

Alternative mixtures to R-600a. Theoretical assessment and experimental energy evaluation of binary mixtures in a commercial cooler

Mélanges alternatifs au R-600a Évaluation théorique et évaluation énergétique expérimentale de mélanges binaires dans un refroidisseur commercial

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ABSTRACT

This work focuses on the exploration of binary mixtures as alternative to isobutane (R-600a) from a theoretical and experimental point of view. To predict the most energy efficient blends, a theoretical model was used that analysed 5445 different blends consisting of 11 pure refrigerants. Three blends were selected for experimental testing in a commercial cabinet: R-1234ze(E)/R-600 (8/92)_{%mass}, R-152a/R-600 (8/92)_{%mass} and R-32/R-600 (2/98)_{%mass}. The results of the 16-hour tests showed that, at their optimum refrigerant charge, the R-1234ze(E)/R-600 (8/92)_{%mass} and R-152a/R-600 (8/92)_{%mass} blends achieved energy consumption reductions of -2.69% and -5.04% , respectively, while the R-32/R-600 (2/98)_{%mass} blend showed an increase of $+0.36\%$. All blends reduced compressor consumption, but increased duty cycles. The results demonstrate the existence of alternative blends that can significantly reduce isobutane energy consumption with similar thermodynamic properties.

1. Introduction

The growing concern to confront the Global Warming has affected to the layers of our society. The refrigeration sector is one of the main contributors to the temperature increment that the planet is facing, as it was the responsible of 7.8% of global GHG emissions in 2018 (International Institute of Refrigeration 2019). To mitigate this impact, the European Commission, via the Regulation N° 517/2014 (European Commission 2014), focused on limiting the use of refrigerants with high GWP. Among other measures, the use of refrigerants with GWP higher than 150 were banned for the domestic subsector and for the majority of commercial stand-alone applications from January 2015 and January 2022 respectively. The use of hydrocarbon as refrigerants has become as one of the best options for these two subsectors, since they have reduced GWP, excellent thermodynamic properties, low cost, high availability and are natural.

The stand-alone appliances dedicated for refrigeration and food counted with more than 2.12 billion of units in 2010 (2 billion related

with domestic purposes and 120 million with commercial ones) (International Institute of Refrigeration 2019). Globally, the main refrigerants used are R-22 and R-134a, however in Europe the new equipment is related with the use of hydrocarbons, being R-600a for small capacities and R-290 for higher capacities the most common (UNEP 2018).

R-600a has become the standard in Europe in many stand-alone applications. However, previously to it, the use of other refrigerants has been deeply discussed in the research community to substitute R-134a. Mota-Babiloni et al. (2014) analysed experimentally the refrigerants R-1234yf and R-1234ze(E) as R-134a drop-ins in a vapour compression test bench, obtaining COP reductions between 3% and 11% and between 2% and 8% respectively. Similarly, Aprea et al. (2016) tried R-1234yf as drop- in a domestic refrigerator originally design for R-134a, concluding that the plant was functionally and provided energy saving of 3% in 24 h. R-152a is another refrigerant that has attracted the attention of researchers. Firstly Sánchez et al. (2017) tested it in a vapour compression test bench, obtaining a slight increase in COP of between 1% and 4.8%. Later, Maiorino et al. (2018) and Sánchez et al. (2022) analysed R-152a in a domestic refrigerator and a commercial

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Acronyms			
COP	Coefficient of performance	w	specific work, $\text{kJ} \cdot \text{kg}^{-1}$
DC	Duty cycle	x_v	Vapour title
GHG	Greenhouse gases	<i>Subscripts</i>	
GWP	Global warming potential (referred to 100 years)	comp	refers to compression
IHX	Internal heat exchanger	dis	compressor discharge
NBP	Normal boiling point, $^{\circ}\text{C}$	e	effective
RH	Relative humidity, %	enc	related to enclosures
VCC	Volumetric cooling capacity, $\text{kJ} \cdot \text{m}^{-3}$	f	related to fans
SH	Degree of superheat in evaporator, K	in	inlet
SUB	Degree of subcooling in condenser, K	iso	isenthalpic transformation
<i>Nomenclature</i>		k	refers to condensing conditions
E	Energy consumption, $\text{kW} \cdot \text{h}$	liq	liquid conditions
h	Specific enthalpy, $\text{kJ} \cdot \text{kg}^{-1}$	m	medium conditions
m	Mass, kg	o	refers to evaporating conditions
p	Absolute pressure, bar	out	outlet
P_c	Total power consumption, W	sat	saturation conditions
s	Specific entropy, $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	suc	compressor suction
t	Temperature, $^{\circ}\text{C}$	vap	vapour conditions
v	Specific volume, $\text{m}^3 \cdot \text{kg}^{-1}$	<i>Greek symbols</i>	
		ε	efficiency

cabinet respectively, reducing the energy consumption by 7.4% and 13.7% respectively. In the same work, Sánchez et al. (2022) additionally analysed the refrigerants R-290, R-1270 and R-744, all of them providing energy savings in relation to R-600a. But not only have pure refrigerants been studied. Saravanakumar and Selladurai (2014) and Yu and Teng (2014) analysed mixtures formed by R-290/R-600a in different proportions as substitute of R-134a, resulting in savings up to 5%. Aprea et al. (2017) also analysed the mixture R-134a/R-1234yf (10/90) in a domestic refrigerator with an energy save of 16% in 24 h. Oliveira et al. (2021) did an experimental evaluation of the heat transfer of the hydrocarbons R-600a, R-290 and R-1270, demonstrating that the R-600a presented the highest heat transfer coefficient among all of them, and concluded that it could be a reasonable substitute for R-134a in residential and commercial refrigeration. Similar conclusions were obtained by Solanki and Kumar (2019), in which the heat transfer coefficients of R-600a were between 64% and 132% higher than those of R-134a under different conditions.

However, little attention has been paid to the search for alternative mixtures to isobutane through mixtures. For first time in 2020, Calleja-Anta et al. (2020) addressed the possibility of raising COP of the isobutane-based systems via mixtures with similar thermodynamic properties. In that study, a theoretical thermodynamic screening was launched, in which a total of 55,440 ternary mixtures were analysed considering an ideal vapour compression cycle with different typologies and different temperatures ranges. The most promising mixtures were R-1270/R-600, R-152a/R-600, R-1234zeE/R-600 and R-290/R-600, foreseeing theoretical COP increments up to 8.6% in relation to R-600a. Subsequently, based on the mixtures obtained in the cited study, Calleja-Anta et al. (2022) experimentally analysed the drop-in of the mixtures R-600a/R-1234yf [92.5/7.5%], R-1234ze(E)/R-600 [10.5/89.5%], R-290/R-600 [89.0/11.0%], R-600/R-1270 [84.5/15.5%] in a commercial fridge for fresh food originally designed to work with isobutane, measuring energy consumption reductions in the first three mixtures (−2.15%, −3.84% and −1.31% respectively). However, the main purpose of that work was the validation of the hypothesis that existed mixtures with better energy consumption behaviour than isobutane but with similar thermodynamic properties, as the appliance did not allow any kind of retrofit, not allowing to show the real potential of the mixtures. Latterly, Calleja-Anta et al. (2022) took a step forward and evaluated the possibility of creating binary mixtures

with isobutane as component but with reduced flammability. The results showed that few mixtures could accomplish with the requirements and with many limitations in terms of mass composition.

The aim of this paper is to continue exploring alternative mixtures to isobutane that can reduce its energy consumption but maintaining similar thermodynamic properties. First, a theoretical screening is conducted to identify mixtures that predict an increment of COP respect isobutane. The most promising fluids are experimentally tested in a stand-alone commercial cabinet initially designed to work with isobutane but upgraded for the selected mixtures by modifying only the expansion system. Energy tests were conducted during 16 h to demonstrate the convenience of using mixtures in a real application under the same operating conditions of heat rejection conditions and cooling demand. Results corroborate the existence of mixtures with better energy performance than R600a that can be used as an alternative achieving energy savings of up to 5.04%.

The novelty that this work present is to prove the real applicability of alternative mixtures to isobutane. The experimental unit used is a commercial plant with higher cooling demands than other plants tested in other works, which allows to obtain more stable test results in which the external disturbances have barely importance. In addition, this unit is equipped with an electronic expansion valve with the capability to adapt its operation to the tested refrigerants, allowing a better adjustment of the system to the refrigerant. These two facts, that might seem minor, have a significant impact in the evaluation of the alternative mixtures, since they allow to evaluate more closely the actual potential of the alternative mixtures analysed.

2. Theoretical obtention of the mixtures

This section describes the model used to foresee mixtures that can provide theoretically higher COP than R-600a. The results obtained are discussed and the mixtures that will be tested are selected.

2.1. Description of the theoretical assessment

Simulations were carried out considering an ideal simple vapour compression refrigeration cycle with an internal heat exchanger (IHx) connecting the outlet of the condenser with the outlet of the evaporator. The intention was to replicate as close as possible the conditions in

which the experimental plant worked. For that, the conditions obtained from the reference test carried out with R-600a at the optimum mass charge were taken as reference and maintained constant for the rest of fluids (the analysis of the test and how the conditions are obtained are explained in detail in the following section and can be seen in Table 4). The evaporation and condensation temperatures (t_o and t_k) were fixed at $-10.2\text{ }^\circ\text{C}$ and $33.25\text{ }^\circ\text{C}$, with a superheating (SH) and a subcooling (SUB) of 13.5 K and 1.3 K respectively. The efficiency of the IHX (ϵ_{IHX}) was considered as 0.85. To lighten the calculation process, pressure drops were neglected. Calculations were performed using the latest version of the Refprop v.10 software (Lemmon et al., 2018), using the program's default interaction coefficients.

Evaporation pressure of the mixtures (p_o), corresponding to the evaporation temperature, was calculated with an iterative method by using the mean enthalpy in the evaporator [Eqs. (1) and (2)]. Following the same criteria, condensing temperature (p_k) was calculated according with a vapour quality (x_v) of 50%, since it coincides with the mean enthalpy [Eq. (3)].

$$h_m = \left(\frac{h_{o,in} + h_{o,out}}{2} \right) \quad (1)$$

$$p_o = f(t_o, h_m) \quad (2)$$

$$p_k = f(t_k, x_v = 0.5) \quad (3)$$

Temperatures at the outlet of the evaporator and the condenser were calculated according to the Eqs. (4) and (5) respectively, in which $t_{sat,vap}$, p_o and $t_{sat,liq}$, p_k are the saturations temperatures in vapour ($x_v = 1$) and liquid state ($x_v = 0$) for the given pressure.

$$t_{o,out} = t_{sat,vap, p_o} + SH \quad (4)$$

$$t_{k,out} = t_{sat,liq, p_k} - SUB \quad (5)$$

Finally, suction enthalpy and inlet evaporator enthalpy were calculated following Eqs. (6), (7) and (8).

$$t_{suc} = t_{o,out} + \epsilon_{ihx} \cdot (t_{k,out} - t_{o,out}) \quad (6)$$

$$h_{suc} = f(t_{suc}, p_o) \quad (7)$$

$$h_{o,in} = h_{k,out} - h_{suc} + h_{o,out} \quad (8)$$

The theoretical model to predict the binary blends is sketched in Fig. 1, which is similar to the one used in Calleja-Anta et al. (2020).

Firstly, the different thermodynamic states through the cycle were calculated according with the cycle previously described. To classify the mixture as "acceptable" to substitute the isobutane, some requirements were set. The mixture must have a GWP below 150 [according to the fifth assessment report (IPCC Climate Change 2013)], an effective evaporation glide ($Glide_{o,e}$) and a condensation glide ($Glide_k$) lower than 10 K and 20 K respectively and a discharge temperature (t_{dis}) lower than $90\text{ }^\circ\text{C}$. Mixtures not accomplishing these requirements were discarded. Formulas used to calculate these parameters can be seen from Eqs. (9) to (12).

$$GWP = \sum_i^n (m_i \cdot GWP_i) \quad (9)$$

$$Glide_{o,e} = t_{f(p_o, x_v=1)} - t_{f(p_o, x_v=0)} \quad (10)$$

$$Glide_k = t_{f(p_k, x_v=1)} - t_{f(p_k, x_v=0)} \quad (11)$$

$$t_{dis} = f(s = s_{suc}, p_k) \quad (12)$$

For the "accepted" mixtures, a second filter based on energy parameters was set. Mixtures with a Volumetric Cooling Capacity (VCC) within a range between 0.7 and 1.3 respect VCC obtained by isobutane

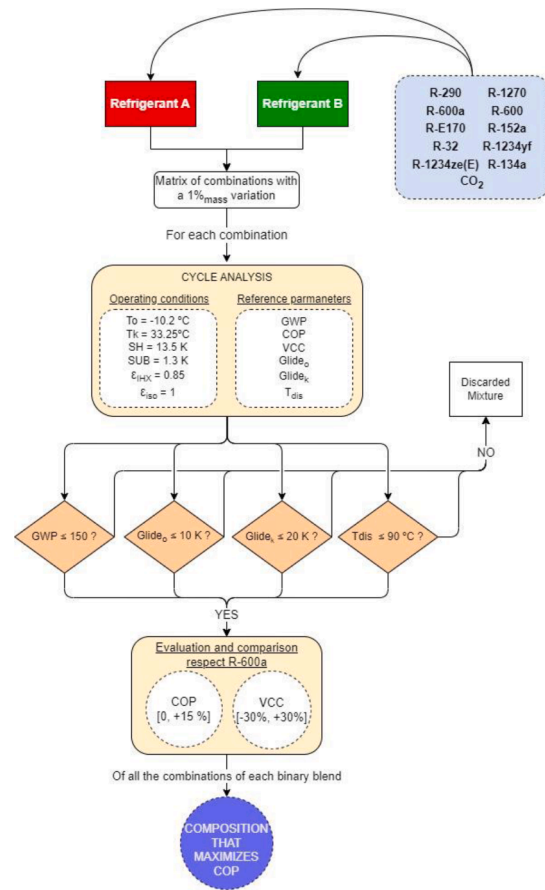


Fig. 1. Sketched of the theoretical model used to evaluate alternative mixtures.

are considered as acceptable. Since the unit used for the experimental tests is equipped with a R-600a compressor, higher deviations on this parameter may lead to a lack of cooling capacity and an excessive duty-cycle. Additionally, only mixtures with a Coefficient Of Performance (COP) between 1 and 1.2 times respect isobutane were considered. Blends with lower values are not of interest for this study and higher values of 1.2 isobutane COP are thought to be unrealistic and may be caused by punctual errors in the mixing rules of Refprop. Eqs. (13) and (14) show how these two parameters are calculated.

$$VCC = \frac{h_{o,out} - h_{o,in}}{v_{suc}} \quad (13)$$

$$COP = \frac{\Delta h_o}{\Delta w_{comp}} = \frac{h_{o,out} - h_{o,in}}{h_{dis,sf(s_{suc}, p_k)} - h_{suc}} \quad (14)$$

11 pure refrigerants were considered as possible constituents of the mixtures (R-290, R-1270, R-600a, R-600, R-E170, R-152a, R-32, R-1234yf, R-1234ze(E), R-134a and CO_2). All of them were mixed together to form binary blends, creating a total of 55 different combinations. For each combination of two refrigerants, the mass composition of the refrigerants was varied in 1%, resulting in a total of 99 different compositions. For all the 99 compositions of each binary blend, it was selected the one which offered a higher COP. In total 5445 different mixtures were analysed in this screening.

2.2. Theoretical results and mixtures selected to be tested

For each pair of refrigerants, the compositions that maximize COP and accomplish with the requirements are chosen. The resultant mixtures can be seen Fig. 2. Highlighted in a red circle are the mixtures which will be tested in the experimental unit. In the same line as the

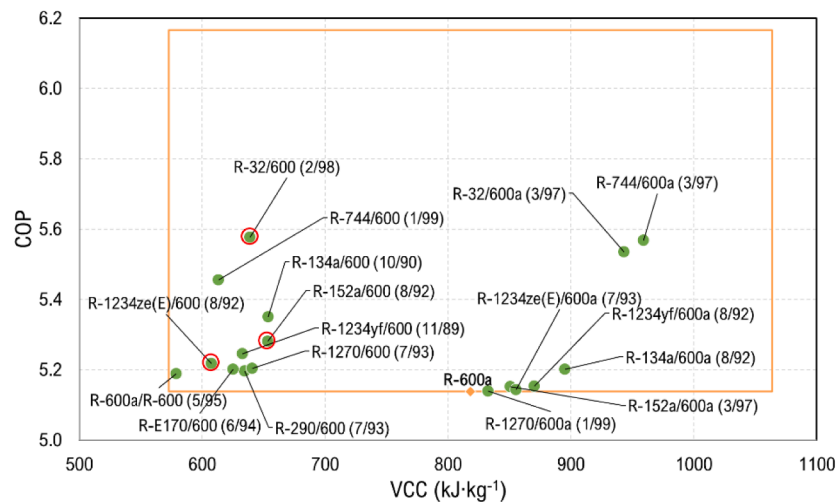


Fig. 2. Results obtained in the thermodynamic screening. For each pair of refrigerants, the composition with higher COP was chosen.

study Calleja-Anta et al. (2020), two different patterns can be observed. At the right of the graph are placed mixtures mainly formed by isobutane and a second refrigerant, while at the left are the mixtures with butane as principal constituent. Mixtures with isobutane, despite of presenting similar VCC than isobutane, are considered of less interest due to their low increments of COP respect isobutane. On the other side, mixtures with butane present increments in COP around 2%. Of all the mixtures, four blends highlight, which are the ones with R-32 and R-744 as constituents in a very small fraction. These results may be due to the uncertainty associated with the calculation program used. In any case, to validate this hypothesis, the mixture R-32/R-600 (2/98) is chosen to be experimentally tested.

A total of three mixtures are chosen to be tested in the experimental unit: R-1234ze(E)/R-600 (8/92), R-152a/R-600 (8/92) and R-32/R-600 (2/98). The reason for choosing the first two mixtures was that it had already been demonstrated in previous work that they could offer energy reductions, while R-32/R-600 (2/98) is chosen for the reason previously explained.

The thermodynamic properties of the selected mixtures and GWP obtained in the theoretical process can be seen in Table 1, as well as their comparison respect R-600a. The three mixtures present a significant VCC reduction and slight COP increments, which may lead to duty cycle increments in the plant.

Fig. 3 represents the pressure-enthalpy diagram and 35 °C and –10 °C isotherms. The three mixtures present similar pressure levels to isobutane. In reference to the latent heat of phase-change at evaporating conditions, all the three mixtures present higher values, as it can be seen in the diagram. Concretely, isobutane present a latent heat of 363.53 kJ/kg, while the mixtures of 374.99 kJ/kg, 381.4 kJ/kg and 390.54 kJ/kg, which represents increments of +3.15%, +4.92% and 7.43%

Table 1

Properties and GWP of the mixtures selected to be tested.

Refrigerant (Mass%)	COP [-] (ΔCOP)	VCC [kJ/kg] (ΔVCC)	Glide _o [K]	Glide _k [K]	T _{dis} [°C]	GWP _{100years}
R-600a	5.14	818.15	–	–	69.12	3
R-1234ze (E)/R-600 (8/92)	5.22 (+1.54%)	607.49 (–25.75%)	2.17	3.87	68.2	3.27
R-152a/R-600 (8/92)	5.28 (+2.78%)	653.42 (–20.13%)	5.21	10.08	65.06	13.8
R-32/R-600 (2/98)	5.58 (+8.52%)	638.85 (–21.92%)	3.02	16.01	58.28	9.75

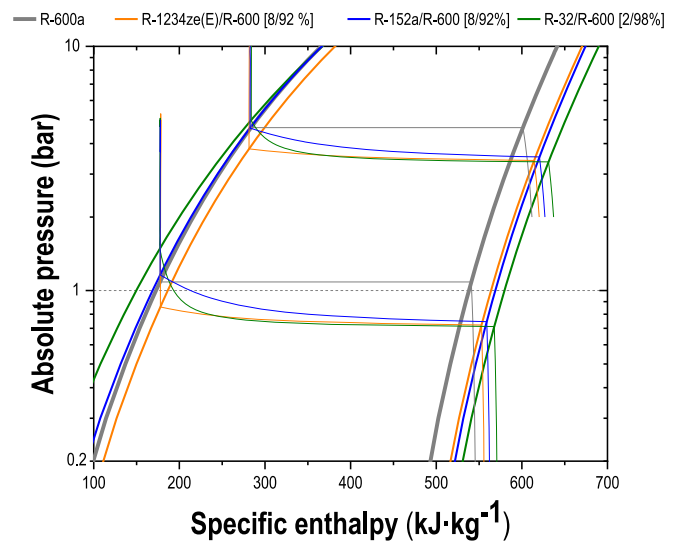


Fig. 3. Pressure-enthalpy diagram of considered refrigerants and isotherms (–10 °C, 35 °C).

respectively. The main difference can be observe in the temperature glides in both temperatures levels. The glide occurs mainly at low vapour quality values, while at high values is much smaller and tend to stabilize. It can be see by the flow of the isotherms that the glide is higher in the mixtures R-152a/R-600 (8/92) and R-32/R-600 (2/98), as the effective glide in Table 1 shows.

3. Methods and materials

This section describes the experimental unit used to perform the experimental tests, as well as the experimental procedure followed and the mixture preparation process.

3.1. Experimental system

The experimental tests were performed in a stand-alone commercial cabinet used for the refrigeration of fresh beverage. Its dimensions are 620 (L)x 2000 (H)x 655 (D) mm with a total inner volume of 440 litres. The schematic refrigeration circuit can be seen in Fig. 4, as well as a picture of the appliance. It consists in a hermetic reciprocating compressor, two condensers (one wired-tube and another finned-tube)

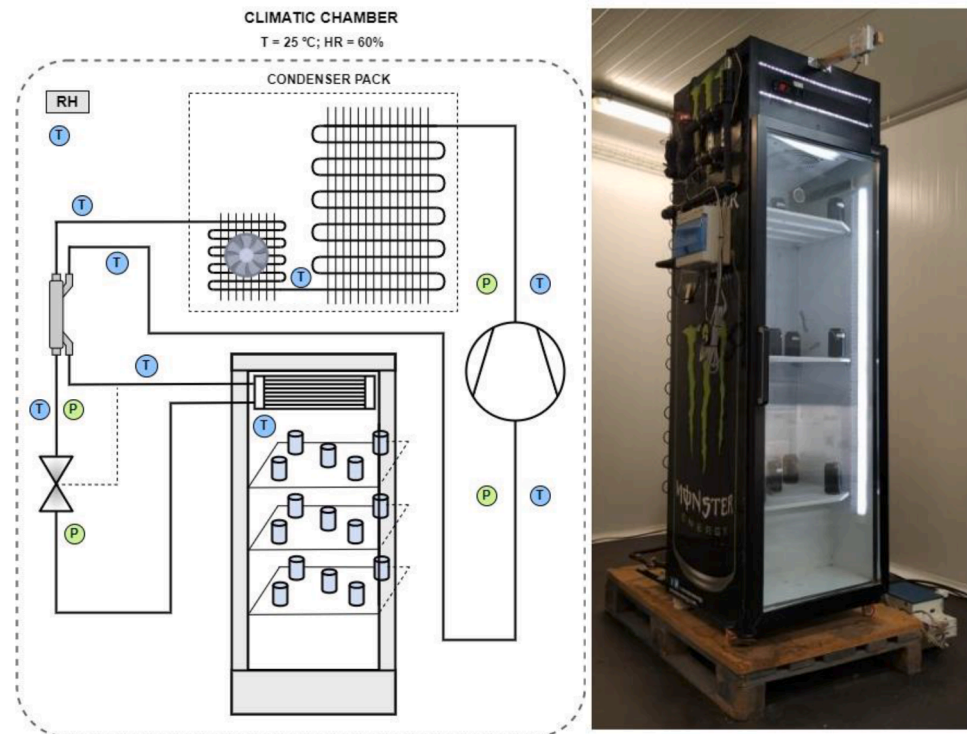


Fig. 4. Picture of the appliance where the experimental tests are conducted (right) and frigorific scheme of its refrigeration cycle with the position of the different sensors installed (left).

in series (to ensure a complete condensation of the refrigerant), an internal heat exchanger (IHX), an electronic expansion valve (whose driver can be configurable to work accordingly with each mixture) and a finned-tube evaporator. The characteristics of each element can be seen in Table 2.

The regulation of the cabinet was done with an ON/OFF control system which activated and deactivated the compressor to adjust the internal temperature of the appliance to the set-point specified temperature by the user, with a hysteresis of 3.5 K. The ON/OFF system also commanded the function of the fans of the evaporator and the second condenser, being their power consumption of 60 W in total. The lights of the appliance and its different controllers were always demanding a constant electric power of 17.7 W. The defrosting periods were programmed each 8 h and finished when the temperature in the surface of the evaporator reached 5 °C. In that period the evaporator fan was activated.

To obtain the different thermodynamic parameters of the refrigerants, the refrigeration circuit was instrumented with 7 T-type

surface thermocouples (T) and 4 pressure gauges (P) [2 high-pressure (0–16 bar) and 2 low-pressure (0–9 bar)]. Additionally, three thermocouple probes at the inlet and outlet of the evaporator airflow were installed. To simulate the product behaviour, 15 test cans filled with a mixture of water/propylene-glycol (67/33%_v) were homogeneously placed inside the cabinet with an immersion T-type thermocouple in them. The position of the sensors can be seen in Fig. 4 (except the evaporator airflow ones, which are not represented). The uncertainty of the T-thermocouple is of ± 0.5 K and of the pressure gauges is of $\pm 1\%$ of the full measuring range. To measure the electric power demanded, a digital wattmeter was used with an uncertainty of $\pm 0.5\%$ of measurement.

The cabinet was placed in a climatic chamber with control of the temperature and the relative humidity. Both parameters were measured with a thermohydrometer with an accuracy of $\pm 2\%$ RH and ± 0.2 K.

3.2. Experimental procedure and mixtures preparation

The objective of the work is to verify experimentally that the mixtures identified in the theoretical study are able to reduce the energy consumption of the isobutane and quantify it. For that, the standard ISO 23,953–2:2015 (ISO 23953-2:2015, 2015) is used as the reference method to conduct the tests. The tests were performed during 16 h in the cabinet previously presented (Sánchez, et al. (Sánchez et al., 2022) demonstrated that, for this particular appliance, the energy consumption recorded during 16 h was proportionally the same than 24 h). The experimental unit was placed inside a climatic chamber at the conditions of 25 ± 0.3 °C and $60 \pm 4\%$ of RH.

The set-point of the ON/OFF controller was adjusted to obtain an average product temperature for all tests of 3.1 °C.

Refrigerant mixtures were prepared in our laboratory installations using fluids with 99.5% guaranteed purity. The mixtures were done in an 8-litre tank, ensuring always that the mixture was in gaseous state. The first refrigerant added in the tank was the one with lower Normal Boiling Point (NBP), followed by the other component, whose quantity was

Table 2
Description of the cabinet elements.

ID	Element	Characteristics
1	Compressor	Hermetic reciprocating compressor originally designed to work with isobutane. Displacement: 14.3 cm ³ , 2900 rpm, 1/4 horsepower, HBP. Model: Embraco NE K6170Y.
2	Condenser pack	1st Wire-on-tube heat exchanger. Natural convection. Heat transfer area: 0.186 m ² 2nd Finned-tube heat exchanger. Forced convection. Heat transfer area: 0.089 m ²
3	IHX	Concentric tube heat-exchanger Heat transfer area: 0.01 m ²
4	Electronic valve	Used as thermostatic expansion valve. Driver configurable to each refrigerant mixture with bubble and dew temperatures.
5	Evaporator	Finned-tube heat-exchanger. Forced convection. Heat transfer area: 0.186 m ²

adjusted to match with the desired proportions. A balance with an uncertainty of ± 0.1 g was used.

The valve was adapted to work with each refrigerant, configuring the controller according to the bubble and dew temperatures of each mixture. The set-point of the SH of the expansion valve was set at 6 K.

The refrigerant charge of the cabinet was done via the service valve of the compressor. The initial charge was around 90 g for each refrigerant (except isobutane, which required a lower initial charge of 72 g). Once the test finished, the cabinet was charged a quantity between 6 and 8 g. This process was repeated still an optimum charge is clearly reached (charge with the lowest energy consumption respect the rest). A reasonable amount of time was left between charges, never less than 4 h, until the device stabilized to the new conditions. The effective test sample chosen for the analysis comprise one whole period between two defrosting periods, the last part of one cycle and the beginning of the other, as it can be seen in Fig. 5. Fig. 5 represents the evolution of the discharge and aspiration pressures, the product temperature (as the average of the 15 test cans inside the cabinet) and the power consumption during by the unit during 16 h of the test R-600a 115 g.

4. Experimental results

4.1. Mass charge optimization

For each refrigerant there is an optimum in the mass charge in which the energy consumption is lower. Each blend is subject to mass charge optimization process, as explained in the previous section. The energy consumption of the appliance for 16 h is calculated with Eq. (15), in which $P_c(t)$ is the total power demanded by the experimental unit in the instant t . Each sample is taken every 5 s. Calculated energy consumption has an uncertainty below 0.5%.

$$E_i = \frac{1}{3600} \int_0^{16h} P_c(t) \cdot dt = \frac{1}{3600} \sum_{j=1}^{16h} \left\{ \left[\frac{P_c(j) + P_c(j-1)}{2} \right] \cdot [t(j) - t(j-1)] \right\} \quad (15)$$

The energy consumption results obtained for each mixture during the optimization process can be seen in Fig. 6. For the four refrigerants tested there is an optimum charge at which the energy consumption is minimum. From that charge, the energy consumption tends to stabilize and increase slightly respect the optimum. When charged with isobutane, at its optimum charge (115 g), the plant consumes 2.627 kW·h during 16 h. With the mixture R-1234ze(E) / R-600 (8/92)%_{mass} at 159 g, the energy consumption of the experimental unit is reduced by -2.69% , consuming a total of 2.556 kW·h in the test period, whereas with the mixture R-152a/ R-600 (8/92)%_{mass} at 165 g, the total energy consumption is 2.495 kW·h, a reduction of -5.04% with respect R-600a. As expected, the R-32/R-600 (2/98)%_{mass} mixture does not provide a reduction on the energy consumption, consuming in practice the same energy as isobutane. Detailed parameters of the tests can be seen in Table 4.

These results verify the conclusions obtained in the theoretical section and even improve the improvement predicted for two of the three mixtures. In the following section, the thermodynamic properties of the refrigerants are analysed at the optimum operating conditions in order to try to explain the results obtained in Fig. 6.

4.2. Optimized configurations

This section aims to analyse the different operating parameters obtained with the experimental unit during the 16-h test. The results analysed here corresponds to the optimum charge of each refrigerant analysed.

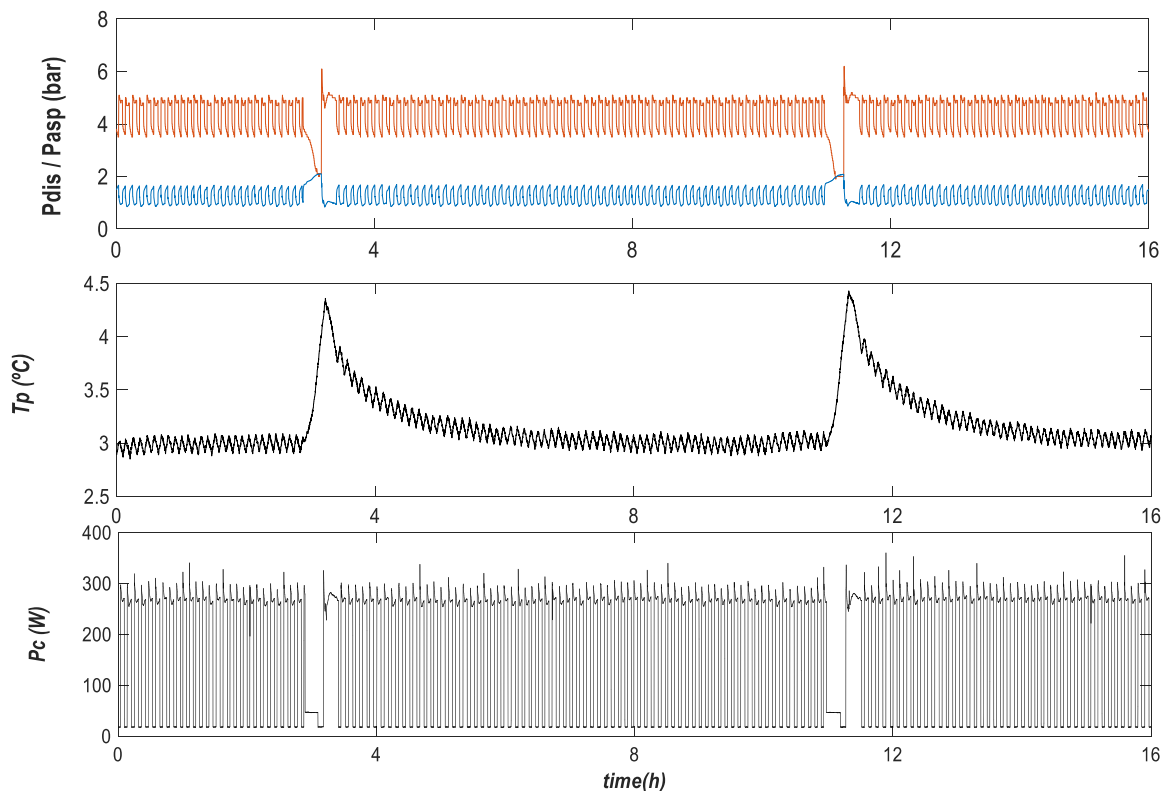


Fig. 5. Evolution of power consumption (P_c), average product temperature (t_p), discharge pressure (p_{dis}) and aspiration pressure (p_{asp}) during 16 h of the test R-600a with 115 g.

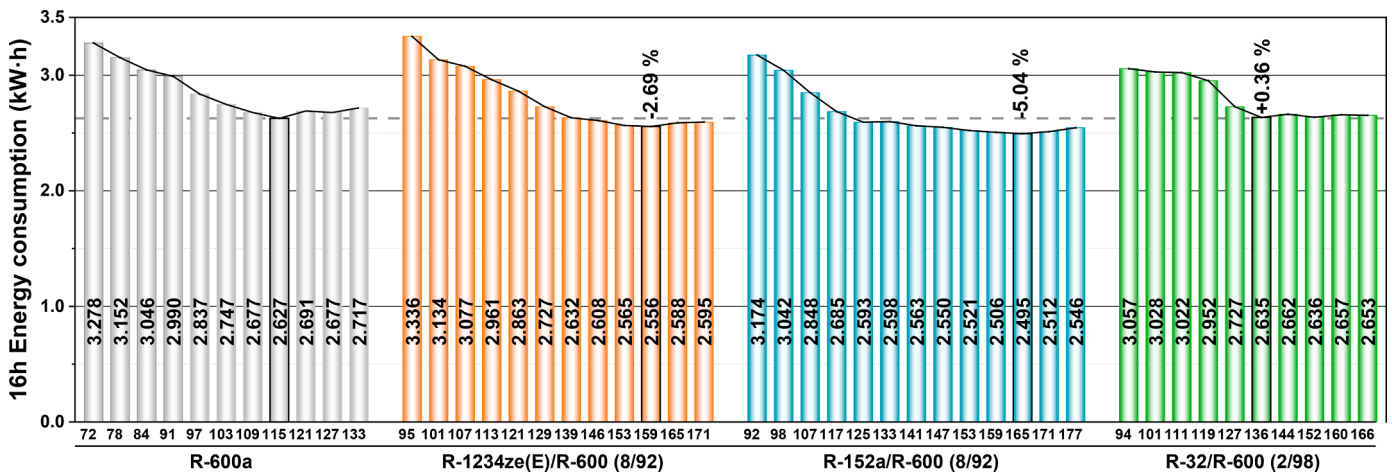


Fig. 6. Energy consumption in 16 h of the isobutane (R-600a) and the alternative mixtures.

4.2.1. Differentiated consumptions

The energy consumption shown in Fig. 6 is the combination of all the energy consumed by the compressor (variable), the fan in the evaporator (28.8 W) and in the condenser (31.2 W) and the lights and electronics (17.7 W). Fig. 7 shows the energy consumption during the 16-h test differentiated by the compressor and by the rest of elements (called “auxiliary power” in the figure). As explained priorly, electronics and lights were demanding a constant power nearly independently to other variables. When the compressor was ON, both fans were activated, while OFF, both were deactivated. During defrosting periods (programmed each 8 h), only the evaporator fan switched on.

It can be observed that for the three alternative mixtures the compressor consumption is lower than isobutane one and the energy reductions are even greater than the observer in Fig. 6. The reductions are 6.82% for R-1234ze(E)/R-600 (8/92), 8.52% for R-152a/R-600 (8/92) and 4.55% for R-32/R-600 (2/98). This indicates that, just considering the refrigeration cycle, the energetic behaviour is better than the isobutane one. However, the consumption by the auxiliary power is higher in all cases, which penalises the overall energy consumption of the plant. This fact can be directly explained through the duty cycle, in Fig. 8.

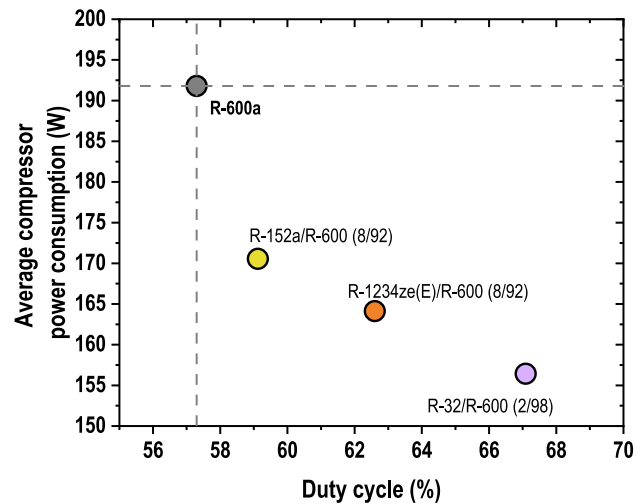


Fig. 8. Average compressor power demand vs duty cycle.

4.2.2. Duty cycle vs power consumption

Fig. 8 shows the comparison of the duty cycle and the average compressor power consumption when the compressor is ON. As expected, the alternative mixtures, principally due to their lower density, require a lower power input by the compressor. While R-600a require a 191.79 W, the other three mixture present a consumption of 170.55 W, 164.12 W and 156.42 W.

However, presenting a lower density has the drawback that, for a given volume, the circulating mass flow is lower, which has impact in the duty cycle. The duty cycles are 57.3% for isobutane, while for the alternative fluids are 59.12% for R-152a/R-600, 62.6% for R-1234ze (E)/R-600 and 67.09% for R-32/R-600. The duty cycle has a high impact on the overall energy consumption in this particular appliance and can be extrapolated to similar ones. As mentioned above, when the compressor is ON, also the fans are ON, adding 60 W of extra power. Thus, for high operation times, the energy consumption by this “auxiliary” power is higher. This can be seen from the fact that refrigerants with lower duty cycles present lower auxiliary power consumption in Fig. 7 and vice versa. This fact goes so far that, for the R-32/R-600 (2/98) mixture, even though the compressor presents a 4.55% reduction in energy consumption with respect to R-600a, the overall consumption for 16 h is even slightly higher.

4.2.3. Operation pressure and temperatures

The operation pressure at the optimum charges is represented in

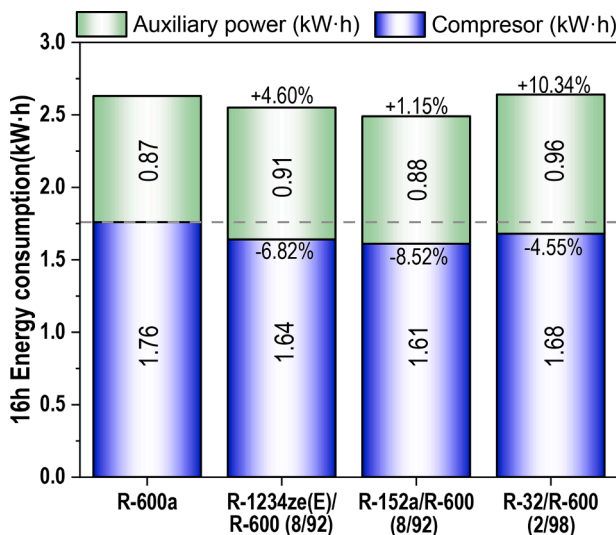


Fig. 7. Energy consumption of each refrigerant differentiated by compressor and the rest.

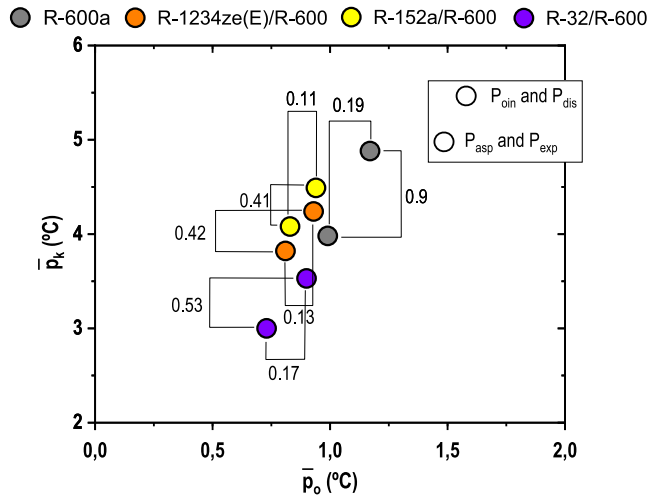


Fig. 9. Representation of the operating pressures of each mixture. Two gauges were installed in each pressure line. The lines connecting the dots represent the pressure drops.

Fig. 9. Two pressure gauges were installed in each pressure level, allowing the measure of the pressure drops. In the figure, each colour corresponds to a different refrigerant. The point at the right and at the top represents the $p_{o,in}$ (should be read at \bar{p}_o) and $p_{o,dis}$ (should be read at \bar{p}_k), whereas the point at the left and bottom are $p_{a,asp}$ and $p_{a,exp}$ (same form of reading it). The lines connecting the dots correspond to the pressure drops.

All the fluids present similar pressure levels to isobutane, not implying any compatibility problem. Due to the big presence of butane (Normal Boiling Point of 0.5 °C), all the alternative mixture present evaporation pressures slightly below 1 bar, being the mixture R-32/R-600 (2/98) the one with lower pressure levels in general. In relation with the pressure drops, isobutane has a pressure drop in the liquid line of 0.9 bar, while the alternative mixtures reduce this value significantly (values vary from 0.41 to 0.53 bar). Similar happens at the vapour line, presenting reductions on the pressure drops. This reduction in pressure drop is probably related to the lower mass flow rate of the mixtures, which is ultimately a consequence of their lower density.

Phase change temperatures are calculated along the activation period of the compressor, according to Eqs. (16) – (18). Evaporation temperature is calculated with the mean evaporation pressure and with the mean enthalpy between evaporator inlet and vapour saturated conditions. A similar procedure is used with condensation temperature.

$$\bar{t}_o = f[(p_{o,in} + p_{asp})/2, (h_{o,in} + h_{sat,vap})/2] \tag{16}$$

$$h_{sat,sat} = f(p_{asp}, x = 1) \tag{17}$$

$$\bar{t}_k = f[(p_{des} + p_{exp})/2, x_v = 0.5] \tag{18}$$

Fig. 10 shows the results obtained with each refrigerant. Perpendicular blue line has a slope of 1:1, in such matter that the fluids at its right present a lower difference between temperatures than the reference and vice versa. R-152a/R-600 (8/92) and R-1234ze(E)/R-600 (8/92) present higher condensation temperature and lower evaporation temperature, probably due to fact that the optimum charge is higher what tends to elevate the pressure levels. However, both fluids are near the blue line, which shows that in practice the relation between both operation temperatures are similar to isobutane. However, the mixture R-32/R-600 present lower condensation and evaporation temperature.

4.2.4. COP estimation

The COP in an experimental compression vapour cycle is the ratio between the cooling capacity and the power demanded by the

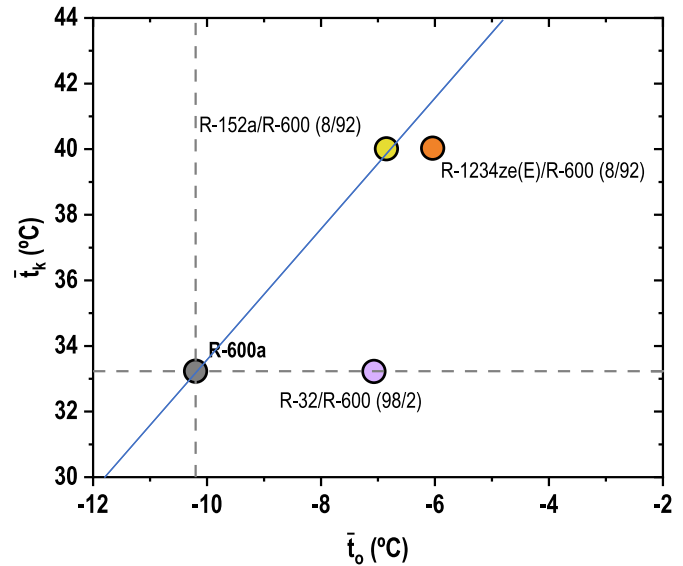


Fig. 10. Operation temperatures of the refrigerants.

compressor for a given time. However, this unit does not count with a mass flow meter that allow to measure the mass flow rate and determine the cooling capacity, so an estimation of COP should be done. For this purpose, the hour before the second defrost period is chosen to be analysed, as it is long and stable enough to be representative.

COP estimation is performed according Eq. (19), in which E_o is the cooling energy to be supplied for one hour and E_{comp} is the compressor energy consumption for the same period. E_o can be divided into the thermal load that comes from the enclosures of the cabinet (E_{enc}) and from the fan of the evaporator ($E_{f,o}$) [Eq. (20)]. Assuming that E_{enc} is equal for all fluids [Eq. (21)] (the inner cabinet and climatic chamber temperatures are equal for all fluids), we can arrive at Eqs. (22) and (23), in which the relation existing between the COP of a mixture and the isobutane depends on the relation of compressors power consumptions and the difference between the consumption of the fans. Eq. (23) can be develop into Eq. (24) in which the difference in fan power consumption is directly related to the difference in duty cycles (DC) ($P_{f,o}$ refers to the power demanded by the fan).

$$COP = \frac{E_o}{E_{comp}} \tag{19}$$

$$E_o = E_{f,o} + E_{enc} \tag{20}$$

$$E_{enc|R600a} = E_{enc|MIX} \tag{21}$$

$$COP_{R600a} \cdot E_{compR600a} - E_{f,oR600a} = COP_{MIX} \cdot E_{compMIX} - E_{f,oMIX} \tag{22}$$

$$COP_{MIX} = COP_{R600a} \cdot \frac{E_{compR600a}}{E_{compMIX}} + \left(\frac{E_{f,oMIX} - E_{f,oR600a}}{E_{compMIX}} \right) \tag{23}$$

$$COP_{MIX} = COP_{R600a} \cdot \frac{E_{compR600a}}{E_{compMIX}} + (DC_{MIX} - DC_{R600a}) \cdot time \cdot \frac{P_{f,o}}{E_{compMIX}} \tag{24}$$

Table 3
Estimation of COP of the alternatives mixtures.

	R-600a	R-1234ze(E)/R-600	R-152a/R-600	R-32/R-600
P_{comp} (W·h)	112.66	101.07	99.31	107.62
$E_{f,o}$ (W·h)	17.11	17.59	16.75	19.86
$COP_{MIX} =$	—	1.11· COP_{R600a} + 0.0047	1.13· COP_{R600a} - 0.0036	1.05· COP_{R600a} + 0.0255

The results of the analysis can be seen in Table 3. Since having similar duty cycles, the term associated with the fans is negligible for the mixtures R-1234ze(E)/R-600 (8/92) and R-152a/R-600 (8/92), having relative COP increments of 11% and 13% respectively. However, in the mixture R-32/R-600 (2/98) the last term is relevant, increasing a 0.0255 the ratio between two COPs, which is 1.05.

COP increments are consistent with the 16-h energy tests, the duty cycles and compressor power consumptions observed. The energy consumption is a trade-off between the COP and the required compressor operation time (duty cycle), resulting in the results in Fig. 6. The mixtures R-1234ze(E)/R-600 (8/92) and R-152a/R-600 (8/92) have a duty cycle that exceed in 5.3% and 1.8% respect R-600a and 11% and 13% relative COP increments. Therefore, the expected energy consumption should be lower than the COP increments and closer to them when lower the duty cycle is, which is the case. However, the mixture R-32/R-600 (2/98) have a significant increment in the duty cycle (10% higher) and a

lower COP increment than the other two mixtures (around 5%), thus penalizing its overall performance.

Compared with the theoretical analysis, COP results obtained experimentally are higher than the predicted theoretically. In any case, the results are coherent with the expected and help to contribute to the hypothesis that the high COP predicted with the mixture R-32/R-600 was not realistic and may be caused by errors in the interaction coefficients of Refprop.

It is important to mention that the results presented in this section are based on estimations. Results are therefore an approximation and should be interpreted as such. Other perspectives should be considered to obtain a more accurate value.

5. Conclusions

Previous works have demonstrated the existence of mixtures that,

Table 4
Reference, operation and energy parameters of the refrigerants evaluated.

Charge (g)	Reference parameters				Operating parameters		Duty cycle	Fractioned energy parameters		Total energy parameters		
	t_p (°C)	$\pm \sigma_{t,p}$ (K)	t_{cam} (°C)	$\pm \sigma_{t,cam}$ (K)	$t_{K,on}$ (°C)	$t_{O,ON}$ (°C)	(%)	$E_{compressor, 16h}$ (kWh)	$E_{aux,16h}$ (kWh)	$P_{C,ON}$ (W)	E_{16h} (kWh)	$(E - E_{ref}) / E_{ref} 100$ (%)
R-600a												
72	3.15	0.25	24.79	0.08	31.68	-11.24	77.61	2.23	1.05	257.36	3.28	n.c.
78	3.06	0.29	24.76	0.08	32.25	-9.84	72.49	2.15	1.00	263.28	3.15	n.c.
84	3.11	0.21	24.77	0.06	32.74	-8.21	67.98	2.08	0.96	269.41	3.05	n.c.
91	3.09	0.26	24.74	0.08	33.03	-7.78	65.62	2.05	0.94	272.55	2.99	n.c.
97	3.16	0.27	24.72	0.08	33.22	-7.83	61.37	1.93	0.90	274.55	2.84	n.c.
103	3.12	0.25	24.76	0.10	33.21	-7.91	59.25	1.86	0.89	274.16	2.75	n.c.
109	3.14	0.27	24.79	0.10	33.23	-8.05	57.55	1.80	0.87	273.90	2.68	n.c.
115	3.16	0.28	24.81	0.08	33.23	-10.20	57.30	1.76	0.87	269.42	2.63	n.c.
121	3.10	0.29	24.88	0.10	33.09	-8.93	58.60	1.81	0.88	270.63	2.69	n.c.
127	3.13	0.29	24.70	0.05	33.72	-8.93	57.82	1.80	0.87	272.60	2.68	n.c.
133	3.15	0.27	24.75	0.06	33.79	-9.01	58.71	1.84	0.88	273.21	2.72	n.c.
R-1234ze(E) /600 (8/92)												
95	3.31	0.36	24.94	0.09	38.36	-6.26	86.11	2.21	1.13	237.97	3.34	26.99
101	3.16	0.32	25.20	0.08	38.09	-6.82	82.23	2.04	1.09	232.98	3.13	19.31
107	3.25	0.31	25.09	0.08	38.26	-6.91	78.96	2.01	1.06	237.08	3.08	17.13
113	3.15	0.32	25.07	0.09	38.37	-6.95	76.15	1.92	1.04	235.60	2.96	12.71
121	3.12	0.33	25.11	0.07	38.46	-6.89	72.86	1.86	1.01	237.00	2.86	8.99
129	3.17	0.30	25.10	0.06	38.79	-6.20	67.69	1.77	0.96	240.89	2.73	3.83
139	3.13	0.30	25.08	0.06	39.01	-5.42	64.40	1.70	0.93	242.87	2.63	0.18
146	3.11	0.29	24.96	0.06	38.94	-5.10	63.87	1.68	0.93	242.31	2.61	-0.73
153	3.19	0.29	24.93	0.06	38.99	-4.99	63.25	1.65	0.92	240.43	2.57	-2.35
159	3.14	0.30	24.93	0.08	40.03	-6.04	62.60	1.64	0.91	241.75	2.56	-2.69
165	3.16	0.29	25.16	0.08	41.26	-4.69	62.15	1.68	0.91	246.29	2.59	-1.49
171	3.08	0.30	25.09	0.08	42.26	-4.66	62.07	1.68	0.91	247.19	2.59	-1.22
R-152a /600 (8/92)												
92	3.28	0.33	25.14	0.08	36.57	-7.89	80.64	2.10	1.08	240.11	3.17	20.84
98	3.15	0.29	25.18	0.08	36.66	-8.24	77.11	2.00	1.04	239.55	3.04	15.80
107	3.14	0.30	25.02	0.10	36.64	-8.00	71.26	1.85	1.00	237.89	2.85	8.42
117	3.25	0.27	25.00	0.08	36.87	-7.01	65.93	1.74	0.94	242.69	2.68	2.21
125	3.10	0.28	25.00	0.08	37.18	-6.33	62.98	1.68	0.92	244.16	2.59	-1.28
133	3.07	0.27	24.98	0.08	37.22	-6.11	62.58	1.68	0.91	245.91	2.60	-1.09
141	3.18	0.28	24.95	0.08	37.25	-5.92	61.61	1.66	0.90	245.88	2.56	-2.44
147	3.13	0.27	24.98	0.08	37.19	-6.05	61.99	1.64	0.91	243.22	2.55	-2.94
153	3.14	0.28	25.53	0.29	37.30	-6.30	61.02	1.62	0.90	244.00	2.52	-4.02
159	3.12	0.27	25.54	0.20	38.49	-6.03	59.82	1.62	0.89	246.72	2.51	-4.60
165	3.07	0.27	24.92	0.14	40.01	-6.85	59.12	1.61	0.88	248.18	2.49	-5.04
171	3.09	0.26	25.23	0.26	39.91	-5.78	59.44	1.63	0.89	248.63	2.51	-4.38
177	3.11	0.27	24.98	0.08	40.92	-5.54	59.78	1.66	0.89	250.94	2.55	-3.10
R-32 /600 (2/98)												
94	3.09	0.24	24.62	0.20	32.69	-6.36	79.57	1.99	1.06	234.25	3.06	16.36
101	3.09	0.25	24.61	0.17	32.70	-6.83	77.92	1.98	1.05	236.37	3.03	15.27
111	3.09	0.26	25.17	0.15	32.59	-7.19	76.63	1.98	1.04	239.31	3.02	15.05
119	3.15	0.24	24.96	0.26	32.83	-7.16	74.46	1.93	1.02	239.72	2.95	12.37
127	3.12	0.29	24.75	0.10	32.77	-7.11	70.61	1.74	0.99	231.87	2.73	3.82
136	3.07	0.33	24.44	0.05	33.22	-7.07	67.09	1.68	0.96	234.05	2.63	0.29
144	3.10	0.33	24.90	0.12	33.61	-6.86	67.78	1.70	0.96	234.50	2.66	1.34
152	3.12	0.36	25.00	0.15	34.16	-8.03	67.65	1.68	0.96	232.63	2.64	0.36
160	3.06	0.34	24.94	0.16	34.13	-6.71	67.28	1.70	0.96	235.46	2.66	1.15
166	3.09	0.35	24.96	0.13	35.68	-6.51	66.45	1.70	0.95	237.77	2.65	0.98

Notes about the table.
- n.c. stands for "not considered".

having similar thermodynamic properties, allow to decrease the energy consumption in relation to isobutane refrigeration systems. This paper addresses that possibility. The aim is the exploration of binary mixtures based on butane as principal component and a second refrigerant from a theoretical and experimental point of view.

To predict the possible mixtures with better energy performance, a theoretical model was launched. 11 pure refrigerants were considered as possible constituents of the mixture. All of them were combined to forms all the possible combinations (55 in total) and their mass composition was varied in steps of 1% (99 possibilities for each pair of refrigerants). In total 5445 different mixtures were analysed. The model simulated an ideal simple vapour compression cycle, operating at $t_o = -10.2$ °C and $t_k = 33.25$ °C, and a SH = 13.5 K and a SUB = 1.3 K. After some filters in terms of glide, t_{dis} , GWP and VCC, the mass composition for each combination of two refrigerants which maximizes COP is chosen. Mixtures R-1234ze(E)/R-600 (8/92), R-152a/R-600 (8/92) and R-32/R-600 (2/98) are chosen to be experimentally tested, as they offered theoretical COP increments of 1.54%, 2.78% and 8.52% respect isobutane.

Experimental tests were conducted in a stand-alone commercial cabinet used for the refrigeration of fresh beverage. The unit was equipped with an electronic expansion valve which was programmed to work specifically with each refrigerant according to its saturation lines. Tests were performed during 16 h in a climatic chamber at 25 °C and 60% RH. For each mixture, an optimization charge process was conducted.

The 16-hours tests showed that the cycle charge with isobutane presented an energy consumption of 2.627 kW·h at a charge of 115 g, while mixtures R-1234ze(E)/R-600 (8/92) accomplished a reduction of 2.69% at 159 g and R-152a/R-600 (8/92) of -5.04% at 165 g. The mixture R-32/R-600 (2/98) showed an increment of +0.36% at 136 g. Compressor consumption was reduced in all mixtures (-6.82%, -8.5% and -4.55% respectively), but duty cycles were higher (+5.3%, +1.82% and +9.79%, respectively). The pressures of the alternative mixtures were compatible with the application.

The COP of the fluids was compared by assuming that the thermal loads by the enclosures were equal for all the tests, showing that the mixture R-1234ze(E)/R-600 (8/92) had an increment of COP of +11%, R-152a/R-600 (8/92) of +13% and R-32/R-600 (2/98) of around +5%.

This paper proves the existence of alternative mixtures that can significantly reduce the power consumption of isobutane with similar thermodynamic properties.

CRedit authorship contribution statement

Daniel Calleja-Anta: Conceptualization, Methodology, Investigation, Writing – original draft. **Daniel Sánchez:** Conceptualization, Methodology, Investigation, Supervision. **Laura Nebot-Andrés:** Methodology, Writing – review & editing. **Ramón Cabello:** Methodology, Funding acquisition. **Rodrigo Llopis:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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