented a very similar energy efficiency ratio though, due to their properties, a compressor change was recommended to achieve better energy performances. The authors presented ARM-20A as the best candidate because its pressure ratio increases more slowly than the other refrigerants concerning room temperature (Shen et al. 2017).

R452B has shown very similar cooling and coefficient capacities to R410A. The operating pressures are very similar, and as a result, the redesign options are minimal (Azzolin et al. 2019). R452B and R447B were also evaluated by Sethi and Motta (2016) through simulations of a residential reversible heat pump. The authors obtained a very similar cooling efficiency and capacity (environment conditions under 35°C) to R410A. For temperatures above 35°C an increase in efficiency from 3 to 4% was obtained with respect to R410A.

In other studies, through simulation in CFD, the leaking condition for R452B was analyzed in a residential cooling unit. It was found that the refrigerant volume fraction was always lower than 4%; hence no risk of flammability was associated with leaks (Elatar et al. 2018). Kujak and Schultz (2016) also analyzed the performance of R452B with respect to leaks in a 4 tons cooling unit; it was concluded that there are not representative sceneries that could lead to potentially flammable events. In et al. (2015) researched the performance of a residential air conditioning at partial load using the refrigerants R32 and R446A. The authors obtained a lower energy consumption for R32 and a higher consumption for R446A. The conclusions showed a reduction in the optimum refrigerant charge of 10% and 20% for R446A and R32, respectively.

Another of the mixtures recently presented as a replacement for R410A are R466A and R463A. R463A was analyzed by Hughes and Minor (2018), demonstrating through thermal stability test, lubricant miscibility, plastics and elastomers compatibility, and the dielectric properties that R463A is an adequate replacement for R410A in commercial applications and air conditioning.

Apart from the alternatives mentioned in Table 5, other mixtures of HFC, HFO and natural refrigerants for heat pumps (Cheng et al. 2017) and air conditioning (Tian et al. 2015) have been evaluated with the aim of increasing their performance and reducing the environmental impact generated when working with high GWP refrigerant fluids. It has been noted that this refrigerant mixtures in different mass proportions have better performances and a higher cooling capacity with respect to R410A, and it has been proved that better performances in the heat capacity of the heat pumps can be achieved with some modifications in the components like the increase in the size of the heat exchangers.

Abdelaziz et al. 2015 and Abdelaziz et al. 2016 evaluated the performance of two air conditioning units designed to operate in high temperature environments with different alternatives of low GWP (R32, DR-55, R447A, R447B, ARM-71A, and HPR-2A). It was concluded that these refrigerants have great potential as replacements for R410A, the results showed an increase of the COP between 2 and 4%, as opposed to HPR-2A and R447A in which the COP was lower than in R410A.

Another study based on the replacement of R410A in heat pumps has been presented by Hakkaki (2015), in which the performance of the R32/R744 mixture was evaluated for a mass composition of 80%/20%, respectively. The author achieved energy savings of up to 12%, in which R32/R744 resulted in a GWP reduction of 16%. Pardo and Mondot (2018) investigated the use of low GWP refrigerants for residential heat pumps, air conditioning and heating systems as replacements for R410A; this study evaluated the refrigerant mixtures HPR2A, R447A, R454B, R459A, and R32; the performances found were very similar among refrigerants; moreover, a reduction between 15 and 24% was found for the refrigerant charge with respect to R410A.

The HFC/HFO mixtures evaluated in heat pumps have shown similar energy performances to R410A. Though these refrigerants are slightly flammable and classified as A2L in the category of safety, they are a good alternative for the reduction of greenhouse gases due to their GWP value which is reduced between 67 and 78% in comparison with R410A.

R32 has been one of the most researched to replaced R410A, from which increases in the COP have been reported and in the cooling capacity. One of the greatest disadvantages in the use of this refrigerant is the increase of the discharge temperature with respect to R410A (Silva, 2019). Nevertheless, this refrigerant has already eliminated the use of

R410A in Japan air conditioning due to its lower environmental impact through better alternatives that are still being researched (Taira, 2016).

R32 is one of the main components of the mixtures, because of this, and that it is considered a substance with good thermophysical properties. The aim of elaborating mixtures is that the disadvantages presented in the use of this pure refrigerant have a minimum effect and to obtain a fluid with better energy and environmental performances concerning R32.

4.1 Properties of the replacement refrigerants for R410A

Table 5 compares the properties of the refrigerants currently proposed as low GWP alternatives to replace R410A in this work. This group of alternatives presents as main characteristic a GWP reduction between 66 and 93%, which generates a positive impact at an environmental level. Concerning the heat transfer properties, an increase from 15 to 20% is observed in the latent heat, excepting ARM-20A and R466A which presented a reduction of 12%. On the liquid thermal conductivity, R446A presents a maximum increase of 27% and a reduction of 12% for ARM-20A; the increase of these values improves the fluids heat transfer which improves the efficiency of the vapor compression cycle. The refrigerant R446A and R447B have an increase in the critical pressure of 16%, thus extending the range of operating pressures when working with these fluids; additionally, the refrigerants present minimum variations in the critical temperature and the boiling temperature for R410A.

As also shown in the table, the refrigerants liquid density decreases around 5%; therefore, an increase in the compressor displacement can be required to counter this variation, to find a better energy behavior in the system, excepting R466A which presents and increase in the liquid density of 20%.

4.2 Energy comparison for R410A replacement refrigerants

Typical operation conditions (high temperature applications) are considered to evaluate the energy performance for each of the mixtures. Figure 9 shows the vapor compression cycle and the *P-h* diagram for the R410A alternative refrigerants. It is noted that the saturation curve for refrigerants ARM-20A, ARM-20B and R463A present a similar behavior to R410A.

According to Figure 10, the obtained values for the COP of the refrigerants evaluated in the last years present small increases for the previously analyzed mixtures. Even though the energy consumption per unit of mass obtained for all the substances surpasses the consumption showed by R410A, ARM-20A and ARM-20B can be considered as one of the best alternatives with respect to consumption and they also present the lowest GWP values.

Refrigeration capacity increases for refrigerants R446A, R447B, R452B and ARM-71A between 20 and 30 %; likewise, the energy consumption per unit of mass in the compression process increases between 21 and 43%. The COP diminishes around 12% for the refrigerants ARM-20A and ARM-20B, and in 8% for the refrigerants R446A and R447B. A reduction in the energy consumption per unit of mass in the compressor of 10% and an increase in the COP of 1% was obtained with the refrigerant R466A. Even if slightly lower COPs are obtained, these alternatives are still feasible due to the GWP reduction of

65% and it is also possible to perform redesigns in the vapor compression system that help to increase the efficiency when considering the properties of these fluids.

4.3 Influence of evaporation temperature for R410A alternatives

Figures 11 and 12 illustrate the Q_v and COP tendencies when varying the evaporation and condensation temperatures. In the performances presented in Figure 12 it is observed that the variation in the performance of the refrigerants is minimal for high evaporation temperatures (between 1 and 4%), showing almost identical behaviors at low condensation temperature (303K). The least efficient alternatives are ARM-20A and ARM-20B, these present a reduction in the COP of around 23% for low condensation temperatures and a reduction in the Q_v of 45% for ARM-20A and 33% for ARM-20B because they present a lower cooling effect and lower operating pressures. R466B presents behaviors closer to R410A with an increase in the COP of around 1% in low and high condensation temperatures.

5. Conclusions

This paper presents the main findings on the new refrigerant mixture alternatives to R134a, R404A, and R410A that have been already considered. An analysis of their main properties and performance is also included.

R445A, R456A, R515A, R436A and other mixtures of R600a/R290 as well as R134a with R1234yf and R1234ze, have been considered in recent years to replace R134a in its different applications. R436A and R430A are the R134a alternatives that present major differences in the main thermodynamic properties and saturation curves to the baseline. R430A presents the closest values to R134a exceeding the COP values for all the working conditions, and the minimum COP is obtained for the mixtures R445A and AC5X.

The replacement of R404A represents the most urgent situation. R448A, R449A, R454C, R455A, R442A, R407H, and R452A are the alternatives considered in previous works but the main characteristics presented by these replacements present significant differences. Therefore, the intended application, is very different between them, depending on the particularities of GWP, flammability, discharge temperature and temperature glide. R455A and R465A present the maximum reduction COP. R442A, R449A, and R407H could represent an energy benefit.

The availability of R410A low GWP alternatives is not so varied as the other applications because the GWP of the pure refrigerant R32 is below the European GWP limit and no urgent solutions are needed. Some possible replacements to R410A appear these years to reduce the drawbacks presented by R32 such as flammability or high discharge temperature and also increasing final energy performance. Among the registered mixtures, R446A, R447A, R447B, R452B, R454B, R459A appears in the previous research as alternatives to pure refrigerant R32 to replace R410A. The greatest COP reduction is seen for the refrigerants ARM-20A and ARM-20B.

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conflict of interest

The authors declare no conflict of interest.

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