Chapter

# An Experimental Study of Synthetics and Natural Refrigerants Gases

*Eraldo Cruz dos Santos, Carlisson Azevedo, Caio Macêdo, Carla Azevedo, Raíssa Araújo, Sílvia Soares Gomes, Lana Baia and Yves Alexandrino*

## Abstract

In Brazil, there has been a significant change in the types of refrigerants used in air conditioning and refrigeration systems. This chapter seeks to compare, based on legislation established by the European Parliament and of the Council, which has been understood and obeyed all over the world, the use of F-gas and different types of fluids intended for use in such systems and also discuss the use of natural fluids such as hydrocarbons, ammonia, and carbon dioxide ($CO_2$), in refrigeration or air conditioning systems, considering the characteristics and properties of these types of fluids, such as thermodynamic and psychometric parameters, the global warming potential (GWP), application limits, flammability factor, and performance as refrigerant. Some specific examples of the use of fluids such as R-R290, R-410a, and R-600a, instead of R-22 fluid, will also be discussed. For this purpose, a test bench was developed with an equipment chiller in the Climatization and Thermal Comfort Laboratory—ClimaTConT—of the Federal University of Pará, in order to compare the types of refrigerant fluids, usually used in air conditioning systems, considering the conditions, evaluating the possibilities of reuse of these fluids, without performance losses, in significant values, always seeking the reduction of the use of synthetic fluids, which are more aggressive to nature, generating pollution and degradation to local environments.

**Keywords:** F-gas, hydrocarbons, natural refrigerants, synthetic fluids, chiller bench

## 1. Introduction

When it comes to environmental pollution, the first idea is the one caused by the operation of a motor vehicle, consuming a fossil fuel, nonrenewable, or the irregular disposal of garbage in areas near urban centers. However, refrigeration and air conditioning systems are highly polluting the local environment, because these systems use refrigerants with specific characteristics, and some of their components can react with the ozone layer or be released into the atmosphere, which is equivalent to a few hundred or thousands of times the emission of $CO_2$.

A great example is a cooling system that works with R-404A refrigerant, which is a synthetic fluid. Under normal operating conditions, this system has no ozone-depleting chemical component. But, if an approximately 10 kg of this refrigerant leaks into the atmosphere, the contribution to the greenhouse effect/global warming will be equivalent to the emission of 40 tons of $CO_2$ [1, 2].

In Brazil, all refrigerants, currently available on the market, are the basis of HCFC and HFC, but these fluids have their days counted for their discontinuation given the contribution to environmental pollution and the action of the Montreal and Kyoto Protocols that made societies aware of the harmful action of these products when released into the local environment [1–3].

Due to these prohibitions imposed by world laws and protocols, the air conditioning and refrigeration market in Brazil aims solutions for the use of refrigerants, which vary between synthetic fluids that has a high value of global warming potential (GWP) and natural fluids, which has a lower value of global warming potential (GWP) than the synthetic ones. However, natural fluids have some impasses that are directly related to their composition, such as ammonia, which has excellent thermodynamic qualities, but it is a highly toxic fluid. The $CO_2$ itself is another fluid that can be used in refrigeration systems, but as a downside, it works under high pressures, close to 100 bar. The hydrocarbon refrigerants, which are better known as R-290 and R-600a, are also excellent thermodynamic fluids, but these fluids are highly flammable and have their maximum amount to be applied to limited climate systems for security reasons [4–10].

In order to encourage the use of natural fluids in air conditioning and refrigeration systems, some laws and protocols have been created in the world to regulate, standardize, and inform mainly about safety issues related to the use of these types of refrigerants [4–6, 11]. From the point of view of use, there are scholarly works in air conditioning and refrigeration systems produced by companies that already work with some natural fluids and have great yields, both on the issue of capacity and cooling efficiency, as the issue of energy consumption [12, 13].

The present work intends to develop a test bench so that reliable data on synthetic and natural fluids can be obtained. In the experimental stage, the refrigerants R-22 and R-290 were used. Nevertheless, in the simulation stage, some data were taken of Danfoss software in order to evaluate the thermodynamic, psychometric, and electric parameters, the ozone depletion potential (ODP), the GWP, the working pressure limits, and the local conditions. Hence, it has become possible to indicate the ideal fluid that should operate in a safe condition and with less aggressive potential to the environment.

## 2. Refrigerant legislation

With the discoveries of the harmful effects of synthetic refrigerants, various organizations and institutions around the world have begun to work together to develop methods for control and to standardize and also to develop some kind of awareness about the use of these refrigerants as a working fluid in refrigeration and air conditioning systems.

Protocols were created first to fight the fluids that negatively affect the ozone layer [1] and later to fight against the use of synthetic fluids, which are massive contributors to the greenhouse effect. Since the 1970s, some scientists have proven that there is a direct relationship between ozone depletion and the use of CFC (fluorine and chlorine-based hydrocarbons) compounds by industry, not only as refrigerants fluids but as aerosol propellants and foam blowing agents. According to photochemical reaction models involving ultraviolet irradiation, the depletion of the ozone layer is the result of a chain effect promoted by chlorine (or bromine) atoms [2].

### 2.1 Montreal Protocol

The Montreal Protocol is an international agreement developed by the United Nations, focusing on the environment. This protocol aims at the gradual reduction to the full transition of synthetic fluids with high ozone layer depletion potential by other types of environmentally friendly refrigerants. Since its inception in 1987, data collection through 2014 indicates that, with the Montreal Protocol, it has been possible to reduce the supply of ozone-depleting fluids by 98%, as most of this amount was used in cooling and air conditioning systems [1]. In European countries, in October 2016, HFC-lowering steps were agreed and became part of the Montreal Protocol, which entered into force on January 2019, pending ratification by 20 states, which appears to be a formality at the moment.

In the Montreal Protocol, in addition to the mechanisms for the gradual reduction and elimination of refrigerant use discussed above, many governments are applying tax measures to reduce the consumption of high potential global warming refrigerants, such as the creation of weighted taxes according to potential for the use of these products.

The production and use of HFCs such as R-32, R-125, R-134a, and R-143A and their mixtures (R-404, R-407C and R-410A) are not regulated by the Montreal Protocol but must be country-specific regulations made individually, so countries such as Spain, Denmark, Norway, and Sweden have imposed taxes on the use of HFCs in their air conditioning and refrigeration systems to reduce their use and control.

### 2.2 Kyoto Protocol

Like the Montreal Protocol, the Kyoto Protocol is an international agreement, managed by the United Nations, that seeks to reduce pollutant emissions into the atmosphere. It is known that the last 150 years of industrial activities related to developed countries generated an increase in emissions and strengthening the greenhouse effect [2].

This protocol was prepared in Kyoto, Japan, in 1997 and, after adjustments, began to be implemented in 2005 and had its first stage, known as the first period, accounted for between 2001 and 2012. During that period 37 countries industrialized, and the European community have if pledged to reduce pollutant emissions by 5% compared to the 1990s. In the second period, in 2012 there was a meeting between the leaders of the countries that signed the Kyoto Protocol and the United Nations. At this meeting it was agreed that between 2013 and 2020 countries would continue to work on reducing emissions by 18% of the values stipulated in the 1990s [2].

### 2.3 F-gas regulation

The 517/2014 Law of the European Parliament and of the Council became known as regulating the use of fluorine-containing gases, known as F-gas, with the main objective of reducing emissions of gases with high potential for the destruction of the ozone layer, because they contribute to the greenhouse effect. Brazil is a signatory to this Law, which defines the rules on storage, recovery of synthetic fluids, as well as conditioning the trade of equipment and the refrigerants themselves in use in the Brazilian territory and also sets the practical limits on the use of F-gas in Brazil [3–5].

The first highlight of 517/2014 Law is the prohibition of the intentional release of any amount of F-gas into the atmosphere; however, it does not cite any criminal implication on anyone caught doing the act of this way.

| Equipment | | Prohibition date |
|---|---|---|
| Household freezers and refrigerators with HFC refrigerant and greater than 150 GWP | | January 1, 2015 |
| Cold rooms for commercial use | HFC with GWP 2500+ | January 1, 2020 |
| | HFC with GWP 150+ | January 1, 2022 |
| Fixed refrigeration equipment with HFC refrigerant and with GWP greater than 2500 | | January 1, 2020 |
| Commercial central cooling system with a capacity of 40 kW or higher that works with GWP 150+ | | January 1, 2022 |
| Mobile residential air conditioning equipment using HFC refrigerant with GWP 150+ | | January 1, 2020 |
| Fixed residential air conditioners with load less than 3 kg and GWP 750+ | | January 1, 2025 |
| *Source: Regulation (EU) N°. 517/2014 [5].* | | |

**Table 1.**
*Equipment with dates for prohibiting the use of refrigerants.*

The Article 4 of this Law establishes that stationary refrigeration equipment, air conditioners, and heat pumps must have an operator that checks for leakage points on the equipment according to the equivalent amount of $CO_2$ in refrigerant charge where 5 or more equivalent tons of $CO_2$ should be checked at least once a year. For equipment with an equivalent load above 50 tons of $CO_2$, this check should be performed every 6 months. Systems with loads over 500 tons equivalent must be checked every 3 months.

Article 13 cites restrictions on the use of F-gas and imposes that from January 2020, the use of F-gas with GWP equal or greater than 2500 shall be prohibited in refrigeration systems with an equivalent load of 40 tons of $CO_2$ or more. Nevertheless, if the fluid used in the system can be recovered, reprocessed, and reused, it will have its utility extended until January 1, 2030.

**Table 1** shows some air conditioning and refrigeration equipment with their respective prohibition dates for their refrigerants.

The questions of the regulation of refrigerants is the application of control mechanisms over the use and disposal of F-gas in each country in order to comply with the dates set out in **Table 1**.

For the purpose of facilitating the understanding about this chapter and the application in HVAC and refrigeration's systems, some definitions used by law and by some educational and research entities and institutions are presented below:

- **Global warming potential (GWP):** This is the direct mass comparison of $CO_2$ that a fluid causes when released into nature over a 100-year period [5].

- **Tons of CO2 equivalent:** Quantity of mass with a global warming potential multiplied by a global warming potential coefficient.

- **Recovery or regeneration:** Process of gathering and direct F-gas storage equipment, i.e., the removal of a refrigerant from system to store it in an external tank [14]. In this process some contaminants found in the systems are removed, like oil, water, oleic acid, and hydrochloric acids. In this sequence, the refrigerant is distilled and then filtered, condensed, and analyzed, and if it complies with ARI 700 Standard (purity, humidity, acidity, non-condensable gases, and maximum allowable residue levels), then it will be refilled.

- **Recycling:** Reuse of F-gas after a treatment process, that is, is the process involving the cleaning of refrigerant by an oil separator and a filter drier for reuse. It is to remove some contaminants like oil, water, and oleic and hydrochloric acids that can be found in system. In this process, the cooling fluid is distilled, filtered, then condensed, and finally, bottled [5, 14].

- **Reuse:** Reprocessing of the refrigerant, involving the manufacturing processes of new products from the refrigerant recovered.
- **Repair:** Restoration of equipment, for some reason, has lost its tightness, and this has resulted in the release of the working fluid to the atmosphere.
- **Leak detection system:** Mechanical or electronic equipment that allows to identify possible leakage points in the system components [14].
- **Destination:** Currently in Brazil there are regeneration plants capable of receiving refrigerants to be reused within the standards required by law.

In underdeveloped countries, such as Brazil, despite the knowledge of the mechanism of ozone layer depletion and the creation of specific legislations to address the issue, there is still no concern with the use and disposal of F-gases, which makes it difficult to meet the dates stipulated by 517/2014 Law [5].

## 3. Refrigerants

Refrigerants can be defined as substances that serve as a means of transport and heat transfer, absorbing heat at low temperatures and rejecting it at higher temperatures [15]. From that definition, in principle, any substance that changes phase in the refrigeration or air conditioning cycle, from liquid to vapor during heat absorption and from vapor to liquid during heat rejection, may function as a refrigerant. Their commercial usefulness depends on the temperature ranges and pressure at which the system will operate and, more recently, the environmental impacts that eventually this refrigerant can cause when released into the environment.

Water and air can also be considered as fluid refrigerants, although they do not show phase change during the process as well as other synthetic fluids or not form aqueous solutions that are characterized by operating at temperatures below 273.16 K (0°C) without crystallizing.

Among the various properties that a refrigerant should include for use in air conditioning and refrigeration systems, the most important are [15]:

i. Favorable thermodynamic properties.

ii. High chemical stability when operating within the system and low chemical stability outside the system.

iii. Nontoxic.

iv. Non-flammable.

v. Having small specific volume (causing less compressor work).

vi. Having high latent heat of vaporization.

vii. Evaporate at pressures above atmospheric (in case leakage air will not enter the system avoiding the risk of explosions).

viii. Having compatibility with the lubricating oil of the compressor.

ix. Having adequate compatibility with the materials of the refrigeration system.

x. Be easy to detect.

xi. In case of leakage, it should not attack or spoil food, should not contribute to global warming, and should not attack the ozone layer.

xii. Not posing a danger to the environment.

xiii. Be commercially available at a reasonable cost.

The refrigerant groups available in the Brazilian market are divided into [15, 16]:

- **CFCs (chlorofluorocarbons):** They are refrigerant fluids whose molecule is formed by the element's chlorine, fluorine, and carbon, for example, the fluids R-11, R-12, R-113, R-114, R-115, and R-502, among others. The lifetime of CFCs in the atmosphere ranges from 60 to 540 years, causing high depletion of the ozone layer. Most CFCs have an ozone layer depletion potential (ODP) index ranging from 0.6 to 1.

CFCs were no longer manufactured by industrialized countries in January 1996 and, with some exceptions, by developing countries. These fluids feature high ODP and high GWP. According to the Montreal Protocol, in 1996 these gases were banned from developed countries, and in 2010 they should be banned from developing countries such as Brazil, but these gases are still found in old refrigeration and air conditioning systems. These fluids are used in automotive air conditioners, commercial refrigeration, and home refrigeration (refrigerators and freezers).

- **Hydrochlorofluorocarbons (HCFCs):** In these refrigerants some chlorine atoms are replaced by hydrogen, as an example of these fluids, have it R-22, R-123, R-401A, and R-4012A. These fluids are used in climate control systems, window air conditioners, split air conditioners, self-containers, cold rooms, etc.

These gases represent the second generation of fluorinated gases and were the main alternative to CFCs. They have lower ODP, but the GWP still between 1000 and 5000, so they are a little less harmful to the environment than their CFC predecessors, considering the ozone depletion. HCFCs are not fully halogenated like CFCs. The atmospheric lifetime of HCFCs ranges from 2 to 22 years, and therefore their ODP ranges from 0.02 to 0.1 [15, 17].

Currently, in Brazil, HCFC-22 or (R-22) has been the most commonly used refrigerant in air conditioning systems since the early 1990s. HCFCs have been used as transition fluids, and their restriction on use and manufacturing started in 2004. According to the Montreal Protocol, the elimination of HCFCs in developed countries is expected by 2030 and in Brazil by 2040. Nevertheless, some countries are already well advanced on their elimination. In the European Union the use of HCFCs was terminated in January 2010 and may still be used until January 2015 in some specific cases.

- **Hydrofluorocarbons (HFCs):** In these fluids all chlorine atoms are replaced by hydrogen, for example, R-134a, R-404A, R-407C, R-410A, etc. These fluids are used in automotive air conditioning systems, commercial refrigeration and domestic refrigeration (refrigerators and freezers), etc.

As there are no chlorine atoms in HFCs refrigerants, they do not cause ozone layer depletion. HFCs are expected to become the most widely used in air conditioning systems in the coming decades. These fluids can be said to represent the third generation of fluorinated gases that have zero ODP and median and high GWP values. Currently, HFCs are largely used in commercial refrigeration and residential air conditioning.

- **Hydrofluoroolefins (HFOs):** The HFOs represent the fourth generation of fluorinated gases, with zero ODP and very low GWP values. It is already being used in automotive air conditioning systems in developed countries (the United States and Europe). They are fluids used in place of R-134a as they are suitable for high temperature applications and operate at similar pressures.

- **Natural refrigerants:** These fluids are generated through natural biochemical processes, so they pose no risk to the ozone layer and have very low or zero GWP indices. The most common natural fluids are R717 (ammonia), R744 ($CO_2$), hydrocarbons, R718 (water), and R729 (air).

Although the application of natural fluids in refrigeration systems is a worldwide trend, each fluid has its own characteristics and requires special care to be implanted.

- **Hydrocarbons:** They consist of a group of nontoxic gases with zero ODP and low GWP. They are environmentally friendly and have excellent thermodynamic properties, allowing good efficiency in similar or even better cooling systems than HCFC and HFC fluids.

Because these refrigerant fluids are considered as flammable gas, hydrocarbon refrigeration systems must meet a number of safety guidelines. Typically, these gases are applied in small systems such as refrigerators or indirect systems and cooling secondary systems with other fluids (such as a CO2 cascade system). This ensures a low risk of fire if a leak occurs.

The most commonly used hydrocarbons in refrigeration are propane (R-290) and isobutane (R-600a). In addition to the GWP, the ozone depletion potential (ODP) is another parameter that compares the ozone layer depletion potential regarding the R-11 refrigerant, which is assigned the value 1. This value is compared to other types of fluids.

Refrigerants can be classified as simple, which are not mixed with other fluids such as R-22, R-134a, and R-32 and natural or blend fluids, which are mixtures of fluids, such as R-410A. The blend fluids may also be azeotropic or non-azeotropic. And this is another classification of refrigerants, which divides them into two broad categories, which are:

- **Azeotropic mixtures:** In these types of mixtures, the components cannot be distilled off. The mixture evaporates and condenses as if it were a single substance. Its properties are totally different from those of its components. As an example, we have CFC/HFC-500, HCFC/CFC-501, and HCFC/CFC-502. For example, HCFC/CFC-501 is a mixture of 75% HCFC-22 with 25% CFC-12 on a mass basis. Azeotropic mixtures causing ozone layer depletion were no longer manufactured in 1996 in developed countries.

- **Zeotropic or non-azeotropic mixtures:** In a zeotropic mixture, its components are separated by distillation process. Thus, the mixture evaporates and condenses at different temperatures. Examples of such fluid types are R-400 and R-401A/B/C. Currently, these are the most promising alternative refrigerants for retrofit in air conditioning and refrigeration systems.

The CFCs and HCFCs are used worldwide in a variety of applications. By the middle of 1980, about 1/3 of CFC consumption occurred in the United States (USA). In 1985, the consumption of these fluids was around 278 tons.

These fluids served industrial sectors of insulating foams, automotive air conditioning, refrigeration and residential air conditioning, and commercial and industrial and other products. The CFC-expanded insulating foams have been widely used in industrial processes. Of this total, 19% was used in automotive air conditioning and 5% in new refrigeration and air conditioning systems. According to ABRAVA the percentage of halogenated refrigerant consumption is as follows: 77% HCFC-22, 10% CFC-11, and 10% CFC-12 [14].

Synthetic refrigerants (CFC, HCFC, HFC, and HFO) are considered safer, simpler to handle, and cheaper; however, most of them present some types of environmental risks. The presence of chlorine in the composition of most synthetic fluids is what makes them harmful to the ozone layer. Fluids that do not have chlorine in their composition are considered ecological but still favor the greenhouse effect, so the group of HFOs represents the promising generation of synthetic fluids.

The natural fluids such as $CO_2$, ammonia, and hydrocarbons are considered more complex and have a higher cost. In addition, they are considered highly flammable, and care should be taken to install the systems that will receive these fluids. They are recommended for low load operations such as vending machines and have good applicability at any temperature.

Ammonia, used in ammonia fluid R-717, is considered toxic and slightly flammable, has good thermodynamic characteristics, and should be used in systems combined with glycol (chiller system), or $CO_2$ (cascade system), for example [18].

The fluids with behavior of one substance, known as simple fluids, are easier to work because they have well defined properties, can be carried gaseous or liquid loads and in case of leaks, composition still the same in the installation, the only change will be in the volume. Azeotropic blend fluids such as R-22, despite being mixtures, have simple fluid characteristics. Non-azeotropic substances (such as R-404A, which has R-125, 44%, R-143 to 52%, R134 to 4%) have fluids with different boiling points and do not mix perfectly, so do not mix well. Thus, do not behave like simple fluid.

The use of these types of refrigerant implies extra care, as in the case of leaks, the composition of the leaked fluid and the composition of the remaining fluid may be unknown requiring a new charge. There is also the characteristic of glide temperature, where the evaporation temperature is not constant.

All these substances used in air conditioning and refrigeration systems are classified by safety groups as defined by AHSRAE. The classification considers the flammability and toxicity of each substance, as shown in **Table 2**, which presents the safety classification according to ASHAE [16]. Each refrigerant group requires a set of safety procedures for their use, installation, and disposal. The refrigerants found in the CFC, HCFC, and HFC categories are mostly classified in group A1 as non-flammable and of low toxicity. They are safe but environmentally aggressive fluids.

HFO refrigerants are less environmentally friendly but are classified in group A2L, i.e., there is a low risk of spreading flames in the event of a leak, and therefore require some caution and safety devices in equipment using these types of refrigerants.

| | | |
|---|---|---|
| High flammability | A3 | B3 |
| Low flammability | A2 | B2 |
| | A2L | B2L |
| Non-flammable | A1 | B1 |
| | Low toxicity | High toxicity |

*Source: ASHRAE Fundamentals [16].*

**Table 2.**
*ASHAE safety classification.*

Natural fluids, while an alternative more environmentally friendly, require a lot of care, and their facilities must follow the safety guidelines defined for each application. Propane and isobutane hydrocarbons are classified as highly flammable (group A3) while ammonia as highly toxic and low flammability (group B2L). Although carbon dioxide falls within group A1, it is a choking gas, so your systems must follow a series of precautions to ensure the safety of the installation.

In a Refrigeration system, the refrigerant is contained within the equipment, there is no direct contact between users and the refrigerant.

When a coolant leak in a refrigeration system and air conditioning, depending on the design and the refrigerant charge amount used in the system, choking problems may occur in people or product contamination.

Most leaks in the air conditioning and refrigeration systems are related to maintenance aspects, from the use of poorly maintained, deteriorated or even inadequate components and equipment as well as precarious labor that only acts when problems occur.

In the refrigeration, the word “retrofit” has been used to designate the adaptations that are made to equipment that works with CFCs so that they can work with alternative fluids (HCFCs, HFCs), making them efficient, modern, and economical. Another solution is the alternative fluid line, also called “blends,” which is a good alternative for converting equipment that is operating in the field as it requires minimal changes to the original system, and in most cases no compressor replacement is required [19].

**Table 3** shows a comparison of the ODP, GWP, and ASHRAE safety ratings of some refrigerants.

In the Brazilian market, as shown in **Table 3**, it is observed that the replacement of refrigerant fluid R-22 (HCFC) with R-410A (HFC) is occurring; however, it is worth noting that this substitution does not alter the potential for global warming.

In a direct comparison, R-134a refrigerant (tetrafluoroethane) has similar physical and thermodynamic properties to R-12, but it has lower ozone depletion potential (ODP) due to the absence of chlorine and the shorter lifetime in the atmosphere (16 years versus 120 years for R012). This fluid has a 90% reduction in greenhouse potential when compared to R-12. In addition, it is non-flammable and nontoxic, has high thermal and chemical stability, has compatibility with the materials used, and has adequate physical and thermodynamic properties. In addition, the R-134a refrigerant is free of chlorine and therefore has good compatibility with elastomers. One of the consequences of this change is that during the maintenance process of the air conditioning and refrigeration equipment, the R-22 fluid is released to nature, without any kind of control.

According to the Brazilian Ministry of Environment (MMA), the most commonly used refrigerant in cooling and air conditioning is HCFC-22, accounting for 82% of consumption [15, 19]. Considering the indicators shown in **Table 3** and the

| Number/name | Formula | ODP | GWP | ASHAE safety classification |
|---|---|---|---|---|
| **CFCs** | | | | |
| R-11/trichlorofluoromethane | $CCl_3F$ | 1 | 4000 | A1 |
| R-12/dichlorodifluoromethane | $CCl_2F_2$ | 1 | 8500 | A1 |
| R-502/CFC blend | R-115 (51%), R-22 (49%) | 0.23 | 5590 | A1 |
| **HCFCs** | | | | |
| R-22/chlorodifluoromethane | $CHClF_2$ | 0.055 | 1700 | A1 |
| R-123/dichlorotrifluoroethane | $C_2HCl_2F_3$ | 0.02 | 93 | A1 |
| **HFCs** | | | | |
| R-32/difluoromethane | $CH_2F_2$ | 0.0 | 650 | A1 |
| R-134a/tetrafluoroethane | $C_2H_2F_4$ | 0.0 | 1300 | A1 |
| R-410a/AZ-20 | R-32 (50%), R-125 (50%) | 0.0 | 1730 | A1 |
| R-507/AZ-50 | R-125 (50%), R-143a (50%) | 0.0 | 3300 | A1 |
| **HFOs** | | | | |
| R-1234yf | $C_3H_2F_4$ | 0.0 | 4 | A2L |
| R-1234ze | $C_3H_2F_4$ | 0.0 | 6 | A2L |
| R-218/perfluoropropane | $C_3F_8$ | 0.0 | 7000 | A2L |
| **Natural refrigerants (NRs)** | | | | |
| R-290/propane, Care 40 | $C_3H_8$ | 0.0 | ~5 | A3 |
| R-600a/isobutane, Care 10 | $C_4H_{10}$ | 0.0 | ~5 | A3 |
| R-717/ammonia | $NH_3$ | 0.0 | <1 | B2L |
| R-718/water | $H_2O$ | 0.0 | <1 | A1 |

*Source: ASHRAE Fundamentals [16].*

**Table 3.**
*Comparison of available refrigerants for air conditioning and refrigeration systems.*

properties listed above, it is important to realize that most refrigerants do not meet the requirements for commercial use in order to comply with Brazilian and worldwide legislation.

The scenario of replacing the R-22 in the refrigeration and air conditioning industry points to a number of alternative fluids. In this context, manufacturers in the refrigeration and air conditioning industry are looking for solutions that meet their goals without neglecting good performance.

According to ABRAVA [14], **Table 4** presents the suggestions of alternative fluids to the use of R-22 according to each application:

In a survey by the members of the UFPA Resfriar Project, in the metropolitan region of Belém do Pará, along with companies that work with the sale, installation, and maintenance of HVAC systems, more than 95% of people involved with the services did not have either training courses or were qualified to develop the services.

In Brazil, it is possible to observe that, in the practical activities, during the maintenance processes, the people qualified for the development of installation,

| Equipment types | Usual application | Main refrigerant substitutes |
|---|---|---|
| Window air conditioners (WAC) | Residential | R-410A |
| Air conditioners and heat pumps | Residential/small commercial air conditioning | R-410A |
| Hot and cold air conditioners (multi-split systems) | Commercial | R-410A |
| Multi-split systems | Residential/commercial | R-407C or R-410A |
| Large air conditioning systems | Commercial | R-134a or R-410A |
| Air condensing chillers | Central systems | R-134a or R-410A |
| Water condensing chillers | Central systems | R-134a |
| Commercial refrigeration | Commercial | R-134a, R-404A, R-410A, or R-507A |
| Industrial and transport refrigeration | Industrial/transport | R -134a or ammonia |

*Source: ABRAVA [14].*

**Table 4.**
*Alternative refrigerants for R-22 refrigerant according to your applications.*

operation, and maintenance activities of air conditioning and refrigeration systems, called in Brazil as "refrigeration professional," are the people who, not necessarily, are technicians of maintenance of air conditioning and refrigeration systems and, in many cases, are called "curious".

It was found that during the development of the analysis and maintenance services, these people either lack adequate equipment, such as a vacuum pump or a refrigerant recovery unit, or lack of knowledge, or because they could not afford to purchase such basic equipment and instruments required to perform the service and release the refrigerants from the equipment to the local environment. Besides that, they always have a recharge for normal system operation and, in many cases, do not have a basic analysis or concern about the consequences of these acts.

This common and uncontrolled practice releases thousands of kilograms of refrigerant fluids per year, to the environment, contributing significantly to global warming.

## 4. Test bench type chiller

In this topic, the theoretical foundations about vapor compression type cooling systems, with synthetic and natural fluids, necessary for the understanding about the experimental apparatus used are initially approached. After that, the experimental apparatus developed in the ClimatCont laboratory to simulate a chiller system has been described.

### 4.1 Theoretical fundamentals

Some scientific studies specifically dedicated to the comparison of natural fluids with the most common synthetic ones, such as R-22 fluid, have been carried out and published. The research conducted by Park and Jung's [20] related the replacement of R-22 with R-290 with the need of electrical adaptations to ensure the safety of the installation, which resulted in performance coefficients (COP) up to 11.5% when compared to the R-22, i.e., the system with R-290 required 11.5% less electrical power to generate the same refrigeration capacity. Another important point was the reduction of compressor discharge temperatures, which were reduced from 358.16 K (85°C) to 338.16 K (65°C), indicating better use of the lubricant life [20].

Sharmas and Babu comparatively analyzed mixtures between HC and HFC in relation to their characteristics as refrigerants, observing that mixtures containing HCs provided the system with a COP up to 2% higher than a system with HFC, also reducing the compressor discharge temperature, up to 295.16 K (22°C), and for the HCs mixture, a reduction of up to 1 kW per cooling tons in electric power consumption had been achieved [21]. In a computational analysis, these authors assessed that the HC mixture provided a COP of 5.35% over R-22, plus 286.16 K (13°C) lower discharge temperature for the same fluid and with reduced electrical power consumption by 5% [22].

Agrawal et al. compared a mixture of HC (R-290 and R-600a) with HFC (R-134a) and found that the optimum charge for the mixture was 60 g, less than half of the original charge 140 g of HFC, and the nearly 40% improvement in COP. With the optimum loads, HFC consumed 0.5 kW/h, and the HC mixture consumed 0.4 kW/h, providing the cooling capacities of 70 W and 76 W, respectively [23].

### 4.2 Chiller test bench

To carry out a practical analysis of the use of types of refrigerants, a test bench with a chiller was developed at the Federal University of Pará (UFPA) in partnership with the Refrigeration and Climatization and Thermal Comfort Laboratories (ClimaTConT) along with the research group "Resfriar Project," from the Energy, Biomass and Environment Group (EBMA). The main purpose of the bench is to create a demonstration of the operation of the refrigeration cycle, considering the local psychometric conditions, with a variety of refrigeration fluids.

In this test bench, all parameters are controlled and components have been assembled to facilitate understanding of fluid behavior and performance. After doing a research in the technical literature and articles on refrigerants and their properties and characteristics as environmental contaminants, the conclusion was that the bench will be a good system for a comparison between the original working fluid, HCFC R-22, and natural fluids, hydrocarbon base, which after investigation of the negative points of natural fluids, were the best suited to the project conditions [17, 24].

The test bench is composed of a condenser unit Elgin TUM-2053E 220 V, 60 Hz, single phase, with 1.6 kW of cooling capacity and power consumption of 880 W, with R-22 fluid and with a 1.5 l capacity liquid tank. The expansion device is a Thermostatic Expansion Valve from Danfoss, model TX2, for R-22, with number 01 orifice, with a maximum capacity of 2.5 kW and a single evaporator made of cooper tube with 3/8" of diameter and 1/16" of thickness, contained in an insulated box that can hold until 45L of water as shown in **Figure 1**.

Systems that use water as a refrigerant can both remove heat and add heat of an ambient making the environment conditioned. Refrigerant circulates inside pipes between the heater and the cooler. These systems can be classified according to operating temperature, flow type, and degree of pressurization [25].

The chilled water system is a type of cooling system that operates with water being a secondary fluid in the temperature range of 277.16 K (4°C) to 286.16 K (13°C), usually between 279.16 K (6°C) and 280.16 K (7°C), with working

**Figure 1.**
*Bench tests with chiller mounted by ClimaTConT.*

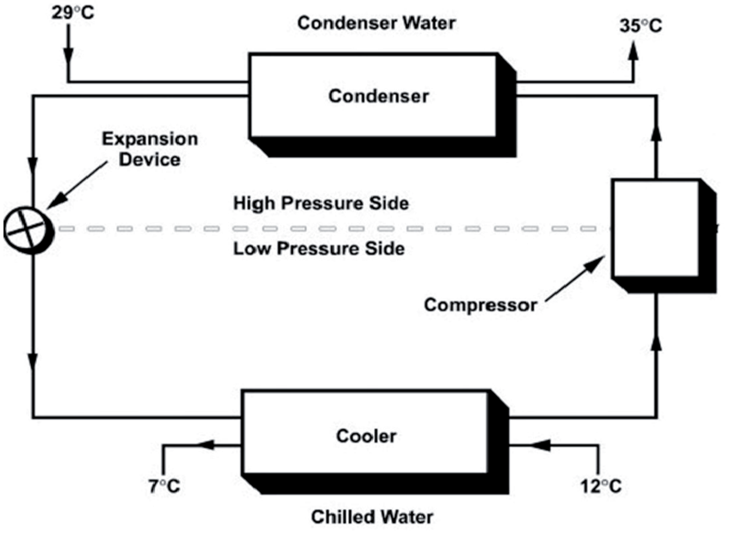


**Figure 2.**
*Schematic representation of the chiller cooling cycle. Source: ASHRAE Fundamentals (adapted) [16].*

pressure close to 800 kPa as presented in **Figure 2**, which shows a schematic of the test bench stand with a chiller, which must be used for the cooling of environments [26].

Preliminary data observed from the test bench with chiller shows that its working pressure is 310.26 kPa (45 psig), which indicates an evaporation temperature of 267.16 K (−6°C); considering the $\Delta T$ of 283.16 K (10°C), the fluid is cooled to 279.16 K (6°C). In this way, the bench tests consisted of evaluating the energy consumption of the R-22 fluid operation, in addition to the working temperatures at specific points, with the values of the refrigerant R-290, which is the fluid with characteristics similar to HCFC.

To measure the temperature parameters, five-point thermometers were installed that acquired the following temperatures: $T_1$, for room temperature; $T_2$, for the temperature in the suction pipe; $T_3$, for the temperature in the discharge pipe; $T_4$, for condenser air outlet temperature; and $T_5$, for water temperature. For the measurement of pressure values in the suction ($p_{Suc}$) and discharge ($p_{Desc}$) lines of the compressor, a digital pressure gauge was installed in the respective test bench pipes. The energy consumed ($E_{Cons}$) during the tests was acquired by a power meter installed on the chiller test bench electrical system, as shown in **Figure 1**.

### 4.3 Weather conditions

In Belém do Pará, which is a city located in the northern region of Brazil, the season with precipitation is overcast, and the dry season is partly cloudy. The city is surrounded by the Guamá River, which is responsible for the high rainfall index of the city.

All year round, the climate of Belém is hot and with high thermal sensation. Throughout the year, the average temperature generally ranges from 297.16 K (24°C) to 309.16 K (36°C), with a relative air unit that is approximately 90%. This city has a thermal sensation ranging from 307.16 K (34°C) to 319.16 K (42°C).

The average altitude of Belém do Pará ranges from 0 to 20 m above sea level, with average barometric pressure of 1010.28 kPa. In summary, Belém do Pará is a city of tropical climate.

## 5. Results and discussions

By using the chiller test bench, the following results were obtained for R-22 and R-290 refrigerants.

### 5.1 Evaluation of R-22 refrigerant in bench tests with chiller

To perform this test, the bench was initially charged with a load of 910 g of R-22 refrigerant. **Table 5** shows the results obtained with R-22 refrigerant on the chiller test bench.

When using the R-22 refrigerant, the test bench responded by reducing the water temperature by approximately 286.16 K (13°C) within 30 min of operation, where 0.5 kW of electricity was consumed to perform cooling.

For refrigerant R-22, which is known by high discharge temperatures that occur during its use in operation, values around 340.16 K (70°C) were measured, as shown in **Figure 3** that presents the variation in discharge temperature. Usually, these high values are disadvantageous given that they influence lubrication and hence compressor life.

**Figure 3** above shows a large variation in the discharge temperature of the chiller test bench, as a function of operating time. In parallel to the measurement of the discharge temperature variation, the values of the system discharge pressure during operation were also measured, because the higher the temperature of the water to be cooled, the higher the condensing pressure, as can be seen in **Figure 4**, which shows the variation of discharge pressure.

The suction pressure determines at which temperature the refrigerant will evaporate, i.e., the vaporization pressure of the fluid. At the test bench, pressures ranged from 489.52 kPa (71 psig) to 335.08 kPa (48.7 psig), which correspond to the

| Time (min) | T1 (K) | T2 (K) | T3 (K) | T4 (K) | T5 (K) | $p_{Suc}$ (kPa) | $p_{Desc}$ (kPa) | $E_{Cons}$ (kW) |
|---|---|---|---|---|---|---|---|---|
| 10 | 303.56 | 292.76 | 340.26 | 309.56 | 289.66 | 489.52 | 1613.37 | — |
| 15 | 304.16 | 280.36 | 340.26 | 309.66 | 280.76 | 380.59 | 1668.53 | 12,019 |
| 30 | 304.26 | 275.96 | 341.96 | 307.96 | 277.66 | 351.63 | 1560.97 | 12,019 |
| 45 | 304.36 | 273.96 | 331.96 | 307.56 | 276.76 | 335.08 | 1548.56 | 12,019 |
| 60 | 304.66 | 273.96 | 327.16 | 308.46 | 276.36 | 344.73 | 1489.95 | 12,020 |

**Table 5.**
*Test results for R-22 refrigerant on the chiller test bench.*

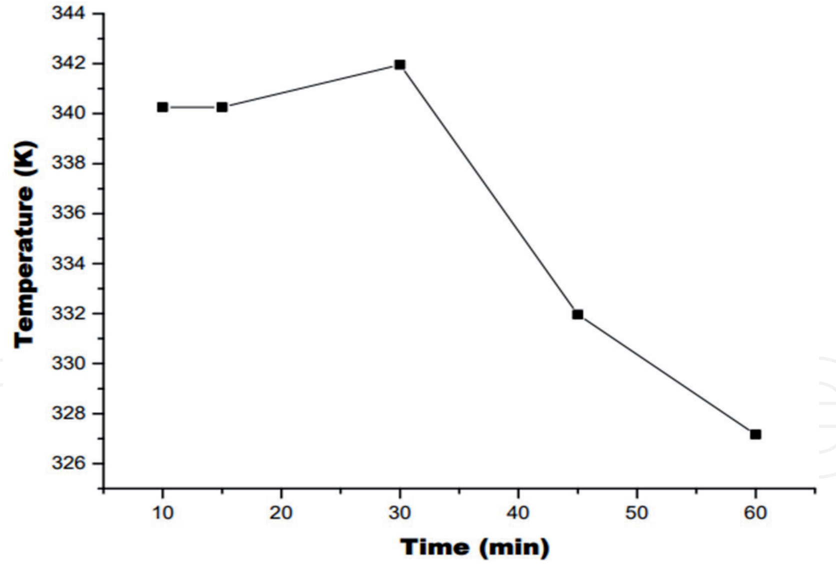


**Figure 3.**
*Variation in discharge temperature on test bench using R-22 refrigerant.*

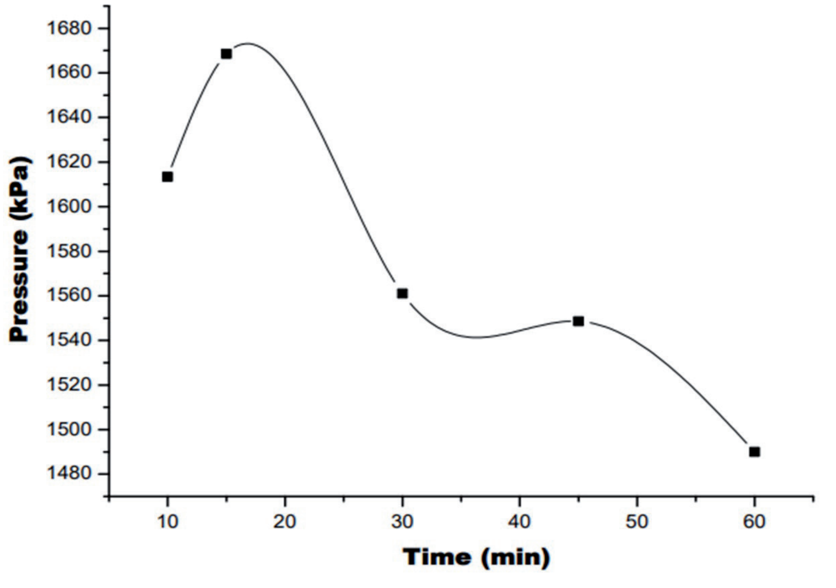


**Figure 4.**
*Variation of discharge pressure on test bench using R-22 refrigerant.*

evaporation temperatures of 278.46 K (5.4°C) and 269.16 K (−4.0°C), respectively. During 1 h of operation, the system was able to reduce the temperature and keep the water between 276.16 K (3°C) and 277.16 K (4°C).

### 5.2 Evaluation of R-290 refrigerant in bench tests with chiller

To perform this, the test bench with chiller was charged with a 370 g load of refrigerant R-290 for 90 min. **Table 6** shows the results obtained with R-290 refrigerant on the chiller test bench.

For the operation of the test bench, the load of R-22 refrigerant was removed and recovered, and then leakage was verified in the components of the test bench with nitrogen. Posteriorly, the bench was charged with 370 g of R-290 refrigerant.

During the tests, it was possible to keep the water temperature close to 274.56 K (1.56°C) and consume 1.0 kW in 70 min of operation. The temperature differences measured at discharge were significantly smaller than those for R-22 refrigerant, as

| Time (min) | $T_1$ (K) | $T_2$ (K) | $T_3$ (K) | $T_4$ (K) | $T_5$ (K) | $P_{suc}$ (kPa) | $P_{Desc}$ (kPa) | $E_{cons}$ (kW) |
|---|---|---|---|---|---|---|---|---|
| 0 | 305.66 | 294.26 | 324.96 | 306.76 | 275.66 | 317.15 | 1206.58 | 12,022 |
| 10 | 305.36 | 292.16 | 331.36 | 309.06 | 275.36 | 320.60 | 1292.76 | 12,022 |
| 20 | 306.56 | 287.96 | 325.16 | 307.46 | 275.36 | 344.75 | 1268.63 | 12,023 |
| 30 | 306.26 | 275.96 | 325.26 | 307.56 | 274.86 | 343.35 | 1268.63 | 12,023 |
| 40 | 306.46 | 275.26 | 325.26 | 307.46 | 274.86 | 341.29 | 1268.63 | 12,023 |
| 50 | 306.16 | 274.96 | 324.46 | 307.06 | 274.36 | 334.39 | 1247.95 | 12,023 |
| 60 | 305.46 | 274.66 | 323.46 | 306.16 | 274.66 | 327.50 | 1206.58 | 12,023 |
| 70 | 305.36 | 274.16 | 323.16 | 306.16 | 274.66 | 327.50 | 1206.53 | 12,023 |
| 80 | 304.66 | 273.76 | 322.76 | 305.76 | 274.76 | 327.50 | 1206.53 | 12,023 |
| 90 | 305.26 | 273.76 | 322.66 | 305.86 | 274.66 | 324.05 | 1213.48 | 12,024 |

**Table 6.**
*Test results with R-290 refrigerant on the chiller test bench.*

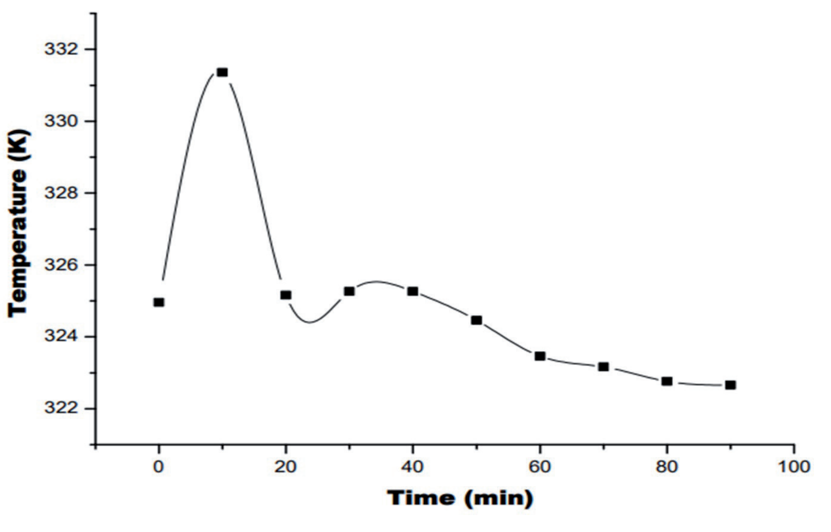


**Figure 5.**
*Variation in discharge temperature on test bench using R-290 fluid.*

shown in **Figure 5**, which highlights the variation in bench discharge temperature with R-290 refrigerant.

It is observed in **Figure 5** that the maximum discharge temperature measured on the chiller test bench, with R-290 refrigerant, was less than 331.36 K (59°C). The discharge pressure compared to that of R-22 refrigerant showed values up to 29% lower, with little fluctuation, as shown in **Figure 6** that presents the pressure variation in the discharge plumbing.

It was observed that the suction pressure ranged from 317.16 to 344.75 kPa (46 and 50 psig), corresponding to the respective evaporation temperatures of 269.16 K (−4°C) and 271.16 K (−2°C).

When comparing energy consumption, the chiller test bench with R-22 refrigerant consumed 1.0 kW of electricity to cool 40 l of water in 50 min of operation, while with R-290 refrigerant consumed 1.0 kW in 70 min of operation, i.e., with R-22 the bench consumed 1.2 kW/h, while with the R-290 the consumption was 0.857 kW/h.

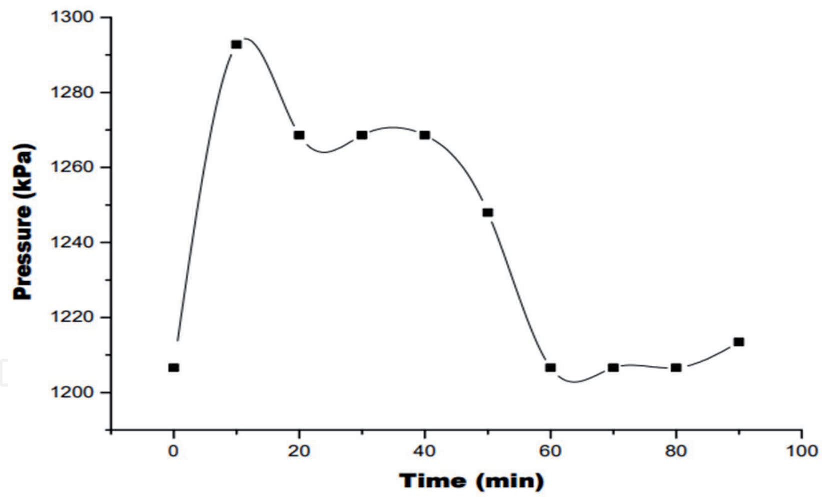


**Figure 6.**
*Variation of discharge pressure on test bench using R-290 refrigerant.*

The cooling capacity of system $\dot{Q}_{Ref}$ was 2326 W, so the performance coefficient (COP) can be calculated as shown in Eq. (1) and Eq. (2):

$$COP_{R-22} = \frac{\dot{Q}_{Ref}}{E_{Cons}} = \frac{2326}{1200} = 1.9334 \quad (1)$$

$$COP_{R-290} = \frac{\dot{Q}_{Ref}}{E_{Cons}} = \frac{2326}{857} = 2.714 \quad (2)$$

As calculated above, the R-290 refrigerant COP was 40% higher than of the R-22 refrigerant.

### 5.3 Comparison between types of refrigerants

The graphs shown below are comparing pressure and temperature of the most common synthetic and natural fluids taken from the Danfoss application [27] and based on the National Institute of Standards and Technology (NIST) [28].

As presented in **Tables 4** and **5**, the R-22 substitute refrigerant is R-410A refrigerant. The R-410A is an almost azeotropic mixture composed of R-125 and R-32. It is a chemically stable product with low temperature glide and low toxicity. According to ASHRAE this fluid is classified as A1 in group L1.

**Figure 7** shows a comparative graph between these two fluids for temperature and discharge pressure.

When compared to other refrigerants, R-410A has the highest working pressure, as shown in **Figure 8**, which evidences a comparative graph between dew temperature and operating pressure. Both refrigerants have 0 (zero) ODP, but the GWP is virtually unchanged around 1700, which implies in no advantage in this replacement. Besides that, R-410A has its days counted for discontinuation given the action of laws and protocols, in order to reduce the environmental pollution [1–3].

It can be seen from **Figure 8** that R-410A refrigerant has higher cooling capacity and works at higher pressures than R-22 refrigerant. Because this product is not azeotropic, it should always be charged in air conditioning and liquid refrigeration systems. This gas is also not miscible with mineral oils, and therefore polyol-esters (POE) should be used.

Some comparative studies [20–23] have concluded that R-290 fluid is the natural one with thermodynamic properties more similar to R-22, as shown in **Figure 9**.

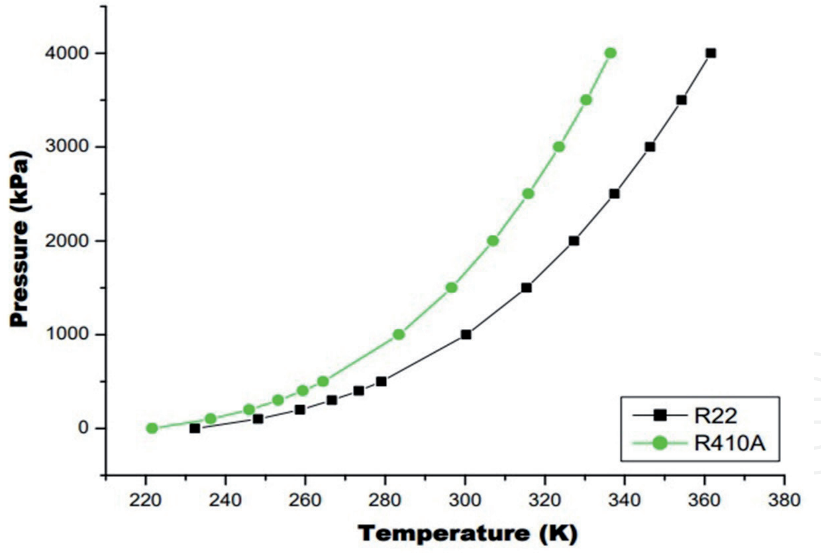


**Figure 7.**
*Comparative graph between R-22 and R-410A refrigerants. Source: Danfoss [27].*

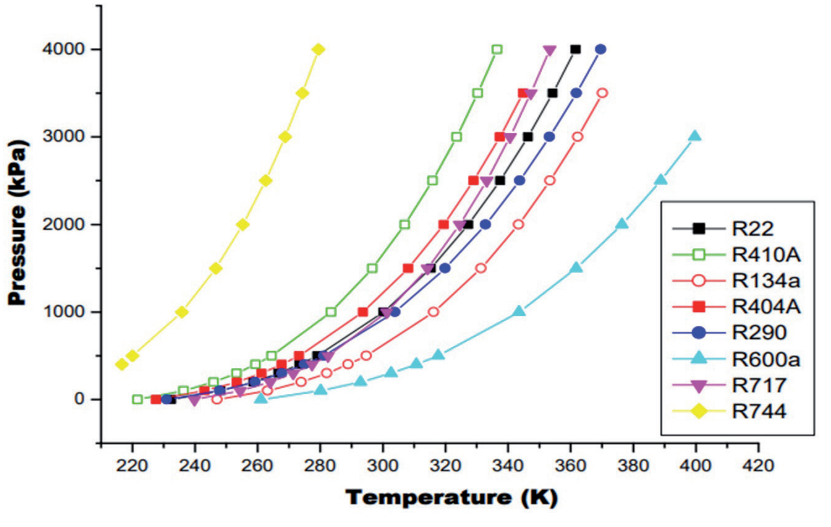


**Figure 8.**
*Comparative graph between the most commonly used refrigerants in Brazil. Source: Danfoss [27].*

Furthermore, it would make it possible to simply replace one fluid to another with less but rigorous modifications to the equipment's electrical system in order to prevent possible fire in case of leakage.

Notwithstanding the similarity with R-22, the R-290 fluid also works at temperatures and pressures close to those of the R-404A, indicating that it can be applied smoothly in these systems, as shown in **Figure 10**.

Between the most commonly used synthetic fluids, it can be seen from **Figure 11** that there is almost a pattern in temperature and pressure variation according to fluid composition.

By observing **Figure 12**, there is remarkable divergence, especially in the case of $CO_2$ due to it is low critical temperature, which does not allow its direct use in air/water condensation systems such as synthetic fluids.

It is important to note that each type of refrigerant has its applications for each type of air conditioning and refrigeration system and that they should not be mixed, requiring specific procedures for replacing the refrigerant charge.

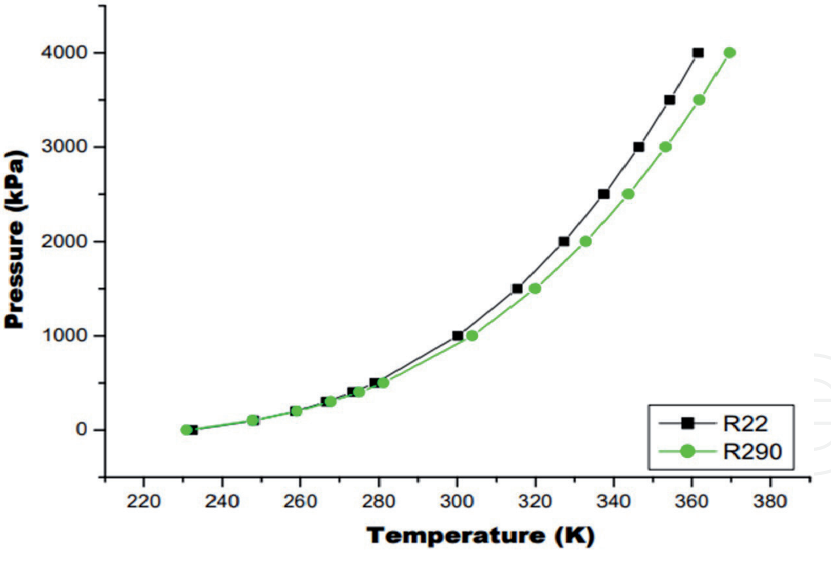


**Figure 9.**
*Pressure–temperature relation between R-22 and R-290 refrigerants. Source: Danfoss [27].*

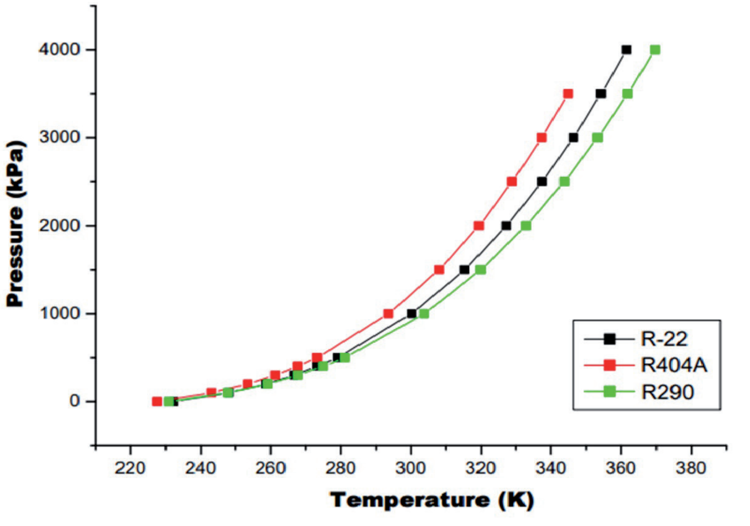


**Figure 10.**
*Parameters of synthetic and natural fluids. Source: Danfoss [27].*

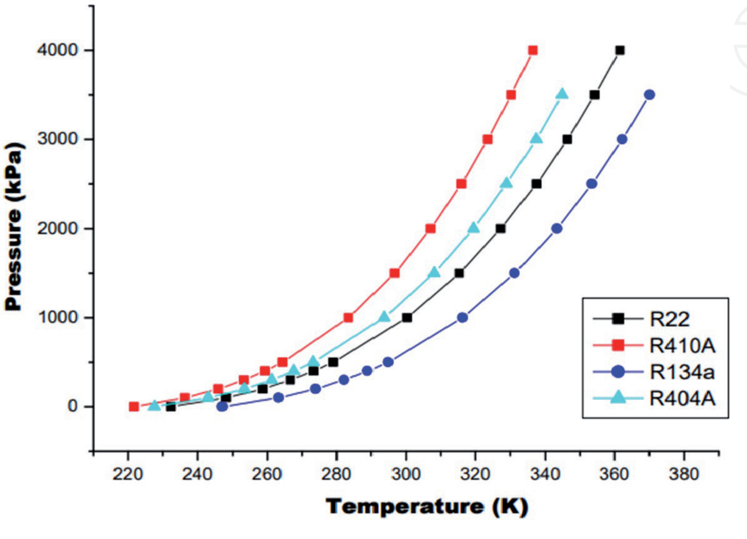


**Figure 11.**
*Pressure-temperature relation between azeotropic and zeotropic synthetic fluids. Source: Danfoss [27].*

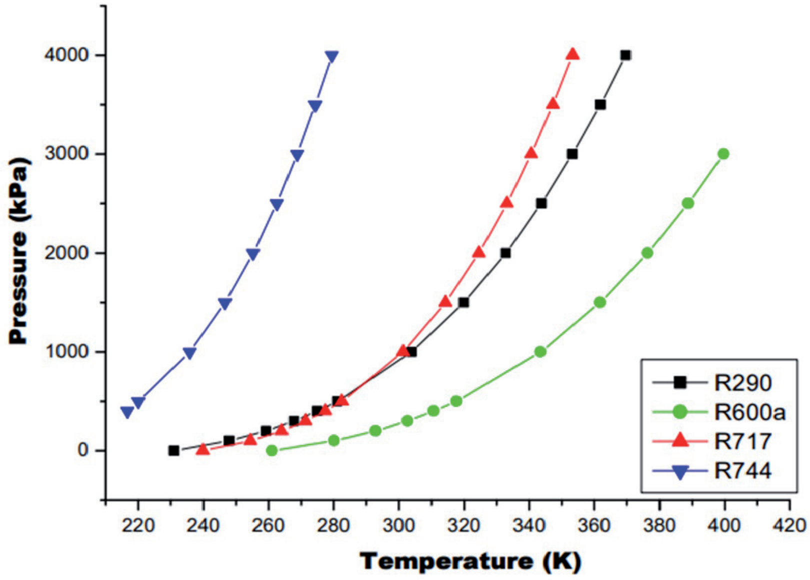


**Figure 12.**
*Pressure-temperature relation between natural fluids. Source: Danfoss [27].*

## 6. Conclusions

What is expected of this work is the development of discussions regarding the use and disposal of F-gases, so that they can create more effective control mechanisms, not only to the process of replacement of refrigerants CFCs by HFCs but also to controlling the use and especially the disposal of these refrigerants in a controlled manner, preventing the reuse and release of these types of refrigerants in nature.

The tests performed on ClimaTConT of the UFPA were extremely satisfactory, and with the information obtained from the test bench with chiller, it is possible to realize that the current replacement of R-22 with R-410A is not necessarily the best choice for air conditioning systems, because the various indicators, such as ODP and GWP, do not vary widely, which does not contribute to the reduction of ozone depletion.

In the face of all the information listed, some immediate actions should be taken:

- Refrigerant replacement or retrofit:
  - The impact of CFCs on the ozone layer is a serious risk to human survival. Therefore, some short-term actions should be taken, such as:
    1. Effecting the transition phase where R-12 should be replaced by R-134a, and R-11 by R-123. Other substitutes with ODP less than 0.05 should be used to replace CFCs. It is important to note that HCFCs themselves will begin to be restricted from the year 2004.
    2. HFCs and their zeotropic mixtures can be used without restrictions: The R-404A replacing R-502 and R-407C replacing R-22. There are refrigeration systems where these replacements can be made with very small cooling capacity losses and efficiency.
    3. Developing control mechanisms for the recovery of refrigerants used in residential, commercial, and industrial air conditioning and refrigeration equipment, such as recovery of fluids for recycling and/or disposal, preventing these fluids from being released into the local environment.

4. Development of studies, individualized, aimed at reducing the refrigerant charge used in air conditioning and refrigeration systems.

    ○ It is important to be careful with the safety equipment required when working with natural refrigerants such as R-290 and R-600a as they are flammable and must have their concentrations controlled.

    ○ Responsible companies must be required to use basic equipment such as a vacuum pump, refrigerant recovery unit, and precision scale for the installation and maintenance of HVAC systems.

- Popular programs must be created with training and recycling courses for those involved in the installation, maintenance, and operation of HVAC systems.

- During the manufacture, installation, operation, and maintenance of air conditioning and refrigeration systems using CFCs and HCFCs, deliberate leakage of these products into the environment should be avoided.

- Avoid emissions of CFCs and HCFCs by recovery, recycling, and reprocessing of refrigerants.

It is important that users are aware of the origin of the refrigerant to be used in air conditioning and refrigeration systems or in industrial processes, obeying the standards of purity and quality, within international standards. One must also pay attention to the classification of flammability and toxicity and know the rules and regulations governing this area (ASHRAE 34 and ARI 700).

According to the experience of the members of the UFPA "Resfriar Project," coupled with the knowledge of ABRAVA [14], **Table 7** points out the alternatives and trends for the replacement of the most commonly used refrigerant in cooling and air conditioning systems according to their applications, in the transition or retrofitting phase.

Considering the actual scenario in Brazil, the lack of reliable information about leaks in air conditioning and refrigeration systems precludes further analysis. In any case, informal data obtained from companies operating in the maintenance

| Application | Refrigerant used | Alternative | Trend |
|---|---|---|---|
| Domestic refrigeration | R-11 to R-123<br>R-12 to R-134a | Recycling | R-600a, HFO |
| Commercial refrigeration | HCFC-22 | HFC-404A, $CO_2$, ISCEON, recycling, HFO, HC, R-134a, glycol | HFC-404A, $CO_2$, ISCEON, recycling, HFO, HC, R-134a, glycol |
| Industrial refrigeration | Ammonia, HCFC-22, HFC-134a | R-134a, ammonia, recycling | Ammonia, R-134a, recycling, HFO |
| Automotive refrigeration | R-22 to R-134a | R-134a, recycling | R-123yf, $CO_2$ |
| Climatization systems | HCFC-22 | HFCs (R-134a, R-290, R-407C, R-410A, and R-600a) | R-290, R-410A, R-32, R-600a, recycling, HFO |

*Source: ABRAVA [14].*

**Table 7.**
*Alternatives and substitution trends of refrigerants according to their applications.*

segment indicate that annual leakage rates can be between 40 and 100%, depending on the frequency of maintenance performed [15].

This work proved that even with the reduction in the refrigerant charge used on the chiller test bench, it was possible to improve the system efficiency by replacing an HCFC refrigerant with a natural refrigerant, following a worldwide trend of reduction of the refrigerant charge used in air conditioning and cooling systems.

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## Author details

Eraldo Cruz dos Santos*, Carlisson Azevedo, Caio Macêdo, Carla Azevedo, Raíssa Araújo, Sílvia Soares Gomes, Lana Baia and Yves Alexandrino
Federal University of Pará (UFPA), Belém, Pará, Brazil

*Address all correspondence to: eraldocs@ufpa.br

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