HFOs and their binary mixtures with HFC134a working as drop-in refrigerant in a household refrigerator: energy analysis and environmental impact assessment

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Abstract

Global warming is a worldwide common theme. Due to the Regulation (EU) no. 517/2014, refrigerants with a GWP (Global Warming Potential) higher than 150 are not allowed from January 1st, 2015 in new domestic refrigerators. Thus, a replacement for HFC134a is needed. In this paper attention is devoted to the drop-in substitution of HFC134a with HFO refrigerant fluids in a domestic refrigerator. An experimental evaluation of the environmental impact in term of the greenhouse effect of the substitution of HFC134a with HFOs has been reported. The greenhouse effect is accounted for the experimental evaluation of the LCCP (Life Cycle Climate Performance) index. The refrigerant fluids that have been tested as a drop-in are: pure HFO1234yf, the mixture HFO1234yf/HFC134a (90/10 % in weight), pure HFO1234ze (E) and the mixture HFO1234ze (E)/HFC134a (90/10 % in weight). The plant working with pure HFOs or with both mixtures achieves the same temperature levels of HFC134a in the freezer and the refrigerator cabinet. The experimental results clearly show that the lower environmental impact in term of global warming can be achieved with both mixtures. The lower LCCP index can be obtained with HFC134a/HFO1234yf (with a 17 % reduction respect to HFC134a).

Keywords: HFC134a, HFO1234ze (E), HFO1234yf, Binary Mixtures, Drop-in Refrigerants, Domestic Refrigerator, LCCP

Nomenclature

A Accuracy [%]
ALR Annual Leakage Rate [%]
$CO_{2,eq,mat}$ CO_2 produced per kg of material [kg_{CO2} kg^{-1}]
$CO_{2,eq,rec}$ CO_2 produced per kg of recycled material [kg_{CO2} kg^{-1}]
$CO_{2,eq,ref}$ equivalent refrigerant CO_2 emission coefficient per kg [$kg_{CO2}kg^{-1}$]
$CO_{2,dir,t}$ total direct CO_2 contribution to global warming [kg_{CO2}]
$CO_{2,indir,t}$ total indirect CO_2 contribution to global warming [$kgCO_2$] COP
COefficient of Performance [-]
E electrical energy consumptions [Wh]
E_{mat} percent of energy for material recycling, %
EOL End Of Life refrigerant leakage [%]
F.S. Full Scale
GWP global warming potential [kg_{CO2} kg^{-1}]
GWP_{adp} global warming potential due to atmospheric degradation product of the refrigerant [kg_{CO2} kg^{-1}]
L average lifetime of the equipment [yr]
LCCP Life Cycle Climate Performance [kg_{CO2}]
m_{mat} mass of material [kg]
m_{rec} mass of recycled material [kg]
ODP Ozone Depletion Potential [-]
P pressure of the refrigerant [bar]
Pel electrical power absorbed [W]
RC refrigerant charge [kg]
RFD CO_2 produced per kg of refrigerant disposal [kg_{CO2} kg^{-1}]
RFM Refrigerant Manufacturing Emissions [kg_{CO2} kg^{-1}]
t time [s]
T temperature [°C] x
independent variable
Y indirectly calculated variable

Greek Symbols

α CO_2 emissions from power conversion [kg_{CO2} kWh^{-1}]
□ compression ratio
δ duty cycle [%]

Subscripts

1y along 1 year
co condenser
cond condensation
cp compressor
ev evaporator
H24 along 1-day
i at inlet
o at outlet

ON	phase of working of the compressor
OFF	phase of stop of the compressor
ref	of refrigerant

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1. Introduction

Nowadays, global warming is a worldwide problem, since human activity in energy consumptions lies among the main reasons to temperature increment on our planet. The consequences arising from this phenomenon could be catastrophic unless we adopt drastic and strong measures to stop or, at least reduce this trend. As a matter of fact, the energy consumption due to industrial and domestic refrigeration is a highly topical issue, since refrigeration and air conditioning cover almost 20% of the whole worldwide energy consumptions [1].

Since 2009, a progressive phase out of HFCs has been established, to reduce greenhouse gas emissions. The 28th Meeting of the Parties (MOP28) [2] to the Montreal Protocol, which was held in Kigali, Rwanda, from October 10 to 14, 2016, led to an international agreement on the phase-down of the production and consumption of HFCs. It represents a milestone agreement. As a matter of fact, the A2 countries (the "developed" countries) are called to decrease their production and usage of HFCs from 2019 (where a -10% is expected), until 2036 (where a -85% is expected). The A5 zone ("developing" countries) are called upon to reduce HFCs consumption from 2024 in freezers to 2045 (where a reduction of -85% is expected). Domestic refrigerators cause the main contribution in energy consumption related to the field of refrigeration. Most of them use HFC134a (GWP = 1430) as refrigerant. The Kyoto Protocol [3], an international agreement linked to the United Nations Framework Convention on Climate Change, and the deriving regulation (EU) no. 517/2014 [4], fixed mandatory targets for greenhouse gas emissions. Among them, in this paper, the attention is devoted to interdiction in Europe, from 1 January 2015, to the use of HFCs refrigerant with GWP greater or equal to 150 in domestic refrigerators and freezers.

The refrigerant class of new generation synthetic refrigerants is Hydrofluoroolefins (HFO) [58] one. HFOs, which present environmentally friend behavior, are unsaturated HFCs, since they descend of olefins rather than alkanes (paraffins). Among them HFO1234yf and HFO1234ze are two fluids with zero ODPs and small GWPs, very promising refrigerants since their features guarantee good miscibility with Polyester and Mineral oil and, in case of accidental dispersion, a brief duration in the atmosphere [9-11]. Akram et al. [12] presented the tribological performance of grey cast iron with different lubricants, namely PAG (Polyalkylene glycol), POE (Polyolester), and Mineral oil, in the presence of environmentally friendly HFO-1234yf refrigerant. They found PAG/HFO1234yf exhibited better tribological performance compared to the other systems. Sedrez and Barbosa [13] evaluated experimentally the relative permittivity (dielectric constant) of mixtures of a POE ISO VG 10 lubricating oil and refrigerants HFC134a and HFO1234yf for temperatures ranging from 25-

55 °C. They found the relative permittivity of the HFO1234yf mixture was slightly lower than that of the HFO134a mixture under identical conditions. Sun et al. [14] measured the solubilities of HFO1234ze(e) in pentaerythritol tetrapentanoate (PEC5). An additional point in favor is the chance to employ HFO1234yf and HFO1234ze(E) as drop-in replacement in already existing VC refrigerators (previously working with HFC134a), as revealed by the related state of the art, since many papers, reporting drop-in test results, have been published. Yataganbaba et al.[15] developed an exergy analysis of HFO1234yf and HFO1234ze(E) in a two evaporator vapour compression refrigeration system. Wang [16] carried out a state of the art of the drop-in of HFC134a with HFO1234yf. He evidenced the COP and heat capacity of HFC134a system might suffer from a direct drop-in replacement of HFO1234yf. The deterioration is around 0-27% depending on the operational conditions. The major part of the theoretical suggestions has been confirmed by the experimental works carried out by MotaBabiloni et al.[17] and Navarro-Esbrí et al. [18]. The Spanish authors performed several experiments to analyse the consequences of the direct drop-in of HFC134a with HFO1234ze(E) and HFO1234yf. Sethi et al. [19] analysed both theoretically and experimentally the influences of the replacement of HFC134a with HFOs for a refrigerated vending machine.

Recent papers report on experimental results obtained on a domestic refrigerator using HFO/HFC mixtures that fulfill the 517/2014 EU normative in terms of GWP [20,21]. Mota Babilon et al. [22] have conducted a theorical study on mixtures composed by the HFC refrigerants: R32, R125, R152a and R134a; and HFO refrigerants: R1234yf and R1234ze(E). They concluded that most of the new HFO/HFC mixtures under-performed the HFC analyzed. In this paper an experimental analysis, conducted on a domestic refrigerator, has been reported about drop-in replacement of HFC134a with HFOs and their binary mixtures with HFC134a (90/10 % by weight), The results are presented in terms of energetic performances, from an environmental impact assessment point of view, evaluating Life Cycle Climate Performance indexes. All the tests have been conducted under subtropical conditions, and the energy consumptions have been measured in accordance with the normative UNI-ENISO15502 [23].

2. The drop-in refrigerants

\In this study the HFOs taken in consideration for dropping-in are: pure HFO1234yf, pure HFO1234ze(E) and the binary mixtures HFO1234yf/HFC134a (90/10% in weight) and HFO1234ze(E)/HFC134a (90/10% in weight). Table 1 contains the main characteristics of the fluids considered, compared with the ones of HFC134a.

Parameter	HFC134a	HFO1234yf	HFO1234ze (E)	HFO1234yf/ HFC134a	HFO1234ze(E)/ HFC134a
Chemical Formula	CH_2FCF_3	$CF_3CF= CH_2$	trans — CHF = $CHCF_3$	$CF_3CF= CH_2$/ CH_2FCF_3	trans — CHF = $CHCF_3$/ CH_2FCF_3
Critical T [°C]	101.1	94.7	79.0	95.3	81
Critical p [bar]	40.59	32.81	36.32	34.51	40.16
GWP [kg_{CO2}/kg]	1430	4	7	133.7	150
ODP	0	0	0	0	0
Safety Class	A1	A2L	A2L	N.A	N.A.

Table 1 - The main characteristics of the drop-in refrigerants [24].

Table 2 reports the refrigerant charge, evaluated with the pull-down tests, for each refrigerant fluid. In these tests the amount of drop-in refrigerant mass has been varied by adding refrigerant into the system in 10 g increments. Whereas, the charge of HCF134a has been fixed at 100g by the refrigerator manufacturer. To identify the optimal charge the lower pulldown time (the time employed to reach the freezer cell temperature of -18°C) and the lower energy consumption have been considered. These tests have been described in detail in the papers [20,21,25].

	HFC134a	HFO1234yf	HFO1234ze(E)	HFO1234yf/ HFC134a	HFO1234ze(E)/ HFC134a
RC (g)	101	115	136	116	137

Table 2 - The charge of refrigerants.

As a matter of fact, pure HFO1234yf and pure HFO1234ze(E) belong to ASHRAE Safety Classification A2L which indicates mildly flammable whom represent one of the principal disadvantages in their employment, together with the excessive costs of HFO1234yf (150 €/kg at today's Italian market price). In this context, it is useful to test the drop-in of the above-mentioned mixtures which are non-flammable [26] and less expensive, since the price of HFC134a is quite low (around 35€/kg at today's Italian market price). As prescribed by the 517/2014 EU normative, refrigerants with a GWP smaller than 150, are banned from domestic

refrigerators starting from January 1st, 2015. Therefore, the two mixtures have been obtained with shrewdness toward the mixing ratio: it has been determined the maximum
mixing ratio of the binary mixture employable as domestic refrigerant whose GWP fulfils the normative. Therefore, the maximum percentage in mass of HFC134a, avoided is given by:

$$\%_{HFC134a} = \frac{GWP_{mixture} - GWP_{HFO1234ze}}{GWP_{HFC134a} - GWP_{HFO1234ze}} \ x\ 100 \qquad (1)$$

as a result, the maximum $\%_{HFC134a}$ resulting is 10.11%. Therefore, the binary mixtures considered is composed by 90% of HFOs and 10% of HFC134a.

3. Experimental apparatus

The drop-in tests with the above-mentioned refrigerants have been conducted on a vapor compression refrigerator conceived for domestic usage, belonging to the A+ energy class. Such refrigerator was originally projected for working with 100 g of HFC134a. The VC refrigerator is constituted by two partitions: the freezer cell, located on the upper side; the cold cell, located on the down side. In Figure 1 the schematic of the refrigerator is illustrated.

The plant consists of: a hermetic reciprocating compressor, a forced air-cooled condenser, a capillary tube and an evaporator operating in forced convection. The forced air that cools the condenser placed near the compressor, cools also the compressor. This leads to a low temperature at the compressor outlet. The evaporator is placed in the freezer and an air distribution system connects the refrigerator to the freezer. A damper valve, moved using a thermostatic mechanical drive, controls the amount of air delivered to the refrigerator compartment. The capillary tube is wrapped for a good portion of its length (>90%) around the suction tube of the compressor. In this way, the refrigerant at the evaporator outlet cools the refrigerant that is laminated. This leads to an increase of the enthalpy variation at the evaporator together with the superheating of the refrigerant at the compressor inlet. The refrigerator is provided by an adaptive defrost control system based on an arrangement of resistors placed close to the evaporator. An exhaustive description and further details about experimental apparatus are contained in other our previous papers [20,21,25].

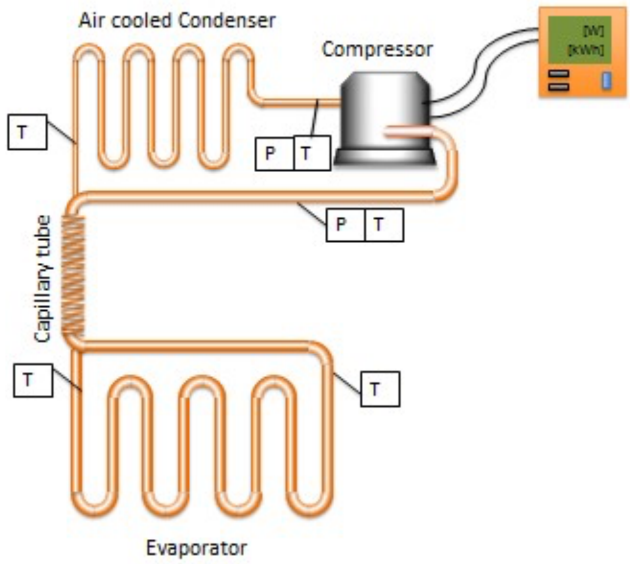

Fig. 1 The scheme of the VC refrigerator, employed for the tests.

In Figure 1, it is possible to appreciate the position of all the sensors along the circuit. Temperature measurements are obtained by means of seven PT100 thermo-resistances (accuracy ± 0.15 K) placed at the inlet and at the outlet of each device. Pressure measurements are carried out using two piezoelectric absolute pressure gauges (accuracy ± 0.2%) located at compressor inlet and outlet. More generally, Table 3 provides all the details about the whole sensor apparatus employed in the experimental tests.

Quantity	Transducer	Range	Uncertainty
Temperature	PT100 4 wires	-100 / 500 °C	0.15°C
Pressure	Piezoelectric absolute pressure gauge	1 /10 bar; 1 /30 bar	0.2% F.S. 0.5% F.S.
Humidity	Protimeter System 996	-100/70 °C 0/100%	0.15°C 1.0% reading
Energy	Energy Test	0 / 1 MWh	1 % reading
Weight	Balance	0/100 kg	0.1 g

Table 3 - The sensor's equipment employed in the tests.

The sensor's equipment is connected to a 32-bit A/D acquisition system which acquires all the data coming up from the sensors. Then, the data are elaborated by Frigocheck 2.0, a virtual instrument developed through Labview, used for real time monitoring of the evolution of pressure and temperature in the domestic refrigerator under test.

The uncertainties of all the derived quantities have been evaluated according to the method of propagation of error [27]. If a generic quantity Y is indirectly calculated from measured values of independent variables x_i:

$$Y = Y(x_1, x_2 \dots \dots x_n) \quad (2)$$

The accidental contribution to accuracy associated to Y is obtainable as a function of the accuracy associated to x_i:

$$A_y = \left[\sum_{i=1}^{n}\left(\frac{\partial Y}{\partial xi} A_{xi}\right)^2\right]^{1/2} \quad (3)$$

According to equation (3) the experimental uncertainty on the compression ratio is ± 0.28 %, Measuring temperature and pressure at some points of the vapor compression cycle allows the evaluation of enthalpy by the software Refprop 9.1 [24]. By analysing the uncertainties of measures and the related error propagation [27], the enthalpy estimation has an accuracy belonging in the range ±1.10-1.95%.

4. Experimental procedure

4.1 Energetic Performances

The energetic performances of the domestic refrigerator have been evaluated under the working condition prescribed by the UNI-EN-ISO15502: the steady state tests must last 24hours (therefore they are called 24-hour tests or 1-day energy consumption tests), under 25 °C as environment temperature and relative humidity belonging to 45 - 75% range. The temperature setting of freezer and cold cell are required to be - 18 °C and + 5°C, respectively. Furthermore, during the 24-hour, at least one defrost cycle must take place.

The refrigerator has been charged with 100 g of HFC134a as indicated by its original datasheet. HFOs and their binary mixtures show different values of charge: the reason lies in making the refrigerator working with the optimal charge of the refrigerant under test. As a matter of fact, in the pull-down tests, it has been evaluated the optimal charge for each refrigerant. During 24-hour tests it has been measured the compressor's duty cycle as follows:

$$\delta = AVERAGE\left(\frac{t_{ON}}{t_{ON}+t_{OFF}}\right) \quad (4)$$

where t_{ON} and t_{OFF} are the time when the compressor has been working (ON) and when the compressor has been kept off (OFF).

4.2 The environment impact assessment

The environment impact has been assessed by means of Life Cycle Climate Performance (LCCP) index. LCCP analysis is based on the TEWI (Total Equivalent Warming Impact) methodology but is more comprehensive than TEWI index. As a matter of fact, both TEWI and

LCCP account direct and indirect contributions in global warming related to the operation of a refrigerator but LCCP includes all the emissions during its whole lifetime from “cradle to grave”. According to [28, 29] the LCCP index is calculated as:

$$\mathrm{LCCP} = \mathrm{CO}_{2,\mathrm{dir,t}} + \mathrm{CO}_{2,\mathrm{indir,t}} \quad (5)$$

$$\mathrm{CO}_{2,\mathrm{dir,t}} = \mathrm{RC} \cdot \left[(GWP + GWP_{adp}) \cdot (L \cdot ALR + EOL)\right] \quad (6)$$

$$\mathrm{CO}_{2,\mathrm{indir,t}} = \alpha \cdot \mathrm{E1y} \cdot \mathrm{L} + \sum \mathrm{m}_{\mathrm{mat}} \cdot \mathrm{co}_{2,\mathrm{eq,mat}} + \sum \mathrm{m}_{\mathrm{rec}} \cdot \mathrm{co}_{2,\mathrm{eq,rec}} + RFM \cdot RC + L \cdot ALR \cdot RFM \cdot RC + RC \cdot (1 - EOL) \cdot RFD \quad (7)$$

As clearly visible from (6), according to LCCP index, direct contribution to global warming is strictly connected to the characteristics of the refrigerant employed (GWP) and to the amount of the fluid charge released in the environment. Direct emissions are comprised of the effects of refrigerant released into the atmosphere over the course of the lifetime of the unit. This includes: annual refrigerant loss from gradual leaks and losses at end-of-life disposal of the unit. The above aliquots are counted again, considering also the atmospheric reaction generates from the breakdown of the fluids in the atmosphere by means of GWP_{adp}. The latter parameter is the Global Warming Potential related to the atmosphere degradation products and measures the consequences of refrigerant decomposition and degradation.

The indirect contribution, as equation (7) reveals, includes the energy-related contributions deriving by carbon dioxide emissions in the environment caused by energy consumptions due to: system ordinary operation, system and components producing and manufacturing, refrigerant making, system and fluid end-of-life recycling/recovering. The typical powerplant technology adopted varies from one country to another. The literature provides some indicative, average levels of CO_2 release per kWh of electrical energy for various countries (). For Italy, the value is 0.435 $kg_{CO2}\,kWh^{-1}$ [30].

In Table 4 are reported the data about GWP, GWP_{adp} and $CO_{2,eq,ref}$ for all the refrigerants considered, provided by the LCCP Guideline (IIR) [28,29].

Refrigerant	GWP	GWP_{adp}	$CO_{2,eq,ref}$
HFC134a	1430	1.6	7.2
HFO1234yf	4	3.3	13.7
HFO1234ze (E)	6	3.3	13.7
HFO1234y/ HFC134a	133.7	3.1	13.05
HFO1234ze(E)/ HFC134a	150	3.1	13.05

Table 4. GWP and Adaptive GWP for all the refrigerant tested.

In Table 5 are reported the references values used for evaluation of LCCP.

L (% yr^{-1})	**EOL (% yr^{-1})**	**L (yr)**	**m_{rec} (kg)**	**RFD (kg_{CO2}/kg)**
2.5	15	15	0	0

Table 5. All the reference values needed to estimate LCCP.

All the leak rates and the CO_2 emissions per material kilo, come from International Institute of Refrigeration (IIR). The CO_2 emission rates per kWh descends by Ecometrica 2011 evaluations [30]; all the estimation about the materials composing the refrigerator under test have been taken, basing on the refrigerator net mass (81 kg) and considering the RAEE standard [31]. In Table 6 are listed the equivalent contributions in carbon dioxide, provided by LCCP guidelines, emissions for all the materials composing the refrigerator.

Material	**m_{mat} [kg]**	**m_{mat} /m_{tot} [%]**	**$co_{2,eq\ mat}$ [kg_{CO2}/kg]**
Aluminum	5.2	6.5	12.6
Copper	2.2	2.7	3.00
Plastic	8.1	10.0	2.80
Polyurethane	12.5	15.4	4.02
Steel	53.0	65.4	1.80

Table 6. Equivalent emissions in terms of carbon dioxide for each material which the refrigerator is made of.

5. **Results and discussions**

5.1 Energetic performances

Figure 2 reports for all the refrigerants the temperature profile of the air temperature inside the freezer and inside the refrigerator in a test sample long 4000 s.

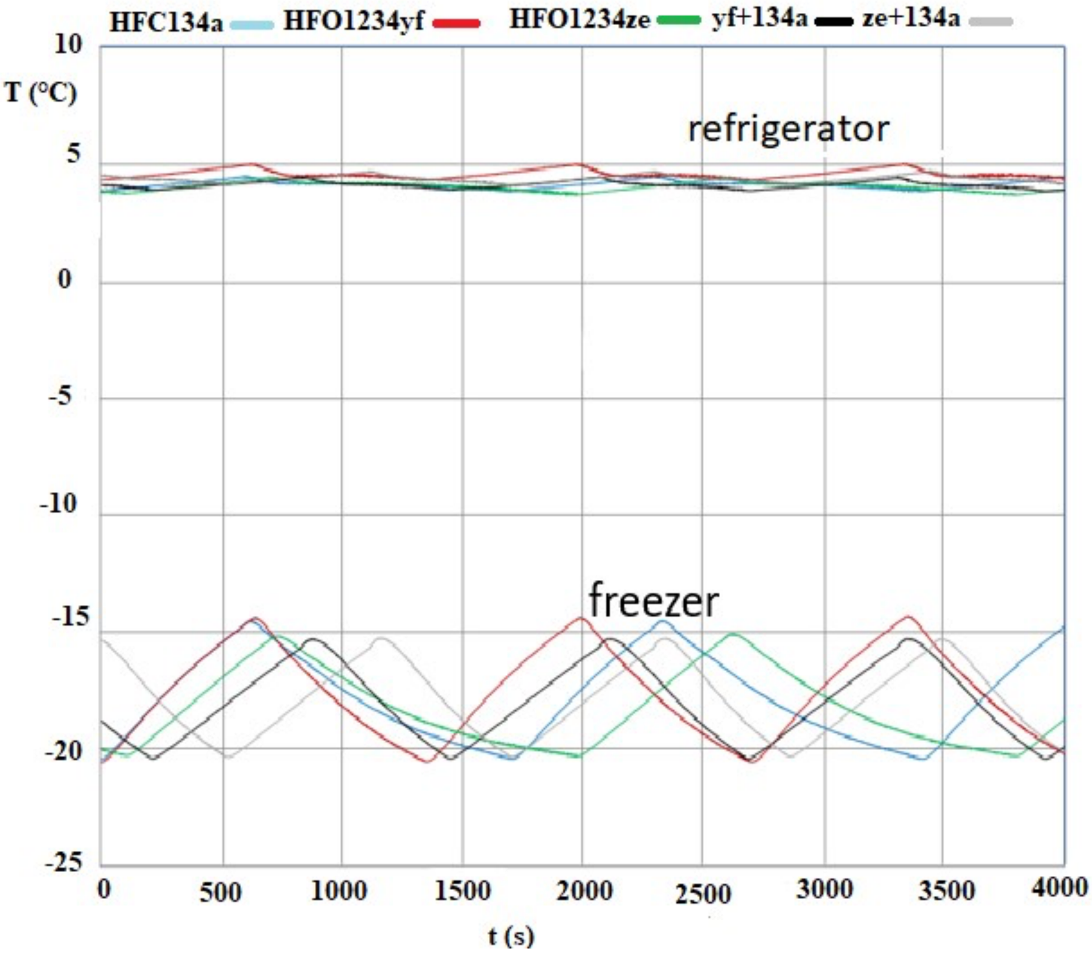

Fig. 2 Air temperature profiles during a sample of the 1-day test.

The profiles there reported show the change of the air temperature inside the freezer and inside the refrigerator. Due to the act of the thermostat that regulates the working of the refrigerator, the air temperature in the freezer has changed between -21 °C and -15 °C, with a mean value equal to -18 °C, while in the refrigerator has undergone smallest variations around the value +5 °C. Such behavior is justified by the greater thermal power dispersed through the walls of the freezer compartment than that dispersed through the walls of the refrigerator compartment because of the higher difference with the temperature of the ambient air. This Figure clearly shows that all the refrigerant fluids have a similar behavior and can maintain the desired temperature in the freezer and in the refrigerator.

Table 7 summarizes the mean values of the experimental results obtained during the 1-day tests (according to the schematic of Figure 1). Table 7 reports for each refrigerant fluid: the optimal charge, the average temperatures and pressures in key points of the refrigerator and the compression ratio. Comparing the temperature values for the different refrigerant fluids, one can observe that the general trends are very similar.

The Table clearly shows that the mean value of the evaporating temperature ($T_{i,ev}$) of the mixture HFC134a/HFO1234yf is very similar to the one proper of HFC134a, whereas the other fluids show mean values slightly higher. Therefore, being the thermal transmittance of both fluids almost the same, they can exchange the same refrigerant power in the freezer. Another important parameter which influences the stability of lubricants and the compressor component is the temperature at the compressor outlet ($T_{o,cp}$). In the presented experimental plant, the compressor is cooled; it leads to a discharge temperature always lower than 50°C.

Table 7 reveals that both the mixtures ensure a discharge temperature lower than the one of HFC134a.

It is more remarkable when the plant operates with a not-cooled compressor, since when the discharge temperature is very high then it may result in breakdown of the lubricating oil, causing excessive wear and reduced life of the compressor valves (mainly the discharge valve).

The pressure levels at the compressor inlet are very similar for all the fluids: for HFC134a and HFO1234ze(E) pure and mixed are lower than the atmospheric value.

Parameter	**HFC134a**	**HFO1234yf**	**HFO1234ze (E)**	**HFO1234yf/ HFC134a**	**HFO1234ze(E)/ HFC134a**
$P_{i,cp}$ (bar)	0.9	1.0	0.7	1.1	0.8
$P_{o,cp}$ (bar)	8.9	9.8	6.9	9.4	7.2
β	9.9	9.8	9.9	8.6	9.0
$T_{i,cp}$ (°C)	27.1	28.2	24.4	25.6	25.2
$T_{o,cp}$ (°C)	44.8	47.5	42.0	43.2	41.3
T_{cond} (°C)	34.8	38.2	36.1	35.1	35.1
$T_{o,co}$ (°C)	34.4	36.9	28.0	34.7	31.6
$T_{i,ev}$ (°C)	-28.6	-27.6	-26.9	-28.5	-25.9
$T_{o,ev}$ (°C)	-22.0	-23.4	-22.4	-23.8	-23.8

Table 7 Average pressures and temperatures in the refrigerator key-points.

One can observe that the HFO1234yf (pure and mixed) high pressure is greater than that of HFC134a. On the contrary, the value pertaining to HFO1234ze (E) (pure and mixed) is lower. Therefore, with HFO1234yf (pure and mixed) the whole circuit is subject to a greater pressure, resulting in increases of losses and mechanical stress for compressor.

The refrigerant mass flow rate in the refrigerator depends on the volumetric efficiency of the compressor and on the density of the refrigerant fluid at the compressor inlet. Both the mixtures show a lower compression ratio. This leads to a higher value of the compressor volumetric efficiency. Therefore, a higher mass flow rate is expected.

In Figures from 3 to 7 is reported the electric power (Pel) absorbed during the 1-day tests for the different refrigerant fluids. The peak of electric power in the Figures represents the defrosting phase required by the normative UNI-EN-ISO15502.

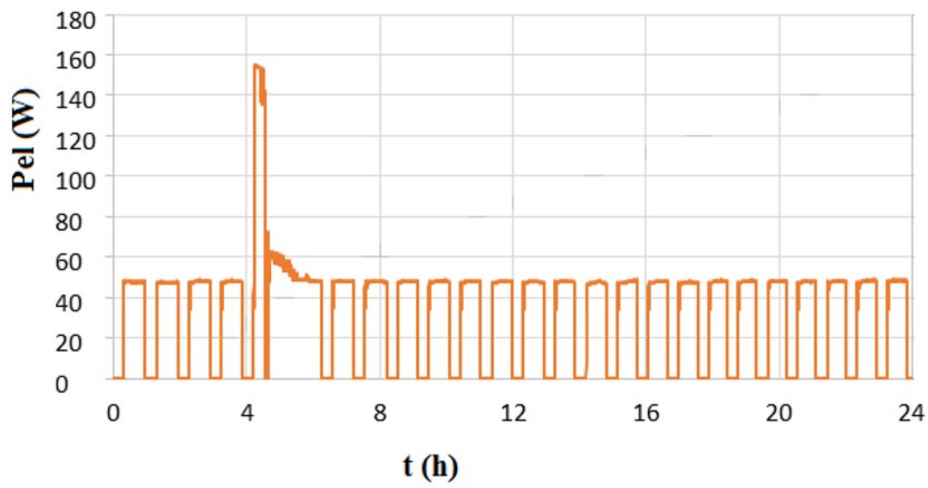

Fig. 3 Electric power absorbed by HCF134a.

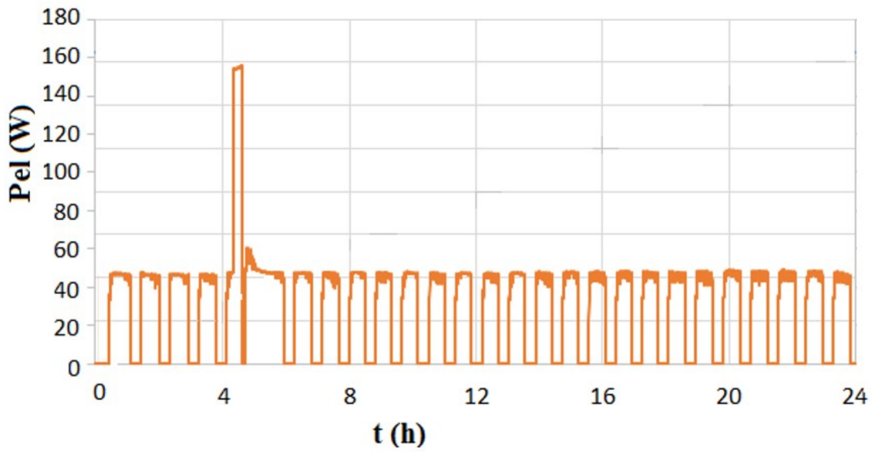

Fig. 4 Electric power absorbed by HFO1234ze.

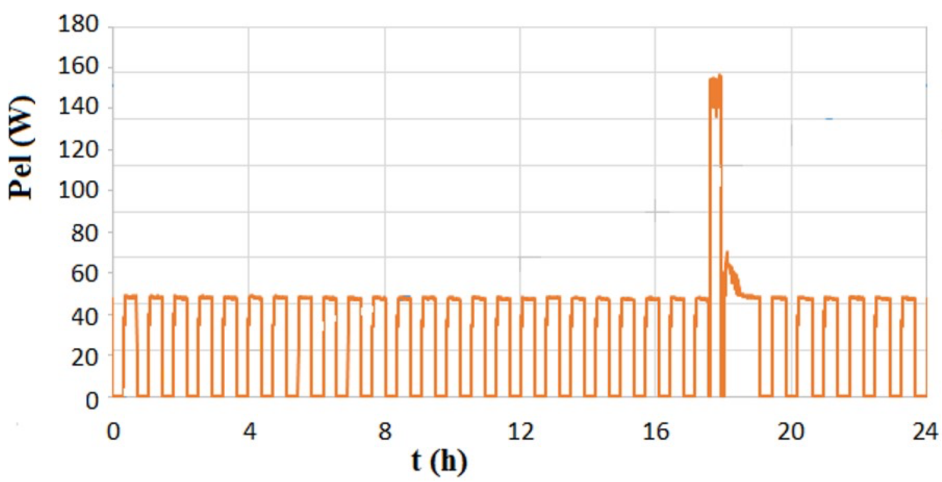

Fig. 5 Electric power absorbed by HFO1234ze/HFC134a mixture.

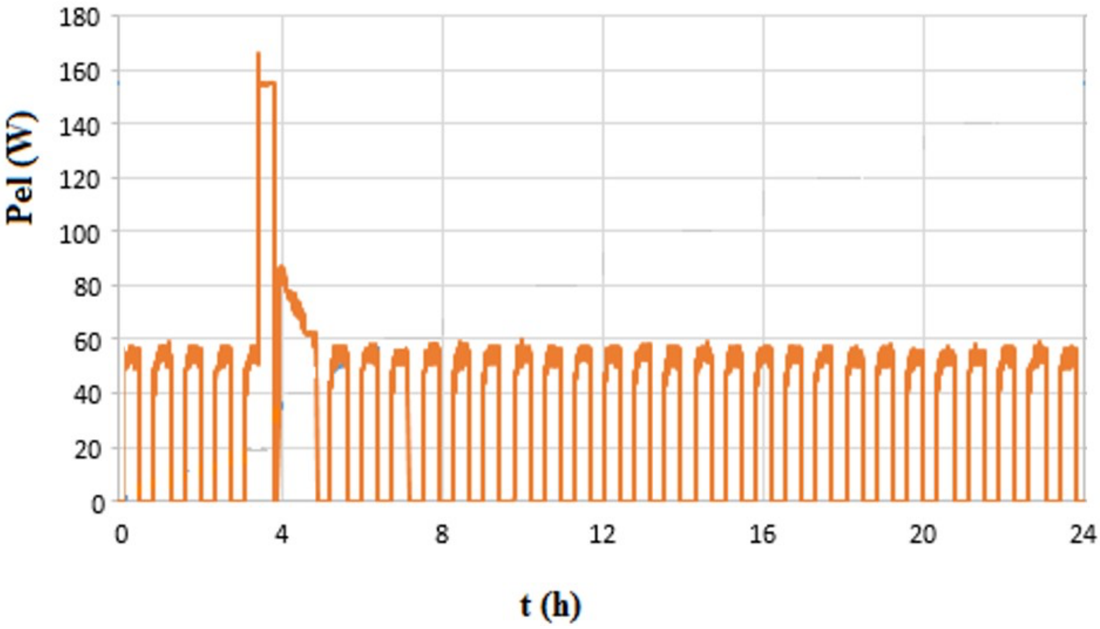

Fig. 6 Electric power absorbed by HFO1234yf.

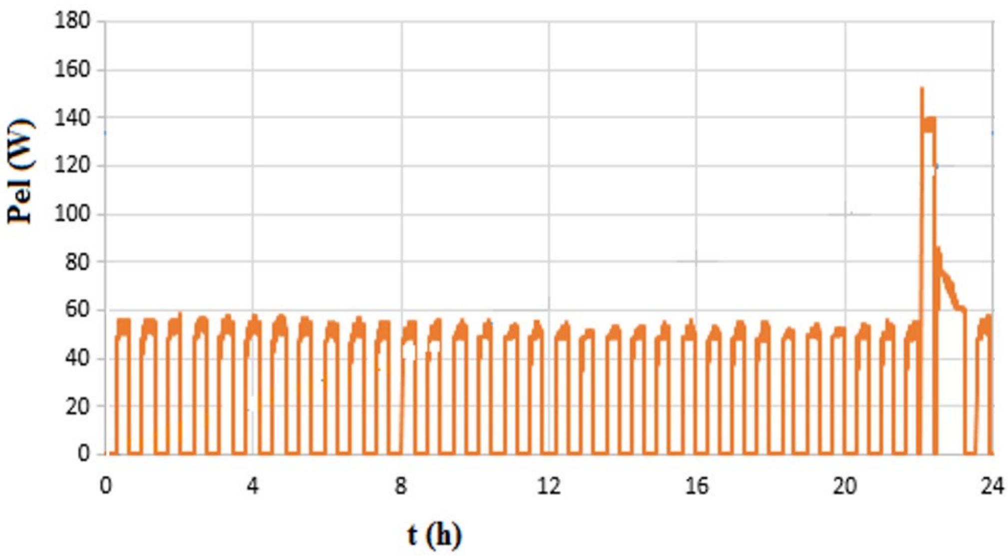

Fig. 7 Electric power absorbed by HFO1234yf /HFC134a mixture.

In Table 8 are reported the average values of: the ON and OFF time (the time when the compressor has been working and has been kept off), the duty cycle, the average electric power consumption during the ON phase of the compressor.

One can observe that the mean ON power are 48 W for HFC134a, 47.6 W for HFO1234ze (E)/HFC134a mixture and 45.8 for pure HFOze (E). Therefore, there is a very limited electric power saving.

The electric power of HFO1234yf and of its mixture is greater than HFC134a one. HFO1234yf and HFO1234yf/HFC134a mixture are characterized by a compressor inlet pressure greater than HFC134a one. This leads to a higher value of the vapour density. The mass flow rate in the circuit depends on refrigerant fluid's density at the compressor inlet and therefore the use of pure and mixed HFO1234yf ensures the highest mass flow rate. As a result, the electric power of the compressor is higher that of HFC134a.

Refrigerant	**t_{ON} (min)**	**t_{OFF} (min)**	□□	**Pel (W)**
HFC134a	35.63	19.83	0.64	48.0
HFO1234ze	32.04	19.77	0.62	45.8
HFO1234yf	24.67	20.90	0.54	54.2
HFC134a/HFO1234ze	24.04	20.30	0.60	47.6
HFC134a/HFO1234yf	20.63	20.70	0.50	51.8

Table 8. Comparison between the different refrigerant fluids.

One can observe that the ON time of HFO1234yf (pure and mixed) and the consequently the duty cycle is significantly lower than that of HFC134a. Therefore, despite the electric power is slightly higher than that of HFC134a, there is a significant energy saving on the daily energy consumption. This is a consequence of a greater values of the mass flow rate that leads to greater value of the refrigerant power.

The ON time of the mixture with HFO1234ze(E) is -32.5% lower than that of HFC134a. This is a consequence of the lower compression ratio that leads to a higher volumetric efficiency of the compressor.

Figure 8 reports the yearly (E_{1y})electric energy consumption for all the refrigerants and the energy saving respect to HFC134a. E_{H24} is recorded over a 24-hours test and E_{1y} is the projection of annual consumptions, calculated as follows:

$$E_{1y} = E_{H24} \times 365 \qquad (6)$$

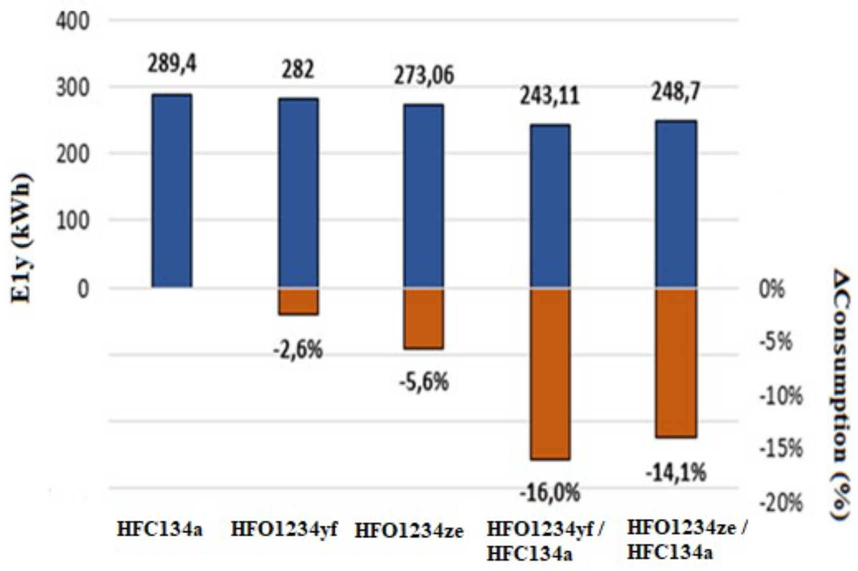

Fig. 8 Yearly electric energy consumption and energy saving for the refrigerant fluids.

Figure 8 clearly shows that the best results can be obtained with both the mixture. Indeed, an energy saving of 16% can be obtained with HFO1234yf mixture and of 14% with HFO1234ze (E) mixture.

5.2 The environment impact assessment

The evaluation of the environment impact assessment of the drop-in replacements of HFC134a in the household refrigerator has been conducted by means of Life Cycle Climate Performance Analysis: the LCCP indexes have been calculated (eq. (3), (4) and (5)). In the LCCP evaluation the experimental parameter used for the analysis are: the RC (evaluated with an accuracy of $\pm$ 0.1 g) and the E1y (evaluated with an accuracy of $\pm$ 1%).

In Table 9 one can appreciate the single CO_2 contributions to direct and indirect emissions aliquots. Data reveals that, for HFOs and their binary mixtures, both the direct and indirect contribution to global warming are smaller than that of HFC134a. The strongest difference lies in the direct emissions, since $CO_{2dir,t}$ for drop-in refrigerant are, on average, 93% lower than HFC134a. The most drastic reduction is registered for HFO1234yf since its direct contribution to global warming is 99.4% smaller than HFC134a. On the other side, the lowest $CO_{2,indir,t}$ belongs to the HFO1234yf/HFC134a mixture, with a reduction of around 14 % instead of working with 101g of HFC134a. Data clearly shows that for all the refrigerant fluids the direct contribution to global warming is negligible with respect to the indirect one

(for HFO based is less than 1%)

Refrigerant	$CO_{2,dir,t}$ [kg_{CO2}]	$CO_{2,indir,t}$ [kg_{CO2}]
HFC134a	75.91	2130
HFO1234yf	0.441	2084
HFO1234ze(E)	0.664	2026
HFO1234yf/ HFC134a	8.33	1829
HFO1234ze(E)/ HFC134a	11.01	1867

Table 9. The direct and direct contribution to global warming for all the refrigerants tested.

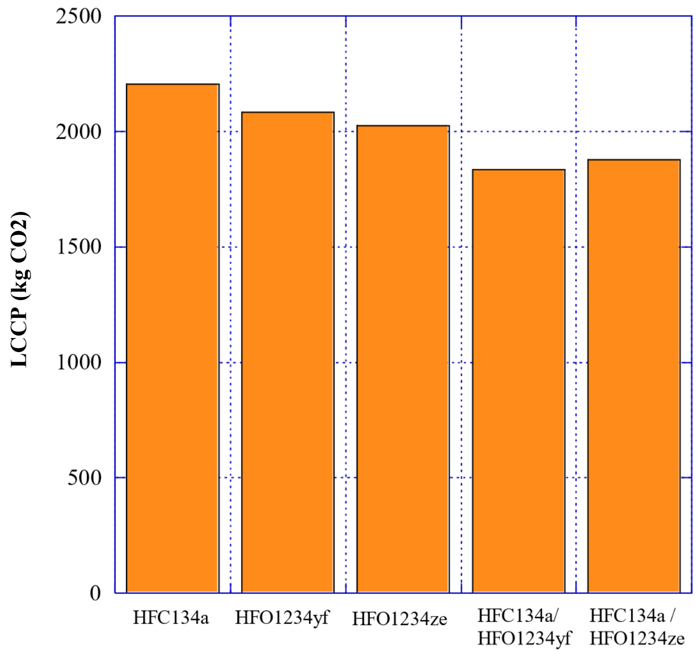

Fig. 9 LCCP for the different refrigerant fluids in Italy.

In Figure 9 is reported the LCCP for all the refrigerant fluids. It is evident that the use of all the HFO based refrigerant fluids leads to a reduction of the LCCP respect to HFC134a. This is due to a reduction of both the direct and indirect contributions to global warming.

Such data are the uppermost significant in the total balance in terms of direct and indirect emissions on global warming: also, from a global point of view, the HFO1234yf/HFC134a mixture provides the lowest LCCP index (-14% respect to HFC134a).

Figure 9 clearly shows that the lower environmental impact in term of global warming can be achieved with both the mixtures. With HFC134a/HFO1234yf mixture there is a 17% reduction of the LCCP respect to HFC134a.

It would be interesting the evaluation of the LCCP index also for a country like Norway, where the electricity is heavily produced from renewable sources. Indeed, for this country the value is 0.017 kg_{CO2} kWh^{-1}. In Table 10 are listed the equivalent contributions in carbon dioxide, provided by LCCP guidelines, emissions for all the materials composing the refrigerator considering that are manufactured with a mixture of virgin and recycled materials.

Material	$co2_{eq\ mat}$ **[kg_{CO2}/kg]**
Aluminum	4.5
Copper	2.78
Plastic	2.61
Polyurethane	4.02
Steel	1.43

Table 10. Equivalent emissions in terms of carbon dioxide for each material which the refrigerator is made of.

In Figure 10 is reported the LCCP for all refrigerant fluids for Norway.

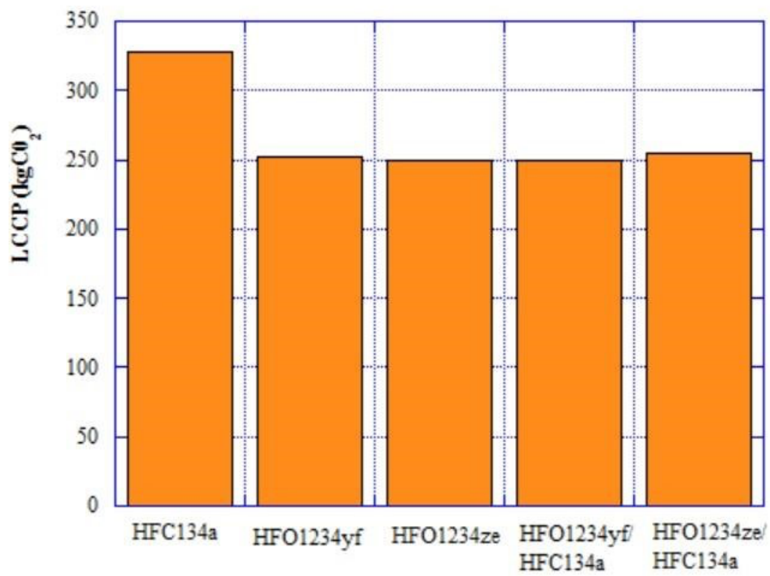

Fig.10 LCCP for the different refrigerant fluids in Norway.

Figure 10 clearly shows that, with the different value for Norway, the direct and indirect contribution to global warming becomes comparable. Therefore, the LCCP values of HFO based refrigerant fluids are significantly lower than that of HFC134a (with a mean value of 23%).

6. **Conclusions**

The replacement of HFCs with environmental friendly refrigerants is a matter of significant importance in domestic refrigeration since GWP limitations affect most of the applications in Europe and possibly, in the rest of the world in the short term. In this paper an experimental comparative analysis between HFC134a and its possible, low GWP, HFOs drop in substitutes is introduced. The comparison has been carried out between HFC134a and: HFO1234yf, HFO1234ze(E), a mixture HFO1234yf/HFC134a (90/10 % by weight), a mixture HFO1234ze(E)/HFC134a (90/10 % by weight). It has been measured energy consumptions of the refrigerator under sub-tropical conditions in accordance with the UNI-EN-ISO15502 standard. In addition, it has been estimated the LCCP to assess the environmental impact of the substitution of HFC134a. LCCP combines the effects of the direct emissions of refrigerants with the indirect effects of energy consumption, since it considers all the relevant indirect emissions related to the entire process of VC refrigerator: refrigerant manufacturing and transportation. The experimental results clearly show that for HFOs and their binary mixtures, both the direct and indirect contribution to global warming is smaller than that of HFC134a. The use of all the HFO based refrigerant fluids leads to a reduction of the LCCP respect to HFC134a. Therefore, a domestic refrigerator working with HFOs provides a lower environmental impact despite of employing HFC134a. The lower environmental impact in term of global warming can be achieved with both the mixtures. With HFC134a/HFO1234yf mixture there is a 17 % reduction of the LCCP respect to HFC134a.

References

[1] 35th IIR Information note “The impact of Refrigeration Sector on Climate Change” (2017).

[2] 28th Meeting of the Parties (MOP28) to the Montreal Protocol. Kigali, Rwanda, October 10 -14, (2016).

[3] Kyoto Protocol to the United Nation Framework Convention on climate change. United Nation Environment Program (UN), Kyoto, JPN, (1997).

[4] EU No 517/2014, European Regulation No 517/2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006, Off. J. Eur. Union, (2014).

[5] J.M. Belman-Flores, V.H. Rangel-Hernandez, S. Uson, C. Rubio-Maya, Energy and exergy analysis of R1234yf as drop-in replacement for R134a in a domestic refrigeration system, Energy, Volume 132, 1, (2017) 116-125.

[6] J.M. Mendoza-Miranda, A. Mota-Babiloni, J.J. Ramírez-Minguela, V.D. Munoz-Carpio, M. Carrera-Rodríguez, J. Navarro-Esbrí, C. Salazar-Hernandez, Comparative evaluation of R1234yf, R1234ze(E) and R450A as alternatives to R134a in a variable speed reciprocating compressor, Energy 114 (2016) 753-766.

[7] A. Mota-Babiloni, J. Navarro-Esbrí, A. Barragan-Cervera, F. Moles, B. Peris, Drop-in analysis of an internal heat exchanger in a vapour compression system using R1234ze(E) and R450A as alternatives for R134a, Energy 90 (2015) 1636-1644.

[8] A.Mota-Babiloni, J. Navarro-Esbrí, F. Molés, Á. Barragán Cervera, B. Peris, G. Verdú, A review of refrigerant R1234ze(E) recent investigations, Applied Thermal Engineering 95 (2016) 211–222.

[9] S. Fukuda, C. Kondou, N. Takata, S. Koyama, Low GWP refrigerants R1234ze(E) and R1234ze(Z) for high temperature heat pumps, Int. J. Refrig. 40, (2014), 161–173.

[10] M.O. McLinden, A.F. Kazakov, J. Steven Brown, P.A. Domanski, A thermodynamic analysis of refrigerants: Possibilities and tradeoffs for Low-GWP refrigerants, Int. J. Refrig. 38, (2014), 80–92.

[11] S. Fukuda, C. Kondou, N. Takata, S. Koyama, Low GWP refrigerants R1234ze(E) and R1234ze(Z) for high temperature heat pumps, Int. J. Refrig. 40, (2014), 161–173.

[12] M.W. Akram, K. Polychronopoulou, A.A. Polycarpou, Tribological performance comparing different refrigerant-lubricant systems: The case of environmentally friendly HFO-1234yf refrigerant, Tribol. Int. 78, (2014), 176–186.

[13] P.C. Sedrez, J.R. Barbosa Jr., Relative permittivity of mixtures of HFC134A and R1234yf and polyol ester lubricating oil, InT. J. Refrig. 49, (2015), 141-150.

[14] Y. Sun, X.Wang, N. Gong, Z. Liu, Solubility of trans-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(E)) in pentaerythritol tetrapentanoate (PEC5) in the temperature range from 283.15 to 353.15 K, Int. J. Refrig. 48, (2014), 114–120.

[15] A. Yataganbaba, A. Kilicarslan, I. Kurtba, Exergy analysis of R1234yf and R1234ze as HFC134A replacements in a two evaporator vapour compression refrigeration system, Int. J. Refrig. 60, (2015), 26–37.

[16] C.C.Wang, System performance of R-1234yf refrigerant in air-conditioning and heat pump system - An overview of current status, Appl. Therm. Eng. 73, (2014), 1412– 1420.

[17] A. Mota-Babiloni, J. Navarro-Esbrì, A. Barragàn, F. Molés, B. Peris, Drop-in energy performance evaluation of R1234yf and R1234ze(E) in a vapor compression system as HFC134A replacements, Appl. Therm. Eng. 71, (2014), 259–265.

[18] J. Navarro-Esbrí, J.M. Mendoza-Miranda, A. Mota-Babiloni, A. Barragán-Cervera, J.M. Belman-Flores, Experimental analysis of R1234yf as a drop-in replacement for HFC134A in a vapor compression system, Int. J. Refrig. 36, (2013), 870–880.

[19] A. Sethi, E.V. Becerra, S.Y. Motta, Low GWP HFC134A replacements for small refrigeration (plug-in) applications, Int. J. Refrig. 66, (2016), 64-72.

[20] C. Aprea, A. Greco, A. Maiorino, An experimental investigation of the energetic performances of HFO1234yf and its binary mixtures with HFC134a in a household refrigerator, International Journal of Refrigeration, 76, (2017), 109-117.

[21] C. Aprea, A. Greco, A. Maiorino, Comparative performance analysis of HFO1234ze/HFC134a binary mixtures working as a drop-in of HFC134a in a domestic refrigerator, International Journal of Refrigeration, 82, (2017), 71-82.

[22] Household refrigerating appliances - Characteristics and test methods, UNI-EN-ISO 15502, (2005).

[23] A. Mota-Babiloni, J. Navarro-Esbrì, A. Barragan-Cervera, F. Moles, B. Peris, Analysis based on EU Regulation No 517/2014 of new HFC/HFO mixtures as alternatives of high GWP refrigerants in refrigeration and HVAC systems, International Journal of Refrigeration, 52, (2015), 21-31.

[24] E.W.Lemmon, M.L. Huber, M.O. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, (2013).

[25] C. Aprea, A. Greco, A. Maiorino, An experimental investigation on the substitution of HFC134a with HFO1234yf in a domestic refrigerator, Applied Thermal Engineering, 106, (2016), 959-967,.

[26] Y. Lee, Y. Kang, D. Jung, Performance of virtually non-flammable azeotropic HFO1234yf/HFC134a mixture for HFC134a applications, International Journal of Refrigeration 52, (2013), 21-31.

[27] R.J. Moffat, Describing the uncertainties in experimental results, Exp. Therm. Fluid Sci. 1,(1998), 3–17.

[28] IIR, “Guideline for Life Cycle Climate Performance index”, (2015).

[29] IIR, 32nd Informatory Note on Refrigeration Technologies / October (2016), “Harmonization of Life Cycle Climate Performance Methodology”.

[30] ISPRA, “Fattori di emissione atmosferica di CO2 e sviluppo delle fonti rinnovabili nel settore elettrico”, (2016).

[31] M. Brander, A. Sood, C. Wylie, A. Haughton J. Lovell, Electricity-specific emission factors for grid electricity, Ecometrica, Edinburg, UK, (2011).

[32] RAEE, Rapporto annuale sul sistema di ritiro e trattamento dei rifiuti da apparecchiature elettriche ed elettroniche in Italia, (2010), Italy.

Highlights

- Substitution of HFC134a in domestic refrigerators.
- HFOs as drop-in substitutes of HFC134a.
- Experimetal evaluation of environmental impact in term of greenhouse effect.
- LCCP index.