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Computational Tool to Support the Decision in the Selection of Alternative and/or Sustainable Refrigerants

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Abstract: There have been consequences regarding the increment of the greenhouse effect, such as the rise in the planet's global temperature, and climate change. Refrigerants have an important contribution to the aforementioned environmental impact. In particular, hydrofluorocarbons (HFCs) contribute to the destruction of the ozone layer and the increase of the greenhouse effect. Protocols, international agreements, and legislation were developed to slow down the emission of greenhouse gases. Prohibition and definition of deadlines for the gradual elimination of various refrigerants have been proposed to replace them with others that are environmentally sustainable. Soon, the refrigeration sector will have to replace some refrigerants with others that are alternative and/or sustainable with minimal or zero environmental impact. A computational tool to support decision-making regarding the selection of alternative and/or sustainable refrigerant to replace the old one is developed to be used by refrigeration companies, manufacturers, and installers. A suggestion of refrigerants with reduced environmental impact is provided, ensuring similar thermal performance and energy efficiency, considering the safety level and renovation cost of the installation and refrigerant itself. This decision support system (DSS) uses an objective function that includes the technical specifications and properties of alternative and sustainable refrigerants. The computational tool is applied in the agri-food sector in three case studies. The results show not only the consistency of the computational tool, but also its flexibility, objectivity, and simplicity. Its use allows companies to choose refrigerants with reduced environmental impact, reduced or zero ozone depletion potential and global warming impact, thus contributing to environmental sustainability.

Keywords: computational tool; HFCs; objective function; environmental impact; alternative refrigerants; sustainable refrigerants; sustainability

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Citation: Jesus, G.; Aguiar, M.L.; Gaspar, P.D. Computational Tool to Support the Decision in the Selection of Alternative and/or Sustainable Refrigerants. *Energies* **2022**, *15*, 8497. https://doi.org/10.3390/en15228497

Academic Editors: Fuqiang Wang, Chao Shen, Dong Li and Zhonghao Rao

Received: 15 October 2022
Accepted: 12 November 2022
Published: 14 November 2022

1. Introduction

Refrigerants are substances or mixtures of substances, which are used in refrigeration systems and air conditioners as mediator fluids, responsible for performing heat transfers, undergoing a reversible phase transition, i.e., from the liquid state to the gaseous state and vice-versa [1]. The heating and cooling equipment involved uses electricity as a source of energy, which is still dependent on fossil fuels, subsequently causing many environmental problems on a global scale. This heavy reliance on conventional energy for the functioning of cooling equipment contributes to the increase in the prices of these energy sources [2].

Refrigeration plays a key role in sustainable development as it has many applications in different areas of daily life. The most commonly used refrigerators and air conditioning systems employ the traditional vapor compression re-chilling system (VCRS). However, the energy consumption of this type of equipment is very high and its working substances (refrigerants) create environmental problems that need to be solved urgently [3].

VCRS systems are responsible for about 30% of the total energy consumption worldwide and this amount can increase when system malfunctions occur, such as refrigerant leaks, however, due to their high coefficient of performance (COP), the use of VCRS will continue to expand worldwide (especially in developing countries) [4].

Chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC) fluids are chemically synthetic substances, generally used as working fluids due to their excellent thermodynamic and chemical properties. Despite the aforementioned advantages, CFCs and HCFCs contain chlorine which reacts with ozone and gradually destroys the atmospheric ozone layer [4].

In 1974, scientists Rowland and Molina published a paper describing the decline in the thickness of the ozone layer, particularly over the continent of Antarctica. Following the presentation of this study, the 'Vienna Convention for the Protection of the Ozone Layer' was organized to take strong measures for the protection of the ozone layer and served as the basis for the 'Montreal Protocol' [5].

The Portuguese agri-food industry is essentially composed of micro, small and medium enterprises [6]. This sector is highly fragmented due to the great variety of products and production processes, but, given its heterogeneity, it is a sector with huge potential to increase its energy efficiency due to delays in the implementation of energy efficiency measures and renewable energy sources, misuse and waste of energy caused by the great diversity of processes [7]. The environmental issues of global warming are currently forcing supermarket owners to adopt alternative technologies that offer a lower cooling load, with consequent reduction of energy consumption and a lower environmental impact. In order to respond efficiently to the problem, natural refrigerants have been receiving increased attention for their use in supermarket refrigeration systems, especially the use of R744, carbon dioxide, in the low-temperature circuit of cascade systems which have become a commercial alternative [8]. Increasing energy demand as well as rising prices have sounded the alarm for the scientific community as well as policymakers to look for other cheaper and available energy sources so that conventional energy use can be checked. The demand for refrigeration and air conditioning using conventional energy can now be reduced to some extent by using solar energy, biogas, biomass, and geothermal energy [2]. Optimization of any thermodynamic process could be a better option from the point of view of energy conservation. There are many parameters that can affect the performance of cooling equipment and a complete study based on the second law of thermodynamics corresponds to the standard methodology to optimize the design of systems for better performance. However, cooling equipment powered by renewable energy also needs to be evaluated in economic terms in order to understand the feasibility and viability of these systems, since this methodology gives more flexibility in realizing a more efficient system [2].

1.1. The Problem under Study and Its Relevance

The use of refrigerants such as CFCs, HCFCs and HFCs has significant detrimental environmental impacts, such as stratospheric ozone depletion and global warming as they contribute about 70% of the man-made ozone depletion potential (ODP) chemicals in the atmosphere [9]. Due to ODP and global warming potential (GWP), several refrigerants have already been banned or deadlines set for their elimination, namely the CFCs that were banned in the Montreal Protocol (1987) [1]. Frozen ready-to-eat products that can be easily prepared and consumed are the big bet of the moment and, in addition, the increase in global temperature has consequently fired the air conditioning market, as refrigerants are better known [10]. Given this growing adherence to refrigeration systems, conventions have been held and protocols signed with the aim of phasing out refrigerants with negative environmental impact. The authorization and provisional solution (until 2040) to use HFCs, which are alternatives to CFCs, was given under the Kyoto Protocol. As the deadline approaches, the search for environmentally friendly alternative refrigerants has become a challenge for researchers working in this area. Natural refrigerants are one of the most desirable alternatives as they have inherently zero ozone depletion (ODP) as well as negligible contribution to global warming increase (GWP) [11]. In the current scenario, all refrigeration systems should also be analyzed, giving importance to economic and environmental issues in addition to thermodynamic aspects. To protect the environment from further degradation, the refrigerants used in any system should have zero ODP and very low GWP seeking to achieve sustainability in the processes [12].

In the context of agro-related industries, from agriculture to retail, and due to the evolution of computational resources, there has been the development of decision support systems (DSS) based on mathematics, statistics and artificial intelligence, to support energy efficiency, production optimization, environmental impact and sustainable management [13]. Some DSS have been developed for irrigation decision-making and water management [14–21], crop yield estimation [22], fruit diseases [23], energy consumption and performance of agri-food facilities [24–27], food logistics and distribution [28,29], commercialization time of perishable food products [30] and their pricing [31,32].

The main objective of this study lies in the development of a computational tool to support decision-making in the selection of refrigerants with reduced environmental impact, ensuring similar thermal performance and energy efficiency, considering the cost of the refrigerant and upgrading the refrigeration system. This tool must have capabilities such as ease of access, as well as the ability to understand, analyze, and interpret the results. After surveying the most diverse characteristics associated with alternative sustainable refrigerants, the model was applied in companies, giving them the best possible solution for their specific case in terms of the replacement of their refrigerant. With the increased demand for efficient, economical, and safe cooling systems for the rapidly growing chilled/frozen food industry, optimizing low temperature refrigeration systems using environmentally friendly refrigerants has now become one of the most important goals to achieve [33].

1.2. Evolution of the Refrigerants

Halogenated refrigerants used in cooling systems currently pose a threat to the environment when vented into the atmosphere because of their ODP and GWP [3]. The first large scale environmental impact caused by the activity of the refrigeration-based industries was ozone depletion. Chlorine-based refrigerants are stable enough to reach the stratosphere, where chlorine atoms act as a catalyst to destroy the stratospheric ozone layer, which protects the Earth's surface from ultraviolet (UV) radiation, altering the dynamic balance of ozone formation and consumption and causing its depletion [34]. Table 1 shows, in chronological order, the measures taken in light of the events held to date and demonstrates the set of restrictions imposed on the use of various refrigerants [35].

Table 1. Historical evolution of refrigerants taking into account their environmental impact.

Year	Event	Measure
1985	Vienna Convention	Recognition of the various consequences of CFC use and demonstration of great concern by major companies
1987	Montreal Protocol	Regulation of the production and consumption of "ozone-depleting substances", focusing particularly on CFC gases, which have a high ozone-depleting potential and, in addition, a high global warming potential
1990	London Amendment	Phase-out definition of all CFC, halon and carbon tetrachloride based refrigerant gases in developed and developing countries.
1992	UNFCC	Inclusion of HCFCs in the list of "ozone-depleting gases" in a phase-out process, in this case only for developed countries, using commonly used refrigerants such as R22 and R123

Table 1. *Cont.*

Year	Event	Measure
1997	Kyoto Protocol	The HCFC phase-out is extended to all countries and the methyl bromide phase-out is scheduled for 2005 and 2015, in developed and developing countries respectively
1999	Beijing Amendment	Tighter controls on HCFC production and marketing
2015	Paris Agreement	Proposed an early freeze date to reduce the damage caused by refrigerants but this was not accepted by all countries Formulation of a long-term low greenhouse gas emission development strategy ("Long-term Strategy")
2016	Kigali Amendment to the Montreal Protocol	Phase-down definition of hydrofluorocarbons (HFCs) due to their high GWP value

Halogenated refrigerants, such as CFCs, HCFCs, and HFCs, are chemical compounds obtained from methane and ethane hydrocarbons by replacing hydrogen atoms with chlorine and fluorine atoms. If the hydrogen atoms are replaced by a halocarbon, it is fully halogenated. When halogenated refrigerants are leaked from equipment during operation or by accident, they contribute to the depletion of the ozone layer and to global warming [4].

Although leakage is usually in small quantities, it is a major source of greenhouse gas (GHG) emissions due to the high GWP of these refrigerants. Moreover, refrigerant released from equipment leads to insufficient system charge and negatively affects the performance of the equipment, resulting in high energy consumption. On the other hand, HFCs contain no chlorine or bromine, but are greenhouse gases that affect the overall temperature of the earth's surface. In short, all these refrigerants contribute significantly to environmental impact and climate change. To effectively meet global environmental issues, all these refrigerants need to be replaced by others with reduced ODP and GWP [1]. In addition, the performance of heat exchangers must be improved to increase efficiency and therefore reduce the indirect emissions of GHG, associated with the energy consumption of the refrigeration systems. One of the alternatives is to replace these halogenated refrigerants with natural refrigerants, such as hydrocarbons (HCs) [1].

1.3. Substitution Strategies

As a result of the Montreal Protocol, CFC production was completely eliminated in developed countries in 1996 and in 2010 in developing countries, consequently, CFCs have been replaced by less harmful HCFC refrigerants. HCFCs are expected to be completely eliminated by the end of 2030 in developed countries and by 2040 in developing countries [3]. Developed countries then started using HFCs, which have no impact on the ozone layer but still have high GWP. Proposals to decrease HFCs are also being discussed under the Montreal Protocol [1]. Countries have generally been aggressive and effective in implementing protocols and their subsequent amendments to slow and reverse the consequences of the presence of refrigerants with high ODP, specifically those containing chlorine and bromine, in the stratosphere [36].

To achieve the desired effect, protocols have been issued over the years, namely in 2006, 2009, and 2014, in which, although the articles have changed slightly, the scope is the same. They all have, without exception, the objective of phasing out refrigerants with a harmful effect on the ozone layer. Regulation 842/2006 of the European Parliament and of the Council of 17 May 2006 was issued with the aim of "containing, preventing and thereby reducing emissions of the fluorinated greenhouse gases covered by the Kyoto Protocol. It applies to the constant fluorinated greenhouse gases . . . " [37].

Regulation No. 1005/2009 of the European Parliament and of the Council of 16 September 2009 was issued mainly for substances that deplete the ozone layer, the scope of which is related to establishing "rules concerning production, import, export, market placement, recovery, recycling, reclamation and destruction of substances that deplete the ozone layer, the communication of information about these substances and the import, export, placing on the market and use of products and equipment containing or relying on these substances" [38].

Regulation No. 517/2014 of the current European Parliament and of the Council of 16 April and 2014 was issued in order to further protect the environment by reducing emissions of fluorinated greenhouse gases [39]. To this end:

- It establishes rules on the containment, use, recovery, and destruction of fluorinated greenhouse gases and on related ancillary measures;
- It imposes conditions on the placing on the market of specific products and equipment containing, or whose functioning relies upon, fluorinated greenhouse gases;
- It imposes conditions on the specific uses of fluorinated greenhouse gases;
- It establishes quantitative limits on the placing on the market of hydrofluorocarbons.

Regarding the evolution of greenhouse gas emissions in Portugal, and according to the most recent update of the National Inventory of Emissions 2021 (for the year 2019), GHG emissions, without accounting for emissions from land use change and forests (LULUCF), are estimated at about 63.6 Mt CO_2e, representing an increase of about 8.1% compared to 1990 and a decrease of 5.4% compared to 2018. Considering the LULUCF sector, total emissions in 2019 are estimated at 55.8 MtCO_2e, corresponding to a decrease of 7.2% compared to 1990 and a decrease of 7.9% to 2018 [40]. After the rapid growth experienced during the 1990s, national emissions slowed down in the early 2000s, with a subsequent decrease in national emissions, particularly after 2005. These trends largely reflect the evolution of the Portuguese economy, which was characterized by strong growth associated with increased energy demand and mobility in the 1990s, followed by a situation of stagnation and recession, especially in the period 2009–2013. In the following years, there was a reversal of that trend. In 2019, GDP recorded a positive variation of 2.2%, slowing down compared to the previous year in which it grew by 2.8%, but maintaining a growth that has been verified since 2014. Total emissions in 2019 decreased by 5.4% compared to 2018, with this reduction being mostly associated with the "energy industries" sector, which registered a sharp drop of 27.2% compared to 2018, as a result of the higher proportion of renewable energy in the national electricity production, associated with the replacement of coal by natural gas in thermoelectric production, and greater use of electricity imports [41].

Both in Portugal and throughout the European continent, a roadmap is being followed for the transition into a competitive low-carbon economy in 2050. This roadmap has been outlined as an economically advantageous way to achieve the necessary emission reductions in the European Union by 2050. Non-CO_2 emissions, including fluorinated greenhouse gases, but excluding emissions from agriculture, are to be reduced by 72–73% by 2030 and 70–78% by 2050 compared to 1990 levels. Based on the full application of existing Union legislation, emissions in 2030 are projected to be 104 Mt CO_2e, which requires a further decrease of approximately 70 Mt CO_2e. The European Parliament then decreed in the same resolution the need to opt for alternative refrigerants by phasing out hydrofluorocarbons on an international scale also following the Montreal Protocol [41].

1.4. Properties of Alternative Refrigerants

Refrigerants play a key role in the refrigeration cycle, influencing its operation and all equipment in the installation, as they allow the heat formed in the cold zone to be absorbed and transferred to a hot zone (outside environment) through evaporation and condensation processes [42]. The thermodynamic properties of a refrigerant are essential to predict the behavior of a refrigeration system and its performance. Excellent thermodynamic proprieties involve a boiling point just below ambient temperature, a critical temperature above ambient temperature, a high normal boiling point, and a high heat of vaporization [4]. There is no refrigerant that gathers all of these desirable properties, this means that when a certain fluid is applied in a certain type of refrigeration installation, it is not always recommended for use in another, even if it is equivalent. The perfect refrigerant is the one that brings together the greatest possible number of qualities, relative to a given purpose and objective [42].

Table 2 specifies a set of proper properties of refrigerants [35].

Table 2. Desirable requisites and properties of refrigerants.

Requirement	Properties
Chemistry	Stable and inert
Health, Safety and Environment	Non-toxic
	Non-flammable
	Low GWP
Thermal	High latent heat
	Critical point and boiling point appropriate for the application
	Low specific heat in vapor state
	Low viscosity
	High thermal conductivity
Others	Reasonable solubility/miscibility with lubricants
	Low melting point
	Easy leak detection
	Low cost

It is a very long list of qualities and none of the refrigerants can be considered ideal and adaptable to all applications. However, special attention needs to be paid to the selection of the most sustainable refrigerant for a given application based on an overall assessment [43]. It is crucial to raise awareness and consciousness for the use of environmentally friendly refrigerants, such as hydrocarbons (HCs), hydro-fluorophenolines (HFO), R744 (carbon dioxide) and R717 (ammonia), as alternatives so that it may be possible to reduce ozone depletion and global warming, and so making refrigeration systems using these refrigerants futureproof. Within these refrigerants, natural refrigerants stand out for the lower environmental impacts that they have and for being more appropriate within the perspective of sustainable technological development [1].

According to the laws established in the European Parliament regarding bans on certain refrigerants in the coming years, as of 2020 R404A will no longer be used in new units and facilities in the European Union and, from that date, facilities may not be loaded with more than 10.2 kg of R404A. In recent years, a range of alternative HFC blends to R404A has emerged, such as R407A, R407F, R442A, etc., all with corresponding trade names. From 2022 onwards, a new F-gas regulation prohibits the use of HFCs in refrigerated cabinets and centralized installations of more than 40 kW [44].

2. Materials and Methods

In order to carry out the development of the computational tool, there is a prior need to characterize in detail the refrigerants in question, analyzing those which are abolished, those which will have the same fate in the near future and finally those alternative refrigerants with reduced GWP and high sustainability. Always keeping in mind the legislation imposed by the European Commission which, over the years, has adopted measures in order to progressively eliminate the production and emission of greenhouse gases and to protect our planet.

2.1. Materials

Many refrigerants have been phased out and those with significant GWP not yet phased out will eventually exit the market in accordance with EU regulations. However, companies still using such refrigerants need to change the refrigerants in their plants and industrial processes soon to meet regulations. To do so, they will have to use refrigerants with low or zero GWP. According to Annex IV of Regulation N°517/2014 issued in 2014, and which is still in force, alternative refrigerants that appeal to sustainability and could be used in industrial and commercial refrigeration processes are as follows:

- R-1234ze (hydrofluorophelines);
- R-170 (Ethane);
- R-290 (Propane);
- R-600a (Isobutane);
- R-717 (Ammonia);
- R-744 (Carbon Dioxide);
- R-1150 (Ethylene);
- R-1270 (Propylene).

Although there is no exact formula when choosing a refrigerant, there are some details that should be considered when making the decision, so that it is possible to acquire the ideal option for a specific case. Therefore, the following factors should be considered in the decision-making process [45]:

- Availability;
- Cost-benefit;
- Quality;
- Safety.

Since the objective of this study culminates with the development of a decision support tool for the consumer for a refrigerant that appeals to sustainability, the technical and thermodynamic data must be known, described, and presented. Next, Table 3 presents the various characteristics of each of these alternative refrigerants that will serve as a basis for the decision system in order to optimize the process of selecting the “ideal” refrigerant for companies in the sector.

Table 3. Operating conditions for alternative and/or sustainable refrigerants.

	Refrigeration			
Refrigerant	**Very Low Temperature**	**Low Temperature**	**Medium Temperature**	**High Temperature**
R-1234ze			✓	✓
R-170	✓	✓		
R-290		✓	✓	✓
R-600a			✓	✓
R-717		✓	✓	✓
R-744		✓	✓	✓
R-1150	✓	✓		
R-1270		✓	✓	✓

Once we have gathered the properties of the coolants that are about to be accepted by companies (consumers) in terms of safety, quality, cost-effectiveness, availability, thermodynamic characteristics, and their contribution to sustainability, we can build a decision support tool that will report the best possible choice for the user, always considering guidelines and needs to maximize satisfaction.

In summary, when comparatively analyzing the refrigerants based on the characteristics and thermodynamic properties that are described in Tables 3 and 4, characteristics must be taken into account in order for the decision support tool to realize the desired goal. This goal should culminate in the selection of the ideal refrigerant for the user in question, based on their economic and financial guidelines and on issues of energy efficiency, cooling capacity, availability of the refrigerant and on the refrigerant's contribution to sustainability.

2.2. Methods

The tool was developed in Excel with the aim of making it accessible to the user insofar as all the operations for the user will be deductive and simple and will allow them to reach a conclusion in a few steps, all of them justified based on user choices, preferences, and guidelines. Figure 1 shows the user interface, which, after the fields are filled in, offers a recommendation of the ideal refrigerant, giving three options in descending order of priority. The decision support system then consists of three parts. The first part requires the identification of the user, the company, and role. The second part consists of a questionnaire with the following questions:

- Do you use any of these old refrigerants?
- Regarding the operating temperature, what do you want?
- Which lubricating oil do you use?
- How concerned are you about the cost/benefit of replacing the refrigerant?
- What is your concern regarding the quality of operation when replacing the refrigerant?
- What is your concern regarding the safety of refrigerant replacement?
- What is your concern regarding availability of refrigerant replacement?
- What is your concern regarding the environmental impact of refrigerant replacement?

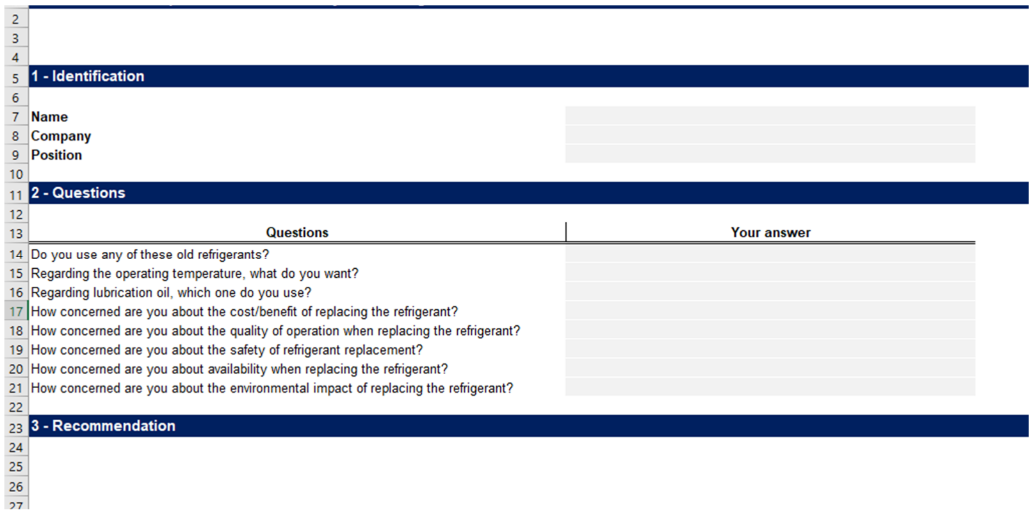

Figure 1. Decision support tool layout.

To make it simple to answer the questions imposed by the program, there are drop-down boxes in the cells where the answers are, in which all the possibilities are presented to facilitate the filling-in process, as shown in Figure 2.

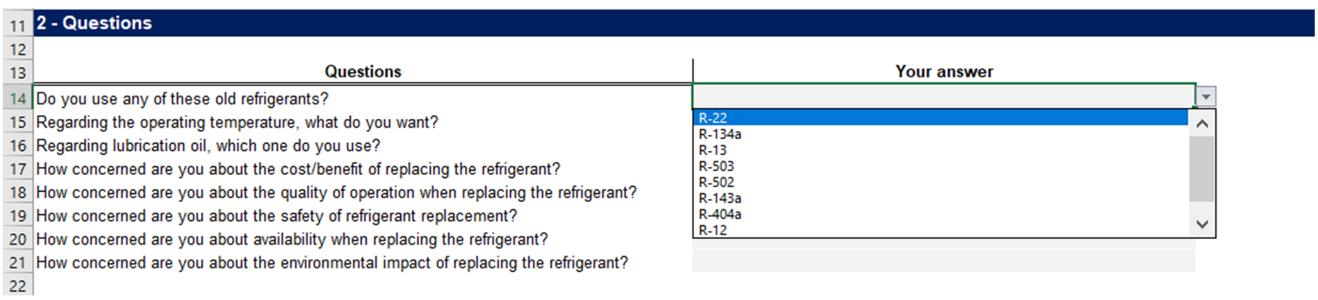

Figure 2. Example of dropdown boxes in the tool.

Table 4. Thermodynamic properties of alternative and/or sustainable refrigerants.

	ODP	GWP	GWP (100)	Boiling Point 1atm (°C)	Critical Temperature (°C)	Critical Pressure (MPa)	Compatible Lubricants	Toxicity	Flammability	Security	Biodegradable	Cost of the Refrigerant	Cost of Installations	Cooling Capacity	Efficiency	Availability
R-1234ze	0	6	6	−19	109.4	3.60	POE	No	Yes	A2	Yes	High	Medium	Medium	Medium	Reduced
R-170	0	6	6	−89	32.3	4.87	Mineral/AB/POE	No	Yes	A3	Yes	Reduced	High	Medium	High	High
R-290	0	3	3	−42	97.0	4.30	Mineral/AB/POE	No	Yes	A3	Yes	Reduced	High	Medium	High	High
R-600a	0	3	3	−12	135.0	3.60	Mineral/AB/POE	No	Yes	A3	Yes	Reduced	High	Medium	High	High
R-717	0	0	0	−33	132.0	11.30	Mineral	Yes	Yes	B2	Yes	Reduced	Very High	Medium	High	Very High
R-744	0	1	1	−57	31.0	7.40	POE	No	No	A1	Yes	Reduced	Very High	Very High	Medium	Very High
R-1150	0	4	4	−104	9.2	50.00	Mineral/AB/POE	No	Yes	A3	Yes	Reduced	High	Medium	High	High
R-1270	0	2	2	−48	91.0	46.00	Mineral/AB/POE	No	Yes	A3	Yes	Reduced	High	Medium	High	High

The third and last stage is associated with the recommendations provided, based on all the data, the restrictions, and conditions regarding alternative refrigerants. The tool provides the user with recommendations, sorting three refrigerant options by priority of use. The answer is given based on an objective function that analyses the answers given by the user to the eight questions, transforming the qualitative answers into data and numerical coefficients. The result is also dependent on restrictions associated with the old refrigerants (making the answer almost straightforward), the lubricating oils used and the temperature conditions in the cooling process.

The decision support tool boils down to the application of a function that depends on five coefficients (varying according to the user's answers to the last five questions), constraints, and data that result from the constant properties of each of the refrigerants, as given by Equation (1). This equation is calculated for each of the eight alternative refrigerants, with higher results meaning more adequate refrigerants for the application in question, considering the user's preferences. Finally, the top three coolants are presented to the user in order of recommendation.

$$\mathrm{R} = (C_1 \times x_1 + C_2 \times x_2 + C_3 \times x_3 + C_4 \times x_4 + C_5 \times x_5) \times y_1 \times y_2 \times y_3 \tag{1}$$

The expression can be divided into three parts in which:

- C's—coefficients;
- X's—refrigerant properties;
- Y's—constraints of the refrigerants.

2.2.1. Coefficients

When the user answers the last five questions that determine the value of the coefficients C_1, C_2, C_3, C_4, and C_5, he introduces qualitative values that correspond to the expressions: "None"; "Reduced"; "Medium"; "High", and "Very High", that is, the coefficients do not correspond to constant values, as they are altered according to the preferences and concerns of those who answer the questionnaire. Since these values are qualitative, there is a need to transform them into numerical data to enable the resolution of the objective function.

This transformation is based on the study conducted by [46], in which the author aims to transform qualitative dependent variables into quantitative ones to culminate with an equivalent conclusion. To achieve such an effect, a sensory analysis is performed through the responses given by consumers. The researcher imposes a certain set of questions on consumers by means of a computational tool from which qualitative data essential for solving the problem is extracted.

After the resolution of the questionnaire by the user, Fonseca [46] processes the data into quantitative values, attributing to each of the answers a value in the scale of 1 to 5 in which 1 corresponds to the worst and 5 to the best result. This way it is possible to express the responses graphically, where they were found to grow linearly. Although this is a study with a different context, the procedure to convert qualitative answers into quantitative values can be adapted to solve an objective function to transmit the best recommendation for users.

Similar to the study presented, the developed decision support tool imposes on the user common questions and a set of possible answers (qualitative data), which will be transformed into a scale in which the values will be separated by the same interval (quantitative data). Following this context, to make Equation (1) possible, a scale from 0 to 1 is attributed as shown in Table 5, to transform qualitative data into quantitative data to quantify the coefficients related to cost/benefit (C_1), operation performance (C_2), safety (C_3), availability (C_4) and environmental impact (C_5). The higher the quantitative value associated with the coefficients, the greater the user's concern in this regard.

Table 5. Scale defined for the objective function coefficients.

Qualitative Value (User Response)	Quantitative Value (User Response)
None	0.00
Reduced	0.25
Medium	0.50
High	0.75
Very High	1.00

2.2.2. Refrigerant Properties

The data referring to the alternative refrigerants that were used in the tool are described and qualitatively characterized in Table 5. These properties are presented as constant values in the objective function which will be multiplied by the previously mentioned coefficients. The characteristics of the refrigerants that serve as analysis and that influence the function are the following:

- Cost of both the refrigerant and the installations;
- Refrigeration quality, analyzing its efficiency and capacity;
- Safety;
- Availability of human and material resources;
- Environmental impact addressing the GWP (100 years).

Similar to the coefficients, the properties to be used in the objective function were transformed into numerical values through a scale set from 0 to 1. However, for the different properties, different scales were considered. Since the objective of the tool is to optimize the objective function to find out which are the best refrigerants, it is necessary to pay special attention to aspects such as cost and environmental impact. In these cases, the higher their qualitative value (described in Table 5) the lower their respective value in numerical terms must be. Thus, the scales were defined as shown in Table 6.

Table 6. Scale defined for the objective function properties.

Quantitative Value	Value (Cost)	Value (Quality of Operation)	Value (Safety)	Value (Availability)
Null	1.00–0.00 = 1.00	0.00	0.00	0.00
Reduced	1.00–0.25 = 0.25	0.25	0.25	0.25
Medium	1.00–0.50 = 0.50	0.50	0.50	0.50
High	1.00–0.75 = 0.75	0.75	0.75	0.75
Very High	1.00–1.00 = 0.00	1.00	1.00	1.00

Finally, the property that addresses the environmental impact, despite being described in Table 4 in numerical terms, was entitled to a specific scale, because, as previously indicated, the higher this factor, the lower must be its value to be used in the objective function. Thus, in this way the scale for the GWP data will be based in Equation (2), wherein the coefficient x_5 refers to the value associated with the GWP of each of the alternative refrigerants.

$$1 - \left(\frac{x_5}{10}\right) \tag{2}$$

2.2.3. Restriction of the Refrigerants

In last place are the refrigerant restrictions that concern the following factors:

- Possibility of directly replacing the refrigerant;
- Temperature conditions used in the refrigeration process;
- Type of lubricant.

These three answers are limiting factors for the result, as they narrow down the range of possibilities for the suggested replacement refrigerant.

As far as the restriction of old refrigerants is concerned, it must be considered that the eight alternative refrigerants being studied and analyzed in this tool can be direct replacements. For the first question, the user has nine possible answers, eight refrigerants that will be abolished in the future, and none of the above.

Depending on the answers given, the tool will direct the objective function in a certain direction. The relationships between the nine possible answers to the first question and the replacement refrigerants are as follows:

- R-22 => R-290, R-600a, R-717, R-744;
- R-134a => R-1234ze, R-600a, R-717, R-744;
- R-13 => R-170, R-1150;
- R-503 => R-170, R-1150;
- R-502 => R-1270;
- R-143a => R-1270;
- R-404a => R-744;
- R-12 => R-600a;
- None => R-1234ze, R-170, R-290, R-600a, R-717, R-744, R-1150, R-1270.

Once again, the answers are presented in qualitative format, and once again there is the need to transform them into numerical data. In this case it is not a scale, but if and else statements that are applied. The if statement is known as the decision statement because it allows for a certain condition or expression. The code inside the if function is executed if the condition is true. However, the code inside the if function is disregarded if the condition is false [47]. In this way, results can assume two logical values, 1 if true and 0 if false. As regards the tool itself, and more specifically the objective function, whenever the user selects an answer, it will assume the logical value of 1. Therefore, in this case, the value of y1 of equation 1 will be quantified. For instance, when the user mentions using R-22 in their facilities, the objective function will only return 1 for refrigerants R-290, R-600a, R-717, and R-744 (y_1 = 1), since the others will be 0 as the result of false conditions, thus shortening the range of possibilities for the recommended refrigerant.

Regarding the temperature range in the refrigeration process, this was established based on Table 3, whereby the user, when answering the second question, defines the operating temperatures and consequently restricts the refrigerants that do not operate on those conditions. Following this context, and once again using the same type of programming established in the previous constraint, should the user enter the answer in the respective dropdown box, it will assume the logical value of 1 if the temperatures are within the range or 0 otherwise; this will be the parameter y_2 of Equation (1). Depending on the answers provided to the tool, the objective function will be directed in a particular direction. Therefore, the relationships between the four possible answers to the second question and the substitution refrigerants are as follows:

- Very Low => R-170, R-1150;
- Low => R-290, R-717, R-744, R-1270;
- Medium => R-1234ze, R-290, R-600a, R-717, R-744, R-1270;
- High => R-1234ze, R-290, R-600a, R-717, R-744, R-1270.

Basically, if the user is given the example of assuming he operates in average cooling temperature conditions, the objective function will be equated only for refrigerants R-1234ze, R-290, R-600a, R-717, R-744, and R-1270, since y_2 = 1 and the others are null, again reducing the set of possible recommendations.

As per the previous constraints, the type of lubricant used is converted to a quantitative value by the same methodology, further reducing the set of possible answers. Once an option in the respective dropdown box is selected, the answer will be associated with the logical value of 1, automatically quantifying the parameter y_3. Depending on the answers provided to the tool, the objective function will be directed in a particular direction.

Therefore, the relationships between the three possible answers to the third question and the replacement refrigerants are as follows:

- Mineral => R-170, R-290, R-600a, R-717, R-1150, R-1270;
- AB => R-170, R-290, R-600a, R-1150, R-1270;
- POE => R-1234ze, R-170, R-290, R-600a, R-744, R-1150, R-1270.

In other words, if by chance the user shows the need to use mineral oil as a lubricant in their refrigeration plants, there will only be compatibility with the R-170, R-290, R-600a, R-717, R-1150, and R-1270 refrigerants, insofar as the objective function will only be considered for these, because their $y_3 = 1$, reducing the set of possible recommendations for replacement refrigerant by the third and final time. Once descriptions of all the components of the tool have been made and all the calculations that culminate in the final recommendation of the replacement refrigerant for the company have been shown, the tool was applied in three case studies for a better understanding of how it works and how it helps users. As the users access the tool and fill out the questionnaire step by step, the final answers associated with solving the objective function are determined and presented, depending on the user's preferences, values, and needs.

3. Case Studies

Over the years, compliance with legislation by companies in the industrial refrigeration sector has led them (once banned from using certain refrigerants) to replace the outlawed refrigerants with others that have similar performance and energy efficiency. However, after contact with the sector, it is possible to verify that thy are not yet aware of the importance of sustainability, so that adoption of the refrigerants referred to as alternative and/or sustainable mentioned in Table 4 will soon be the solution for several companies in their refrigeration processes. One of the sectors that proves this fact is the Portuguese agri-food industry, which in 2016 was limited to a set of refrigerants with high GWP. The refrigerants R-32, R-404a, R-22, R-422, and R-449 represent a large share in the percentage distribution of refrigerant used in Portugal. These refrigerants will be discontinued, giving rise to concern for the replacement of refrigerants by other environmentally friendly ones [48]. Awareness of and sensitivity to the use of more ecological refrigerants will become crucial to make refrigeration systems that use these refrigerants futureproof, since they present a minimum environmental impact and because they are governed by the perspective of sustainable and efficient technological development and growth. To consolidate what is presented above, companies in the sector were questioned and three practical cases were obtained to be studied and applied in the decision support tool so that it might give the best possible recommendation to the companies and transmit the best solutions considering the situation they are facing. Therefore, the cases to be studied, analyzed, and applied in the tool concern the search for alternative refrigerants that will replace R-449, R-422 and R-32, based on the preferences and guidelines of the companies themselves, which, once they provide information for the tool in Excel, will obtained feasible answers and recommendations.

3.1. Case Study One

On contacting the refrigeration company, the information was obtained that the refrigerant in use is R-449, which is characterized by its low environmental impact and low GWP compared to HFCs. Its thermodynamic properties are balanced, it is used in low and medium temperature conditions in commercial and industrial applications and the lubricating oil used in the installations is miscible with POE oils [49]. These coolant data are key to obtaining and transmitting a recommendation from the tool to the user. Firstly, to gather all the possible conditions for solving the problem, the company was asked in the DSS about the refrigerant used to date (in this case R-449), the temperature conditions (averages) and the lubricating oil (POE). Following these first three questions, the parameters associated with the constraints were quantified as shown in Figure 3.

10		
11	**2 - Questions**	
12		
13	**Questions**	**Your answer**
14	Do you use any of these old refrigerants?	R-449
15	Regarding the operating temperature, what do you want?	Medium
16	Regarding lubrication oil, which one do you use?	POE

Figure 3. Filling in the parameters of the restrictions in the case of R-449.

The next and last step before the recommendation is resolved boils down to five questions imposed on the user of the tool about their degree of concern for:

- Cost/Benefit;
- Quality of Operation;
- Safety;
- Availability;
- Environmental Impact.

Following these questions, which are again based solely on the user's opinion in the context of the refrigeration process used in their company, the following answers were obtained in the respective Excel cells as shown in Figure 4. The objective function coefficients were thus quantified, giving rise to the single solution for this case, replacement by R-744 (carbon dioxide).

17	How concerned are you about the cost/benefit of replacing the refrigerant?	High
18	How concerned are you about the quality of operation when replacing the refrigerant?	Very High
19	How concerned are you about the safety of refrigerant replacement?	Medium
20	How concerned are you about availability when replacing the refrigerant?	Medium
21	How concerned are you about the environmental impact of replacing the refrigerant?	Medium
22		
23	**3 - Recommendation**	
24		
25	**1st**	R-744
26		

Figure 4. Solution of practical case one using average temperatures.

According to the data collected from this company, there is extreme concern about the replacement of its coolant by another with excellent properties in terms of capacity and efficiency in refrigeration. Furthermore, there is concern that this does not lead the company to spend large sums of money on the acquisition of the coolant or on changing facilities. Regarding the other factors, no major concerns were presented, giving rise to the answer presented. In case the company, under its conditions, wanted low temperatures in the cooling process, with the same responses to the other parameters, the recommendation would end up being the same, as shown in Figure 5.

11	**2 - Questions**	
12		
13	**Questions**	**Your answer**
14	Do you use any of these old refrigerants?	R-449
15	Regarding the operating temperature, what do you want?	Medium
16	Regarding lubrication oil, which one do you use?	POE
17	How concerned are you about the cost/benefit of replacing the refrigerant?	High
18	How concerned are you about the quality of operation when replacing the refrigerant?	Very High
19	How concerned are you about the safety of refrigerant replacement?	Medium
20	How concerned are you about availability when replacing the refrigerant?	Medium
21	How concerned are you about the environmental impact of replacing the refrigerant?	Medium
22		
23	**3 - Recommendation**	
24		
25	**1st**	R-744
26		
27		

Figure 5. Solution for practical case one using low temperatures.

In short, the R-744 (carbon dioxide) refrigerant was selected as the recommendation for this company, as it ends up being its direct substitute, given that out of the eight possibilities it is the only one with similar thermodynamic properties, temperature conditions and lubricating oil as the R-449, despite the potential need to change the refrigeration installation (compressors, piping, valves, etc.).

3.2. Case Study Two

The procedure is the same as in the first practical case, differing only in the refrigerant used and to be changed by the company, designated R-422. This is characterized by its application in low, medium, and high temperature conditions in refrigeration (industrial, commercial, and domestic) and conditioning (residential and commercial) applications. Furthermore, it is highly compatible with both traditional and new generation lubricants and is therefore miscible with AB, mineral and POE oils [50]. In contrast to the first case study where the recommended refrigerant was the same for the two existing possibilities, in this second case study the company in its replacement process has nine different possibilities as it can choose between three temperature conditions and three types of lubricating oil. The company was also asked about their level of concern regarding cost, quality of operation, safety, availability, and environmental impact when replacing the coolant whose answers are shown in Figure 6.

17	How concerned are you about the cost/benefit of replacing the refrigerant?	Very High
18	How concerned are you about the quality of operation when replacing the refrigerant?	Very High
19	How concerned are you about the safety of refrigerant replacement?	Medium
20	How concerned are you about availability when replacing the refrigerant?	Medium
21	How concerned are you about the environmental impact of replacing the refrigerant?	Medium
22		

Figure 6. Filling in the parameters of the restrictions in the case of R-422.

Subsequently, the dropdown boxes for temperature conditions and lubrication oils were also filled in, and, depending on the data provided by the user, different recommendations were obtained when solving the objective function by the support system. This way, the company has at its disposal a range of possible solutions described in a decision tree as shown in Figure 7.

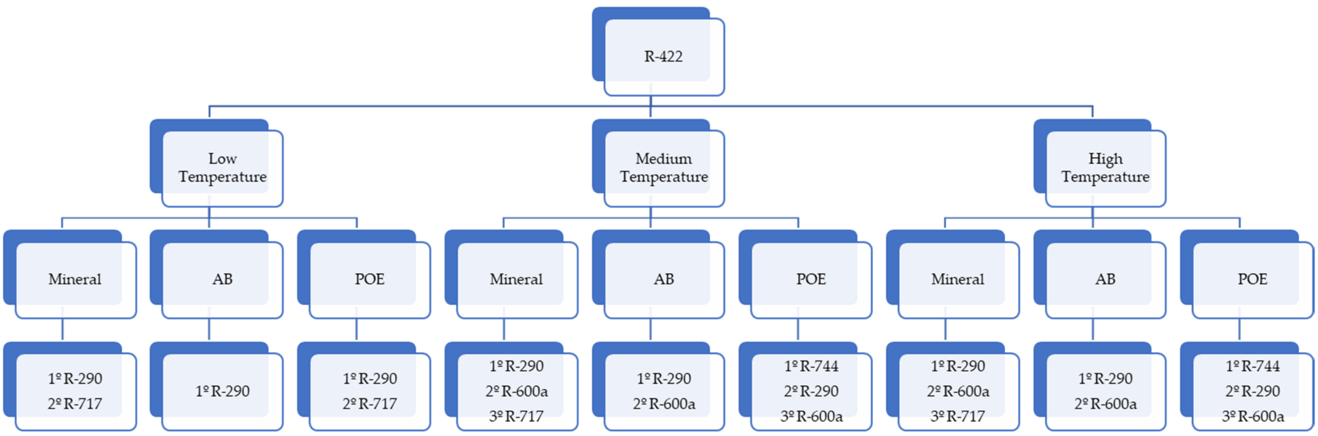

Figure 7. Decision tree for R-422 refrigerant replacement possibilities.

Depending on the company's intentions regarding the temperature conditions and the oil used for lubricating the installations, it can be seen from Figure 7 that the recommendations vary and, thanks to the versatility of the tool itself, the three best alternative and/or most sustainable refrigerants for the specific case in question are provided, whenever possible, considering the various constraints presented. When analyzing the results shown in Figure 7, one can see a trend towards the recommendation of R-290 (propane), regardless of operating temperature and lubricating oils.

3.3. Case Study Three

Finally, another company in the industrial refrigeration sector was contacted and questioned about the replacement of refrigerants, once again registering the sector's lack of awareness on the subject. The company in question still uses the R-32 refrigerant, which will also be discontinued in the future. It is characterized by being miscible with POE lubricant, is used in low-temperature conditions, and has a relatively high GWP of 550, contributing to ozone layer depletion [51]. Again, the computational tool was presented, and the methodology was the same as in the previous cases, with the answers to the questions imposed by DSS represented in Figure 8.

11	**2 - Questions**	
12		
13	**Questions**	**Your answer**
14	Do you use any of these old refrigerants?	R-32
15	Regarding the operating temperature, what do you want?	Low
16	Regarding lubrication oil, which one do you use?	POE
17	How concerned are you about the cost/benefit of replacing the refrigerant?	Very High
18	How concerned are you about the quality of operation when replacing the refrigerant?	Very High
19	How concerned are you about the safety of refrigerant replacement?	Medium
20	How concerned are you about availability when replacing the refrigerant?	Medium
21	How concerned are you about the environmental impact of replacing the refrigerant?	Very High
22		
23	**3 - Recommendation**	
24		
25	1st	R-290

Figure 8. Answers from the company for the replacement of R-32.

Similar to practical cases one and two, this company is essentially concerned with the costs involved in purchasing the refrigerant and changing the refrigeration equipment, as well as with maximizing cooling capacity and efficiency. However, since the company is still using a refrigerant that will be discontinued in the future, there is a need to replace the refrigerant with one with excellent thermodynamic properties, temperature conditions, similar or compatible lubricant, and low environmental impact. For this purpose, none is better than R-290 (propane), because, according to DSS itself, this refrigerant is the direct substitute for R-32, given the characteristics of both.

In conclusion, the tool has been successfully applied in the three cases studied, thanks to its flexibility and accessibility for the user. In addition to helping solve some of the problems faced by companies during the phase-out of GWP and ODP refrigerants, the tool has the ability to advise companies on the possibility of imposing other conditions on temperatures and types of oil, always seeking the maximum satisfaction of the user of the DSS, providing them clearly and objectively with all possible recommendations for the future replacement refrigerant.

4. Discussion

Although the tool provides the best recommendation for the user, answering the initial problem with solutions for the specific cases presented by the companies in the sector, it can be improved and optimized. The developed DSS is consistent and flexible throughout its process, transmitting clear and objective answers, being in turn easy to use and understand for the user. However, the decision support system can eventually enhance its parameters considering the following factors: form; quantity; and quality.

After the transformation of qualitative data into quantitative data through specific scales, these are now represented through discrete numerical values. One of the improvement perspectives for the future of DSS is the implementation of continuous data with the purpose of providing even more data for each of the refrigerants, consequently substantiating the answers and recommendations presented for the sustainable refrigerants to be an option for the companies in the sector.

In relation to the amount of data available to the decision support system, for each of the coolants, DSS uses three constraints (condition of the coolants previously used, operation temperature, and type of oil used for lubrication), five coefficients (cost, operation quality, safety, availability, environmental impact) and seven constant data associated to these coefficients to be determined by the user. To increase the flexibility of the tool, to make it more solid and secure in the answers that it provides, this tool can present a possibility of expanding the number of parameters to be used by the objective function, namely the restrictions, coefficients, and the properties inherent to the alternative refrigerants.

Regarding quality, the demonstration of the recommendations to the user can also be improved. Whenever the result is presented, only the names of the sustainable refrigerants to be recommended are displayed (in order). However, this same presentation can be accompanied by a detailed, concise description of the refrigerant in question. For this purpose, a dropdown box could be implemented, similarly to those already presented to the user.

In short, the optimization of these three factors will lead to an increase in the consistency, efficiency, and accuracy of the results of the decision support tool.

5. Conclusions

5.1. General Conclusions

The industrial refrigeration sector has become increasingly focused on the importance of and need to apply safe designs, with appropriate safety devices, in accordance with international safety legislation. Currently, the use of systems containing HFCs implies compliance with emission targets and rules that, in case of non-compliance, are subject to sanctions. These targets and rules aim to contribute to the reduction of global warming.

Over the years and with the implementation of numerous protocols, namely those of Kyoto and Montreal, and in accordance with the agreements imposed, halogenated refrigerants have been progressively eliminated in a move towards sustainability. This move aims to protect the planet from the harmful emissions that culminate in the degradation of the ozone layer and contribute to global warming.

The replacement of refrigerant fluids that are some of the main manmade polluting agents present in the atmosphere—through their contribution to the destruction of the ozone layer and the increase of the greenhouse effect—by others that appear to be less harmful to the environment requires an extensive in-depth study. The study carried out for this research was focused not only on the direct consequences of these refrigerants on the environment, but also on the analysis of the energy and exergetic performance of the refrigerants in general. Following this context, the general study of several alternatives for replacement, in the short and long term, for the most used refrigerants was defined.

For that purpose, during the work, the general aspect of refrigeration was approached, with the presentation of the main techniques used to produce cold, giving special attention to the cycle under study: the vapor compression refrigeration cycle. Subsequently, the general characteristics and properties of refrigerants are discussed, allowing their rapid classification according to the type and family of refrigerant fluid. The main events that have marked the history of the evolution of refrigerants are described, with emphasis on the legislation published in this area.

After the issuing of regulations N° 842/2006, N° 1005/2009, N° 517/2014 by the European Parliament, not only all refrigerants to be eliminated considering their destructive content for the ozone layer, but also alternative refrigerants with zero ODP and reduced GWP were mentioned, thus appealing to the much sought-after sustainability. In turn, the main objective of this work lies essentially on the implementation of these same refrigerants in companies based on a decision support tool, to the extent that users according to their perspectives, values and wishes will have the answer to their future replacement of halogenated refrigerants.

In short, the computational tool involves an Excel database that evaluates both qualitative and quantitative thermodynamic properties associated with an objective function that depends on the constraints of each of the alternative and/or sustainable refrigerants under analysis and the user's answers to the questions imposed on it. This decision support system gives extreme importance to the user's opinion and specific case for the recommendation of a well-suited refrigerant.

5.2. Specific Conclusions

The execution of the DSS depends fundamentally on constant parameters and specific conditions relative to each of the alternative refrigerants that constitute the possible answer for the substitution process. The objective function programmed in the computational tool is equated based on the restrictions and properties associated with the eight fluids under analysis. Depending on the coefficients to be introduced by the user, the decision system will dictate three recommendations by order of relevance. These restrictions and properties, unique to each of the refrigerants, are obtained and determined based on an evaluation of qualitative and quantitative data previously acquired, namely through the comparison of these alternative refrigerants with the halogenated ones already abolished or that will be discontinued in the future. This same scientific research is supported by the literature review carried out. To enable the resolution of the equation, the qualitative data was transformed into quantitative data through regular scales established for all necessary cases.

Although the sustainable refrigerants present excellent thermodynamic properties, reduced cost when compared to HCFCs and present themselves as excellent solutions for industrial cooling process, they show, however, certain ambiguities that require further research with qualitative and quantitative analysis, in order to develop appropriate recommendations. The development of the study and of the tool leads to a specific and not generalized conclusion due to the simple fact that each of the replacement refrigerants is not the ideal solution for all cases, but rather for a specific situation, because although they all have excellent characteristics and properties, they are associated with different operating conditions in the refrigeration process, lubrication oils and in many cases can be the direct replacement refrigerants for the old ones, which were used until then, without the need for major changes in the pre-existing installations.

Author Contributions: Conceptualization, P.D.G.; methodology, P.D.G. and M.L.A.; validation, P.D.G. and M.L.A.; formal analysis, P.D.G., M.L.A. and G.J.; investigation, M.L.A. and G.J.; resources, P.D.G., M.L.A. and G.J.; data curation, M.L.A. and G.J.; writing—original draft preparation, G.J.; writing—review and editing, P.D.G. and M.L.A.; supervision, P.D.G.; project administration, P.D.G.; funding acquisition, P.D.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded as part of the project "PrunusPós—Optimization of processes for the storage, cold conservation, active and/or intelligent packaging and food quality traceability in post-harvested fruit products", project n.° PDR2020-101-031695, Partnership n.°87, initiative n.°175, promoted by PDR 2020 and co-funded by FEADER within Portugal 2020.

Data Availability Statement: More information on the project PrunusPós can be found at https://www.prunuspos.pt/ (accessed on 10 November 2022).

Acknowledgments: This work was supported in part by the Fundação para a Ciência e Tecnologia (FCT) and C-MAST (Centre for Mechanical and Aerospace Science and Technologies), under project UIDB/00151/2020.

Conflicts of Interest: The authors declare no conflict of interest.

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