Handbook of Research on Advances and Applications in Refrigeration Systems and Technologies

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Chapter 6
Current and Future Trends of Refrigerants Development

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ABSTRACT

In this chapter is addressed the thematic of refrigerants: its historical evolution; properties; legislation applied in the area and future trends. The first refrigerant being marketed on a large scale was ethyl ether (R610), in 1834. Since then, the evolution of the utilized refrigerants was stimulated, initially due to constructive issues in the refrigeration system and later to environmental issues. This evolution may be divided into four generations: 1st use of any fluid that worked; 2nd safety and durability of the equipment; 3rd ozone layer protection and 4th increase of global warming concerns. During the process of evolution many refrigerants were tested to understanding of their properties. Currently, environmental concerns are taken as guide in the search for new refrigerants. The most promising refrigerants to be used in future are the HFES, HFOs and HFCs with low-GWP, natural refrigerants and blends between (HCs/HFCs and HFCs/HFOs) refrigerants.

INTRODUCTION

Refrigerants are all the fluids that have a high capacity to “absorb” large amounts of thermal energy during the evaporation process at low temperature. This characteristic makes it ideal for use in refrigeration systems that operate a refrigeration vapour compression cycle, the cycle applied in air conditioners, heat pumps and cooling systems. Refrigerants can be classified as primary or secondary. Primary refrigerants are those that circulate inside the cooling system, being compressed in the compressor and expanded in the expansion device, i.e. those whose width of biphasic zone measured in (p, h) diagram is important. Some examples of primary refrigerants are the halogenated compounds, hydrocarbons, inorganic compounds, azeotropic and zeotropic mixtures. Secondary refrigerants are usually liquids used...
as heat carriers at low temperature from primary refrigerant to other fluid. This type of refrigerants is only used in refrigeration vapour compression systems that operate by indirect expansion. Are examples of secondary refrigerants, the brines and antifreezes.

Exceptionally, absorption refrigeration systems use two substances (refrigerant and absorbent). In these systems it is intended to take advantage of the chemical affinity existing between these two fluids, in order to its combination and dissociation allows the desired cooling effect.

The ethyl ether (R610) was the first fluid known with excellent thermodynamic properties that makes it a good refrigerant (i.e. the evaporative effect at low temperature). This characteristic was perceptible when a small amount is spilled on the hand. The almost instantaneous evaporative effect causes a cooling sensation in the skin, while a portion of substance is evaporated “stealing” thermal energy at hand.

For this reason, the ethyl ether (R610) was used in the first refrigerating machine patented to operate a refrigeration vapour compression cycle, machine built in 1834 by Jacob Perkins. This was the first refrigerant marketed in a large scale (Dinçer & Kanoglu, 2010).

Since then, there has been an impressive evolution of the used refrigerants, stimulated initially due to constructive issues related with the refrigeration system and later as environmental issues.

This evolution may be divided into four generations (Calm, 2008):

- **1st** marked by the use of any fluid that worked – the natural refrigerants were the firsts to be used because they abound in nature. But the use of some natural refrigerants was very dangerous as they are highly toxic and flammable, having occurred several accidents, including people’s death;
- **2nd** marked by the safety and durability of the equipment – in attempting to find more stable refrigerants whose use was safer for equipment and users, were discovered the CFCs compounds in 1928. These compounds revolutionized the chemical industry, having been used in several applications beyond refrigeration;
- **3rd** marked by the ozone layer protection – for being too stable the CFCs compounds are very harmful to environment, with great participation in the destruction process of ozone layer and increase of global warming;
- **4th** marked by the increase of global warming – currently, the trend is towards the disuse of CFCs and HCFCs compounds and bet on HFCs with a low-GWP, HFOs, HFEs and the return to natural refrigerants.

In this chapter are discussed the thematic related with the refrigerants and its historical evolution, taking into account the main events that marked this evolution. The main characteristics and properties that characterize the refrigerants in order to allow its classification according to the respective family also are presented. Finally are discussed the different replacement possibilities for the currently most used refrigerants and those that are indicated as long-term future possibilities, the different substitution methods and collection and recycling of refrigerants.

**FRAMEWORK**

Refrigerants are currently used in air conditioning systems, commercial refrigeration systems, domestic refrigerators and freezers, mobile refrigeration systems, cryogenic and low temperature freezers and industrial refrigeration systems.
Air Conditioning Systems

The unitary air conditioning systems (including heat pumps) have an average lifespan of 15 years. China is the largest manufacturer of air condition equipment, holding about half of world production of these systems. The electrical power consumption of these devices ranges from 1 - 135 kW and the refrigerant charge between 0.5 - 90 kg. Estimative indicate that air conditioners were responsible for the emission of 91 million metric tonnes of carbon dioxide equivalent (MMtCO₂-eq.), equivalent to 8% of global consumption of HFCs refrigerants in 2010. Unitary air conditioning systems are responsible for 11% of refrigerants consumption in the refrigeration/air conditioning sector. It is expected that this percentage will rise to 38% in next year’s due to transition from HCFCs to HFCs refrigerants with low-GWP value. This growth is driven by the increasing use of air conditioning systems in developing countries (U. S. EPA, 2010a).

The most used refrigerant in unitary air conditioning systems is R22 (HCFC), used in about 60% of worldwide systems in 2010. Since 2000, in developed countries began to be used the refrigerants R410A and R407C (both HFCs). In 2010, these refrigerants were used in approximately 39% of air conditioning systems worldwide. In the same year, unitary air conditioning systems are already being marketed using R290 (HC), representing about 1% of worldwide systems. In addition to propane (R290), are also being studied for application in air conditioning systems the CO₂ (R744), HFCs (R32) and HFO (R1234yf).

In several service buildings (i.e. offices and hospitals), chillers are used for distribution of cold water in the buildings. The cool water is used to cooling the air in the individual rooms. Previously these systems operate with CFCs, HCFCs and HFCs refrigerants, but recently, ammonia based and hydrocarbon based refrigeration systems started to be used. Some small systems based on HFCs refrigerants (with charge below 10 kg) are still being commercialized (Pedersen, 2012).

Commercial Refrigeration Systems

Commercial refrigeration systems include all refrigerated equipment existing in supermarkets, convenience stores, restaurants and other food service establishments (including vending machines). These systems can be characterized according to its level of operating temperature: chilled food in the range of 1 to 14 °C and frozen food in the range of -12 °C to -20 °C (Devotta et al., 2005), influencing this characteristic the choice of ideal refrigerant to used.

In 2006, there were about 530,000 supermarkets worldwide, containing about 546,000 metric tonnes of refrigerant. From this amount 55% are HCFCs, 30% CFCs and 15% HFCs. Estimative indicate that commercial refrigeration systems are responsible for the emission of 346 million metric tonnes of carbon dioxide equivalent (MMtCO₂-eq.), equivalent to 32% of global consumption of HFCs refrigerants in 2010. From this value, the developing countries are responsible for an estimated 131 million metric tonnes of carbon dioxide equivalent (MMtCO₂-eq.) or 38% of the global HFCs consumption in this end-use.

Commercial refrigeration systems have a lifespan range of 15 - 20 years and an approximate refrigerant charge between 0.15 - 20 kg. Several designs of refrigeration systems and its components have been studied in order to reduce: the amount of refrigerant required for systems; the probability of leakage and the risk of use toxic or flammable refrigerants (U. S. EPA, 2010b).

Today the most used refrigerants in commercial refrigeration systems are R22 (HCFC), R134a, R404A, R407C and R507A (HFCs). In 2010, the R22 (HCFC) was the most widely used in multiplex
rack systems. As alternative refrigerants to be used in this type of refrigeration systems are highlighted the hydrocarbon compounds (R290 and R600a), propylene (R1270), ammonia (R717), CO2 (R744) and other alternatives as mixtures between the HFCs and HFOs compounds.

In 2007 a group of international companies launched the program called “Refrigerants Naturally”. With this program, companies intent to promote the utilization of alternative HFCs-free refrigeration technologies in the food and drink, food service and retail sectors. This program stimulated the use of R290, R744 and R600a refrigerants. Unilever Company has introduced freezers for ice cream conservation using R290 refrigerant, about 2000 units in Europe with a refrigerant charge of 90 grams. These devices present an increased efficiency of 9% and do not require a greater maintenance when compared with traditional devices using R404A refrigerant. To the same application, Embraco and Nestlé have developed freezers using R744 (replacing the R404A freezers). Currently, several units using the R744 are being tested in Europe (Melo, 2011).

Transcritical CO2 systems technology is currently the most used in the construction of new refrigeration units in supermarkets exceeding 10 kg of refrigerant. It was estimated that in 2011, the total amount of transcritical CO2 systems existing in supermarkets was about 2000 units (Pedersen, 2012).

**Domestic Refrigerators and Freezers**

The expected life time for domestic refrigerators and freezers varies between 15 - 20 years. In 2009, it was estimated the existence of 1.5 - 1.8 billion of this equipment operating worldwide. Every year are produced approximately 100 million units of new refrigerators and freezers systems typically containing between 0.05 - 0.25 kg of refrigerant. The amount of refrigerant charge in this type of equipment has been reduced due to the introduction of technological innovations in the system and its components.

Domestic refrigeration systems were responsible for the consumption of about 2% of global HFCs refrigerants consumed in 2010. In developing countries, the global consumption of HFCs refrigerants was approximately 12% of the total amount consumed by the refrigeration/air conditioning sector in 2010.

R12 was the first to be used on a large scale in domestic refrigerators and freezers. Due to CFC compounds phase-out, the refrigerant R134a was selected as a substitute, although the hydrocarbon compounds (HCs) would start to be used in Europe and Japan. A large part of refrigerators/freezers still use the R134a refrigerant. In China, 75% of new refrigerators/freezers use isobutane (R600a) as refrigerant (U. S. EPA, 2010c).

R600a dominates the market of domestic refrigerators in Europe and Asia, but is not used in USA due its high flammability. In Europe, 95% of domestic refrigerators used operate with R600a. Since 1993 more than 200 million of R600a refrigerators and freezers have been commercialized and until the moment no accident (in normal operation) has been reported. Refrigerators using R600a are more silent and efficient than R134a refrigerators (Melo, 2011).

**Mobile Refrigeration Systems**

As in other applications, also in Mobile Air Conditioning - MAC (i.e. the refrigeration systems installed in cars, trains, aircrafts, ships and containers) the refrigerant R134a (HFC) come replaced the R12 (CFC) due to impositions agreed in the Montreal Protocol. R134a refrigerant has been employed in other types
of refrigerating systems, but was in the automotive air conditioning systems that became famous (Min-
jares, 2011). Normally a typical refrigerant charge of R134a is 0.8 kg for an existing car (i.e. refill), 0.6
kg for new cars, 1.5 kg for a truck and 5 – 12 kg for a bus. The leakage rate is about 10 - 20% of the total
charge per year (Pedersen, 2012).

With the European MAC Directive publication in 2006, occurred the abolition of refrigerants with a
GWP value > 150 (low-GWP). As the refrigerant R134a presents a high-GWP value, this was abolished,
being in progress its phase-out (until January 1, 2017). The R134a refrigerant is already being replaced
by R152a (HFC) that presents a GWP = 120. The function of R152a refrigerant is to ensure the transition
to a refrigerant that presents a residual GWP value, at least this is the desire of the European Union.

R1234yf was chosen by the automotive industry in 2009 to replace the currently used refrigerant
R134a. After this decision a manufacturer (Daimler) was questioned the safety of R1234yf use. This
situation leads the KBA (German Motor Authority) to proceed with its own testing. The automotive in-
dustry has developed the risk assessment and fault tree analysis of the use of R1234yf in MAC systems,
in cooperation with SAE International, which concludes that this refrigerant was safe to use in MAC
systems (EU, 2014a).

A compilation of information developed through SAE Cooperative Research Programs, chemical sup-
pliers, Original Equipment Manufacturers (OEMs), and other sources, EPA (US Environment Protection
Agency) has approved through its SNAP (Significant New Alternatives Policy) program three low-GWP
refrigerants candidates to be used in air conditioners in new light-duty vehicles. Are also presented the
respective use conditions concerning to security features for each alternative: R152a; R744 and R1234yf
(Sciance, 2013). Presently, automobile and refrigerants manufacturers together with the European Union
try to reach an agreement to which is the refrigerant to be used in this application, in future.

General Motors account already with the following vehicle models on the market using the R1234yf:
in North America (Cadillac XTS in May 2012 and Chevrolet Spark Battery Electric Vehicle in June
2013) and in Europe (Chevrolet Malibu in 2012, Chevrolet Trax and Opel Mokka in January 2013). GM
already has more than 100,000 vehicles on the roads globally, using as refrigerant R1234yf. In Europe,
there are several OEMs (as Hyundai, Subaru, Ford and BMW) that produce components for air condi-
tioning systems of passenger vehicles using R1234yf (Sciance, 2013).

Refrigerated transport growth significantly since the 50s. According to last RTOC report that evalu-
ates in 4 million the terrestrial fleet of refrigerated transport equipment in service worldwide in 2010.
The worldwide fleet of marine reefer containers is evaluated to 850,000 units in 2013. In European
Union-27, the overall refrigerated terrestrial transport equipment is estimated on some 1.1 million equip-
ment in 2012 by Cemafroid. The refrigerated transport sector is dominated by one technology based on
vapour-compression systems using HFCs as refrigerant, namely R404a and R134a. The phase down of
HFCs with high-GWP in European Union (i.e. FGas regulation revision in 2014), in the next years will
directly impact refrigerated transport equipment technology. The transport refrigeration units must change
tremendously during the next years. Between the alternatives, CO2 is considered as a possible long term
alternative in the coming 5 to 10 years. New HFCs and blends of HFCs may be a transitional solution
for short term. The utilization of HFOs is still considered a possibility. Hydrocarbons are certainly too
flammable (Michineau et al., 2014).

In Iceland and Norway, about 20 – 30% of fishing vessels use ammonia as refrigerant. New large
fishing vessels build in Norway have CO2/ammonia cascade systems. To air condition in trains and 
aircrafts a cold-air refrigeration system has been developed, using air as refrigerant (Pedersen, 2012).
Cryogenic and Low Temperature Freezers

Cryogenic systems and low temperature freezers are a particular area of refrigeration widely used in laboratories. This equipment normally consists on a cascade system. The R507, or R23 or R508 refrigerants can be used in the stage of high temperature (approximately -50 ºC) and hydrocarbons to the stage of low temperature – ethane R170 (approximately -80 to -90 ºC) and ethane R1150 (approximately -100 to -120 ºC). As R23, R507 and R508 present very high-GWP values, these have been replaced by propylene R1270 (Pedersen, 2012).

Industrial Refrigeration Systems

Industrial refrigeration systems are normally very large systems, used in process of refrigeration and cold storage on food industry, chemical/biochemical industry (oil and gas industries) and ice-making industry. This type of systems is built on site (Pedersen, 2012).

The capacity of units may vary from 25 kW to 30 MW and with a refrigerant charge size between 20 to 60,000 kg. These types of refrigeration system are normally located in industrial areas with limited public access, and ammonia is the most widely used refrigerant. The current big trend is to use indirect refrigeration in order to reduce the refrigerant charge (in 75 to 85%) and avoid ammonia in working areas (due to its high toxicity). The use of industrial refrigeration plants with CO$_2$ operating a refrigeration cycle at low temperature in cascade systems is becoming common, in which the ammonia is used in the high temperature stage and CO$_2$ in the low temperature stage (Pedersen, 2012; Devotta et al., 2005).

Refrigerants Used in the European Union

In UE-27, CO$_2$-eq emissions have decreased from 170 metric tonnes in 1990 to 147 metric tonnes in 2010, a decrease of 13.5% in 20 years (Figure 1), despite the use of refrigerants having more than doubled in the same period from 200,000 metric tonnes in 1990 to about 510,000 metric tonnes in 2010, as can be seen in Figure 2, meaning an average market growth of 8% per annum. This increase may be due to the accelerated phase-out of CFCs and HCFCs refrigerants under the EU ODS Regulations and introduction of the EU F-Gas Regulation in 2006 (Clodic & Barrault, 2011).

Although the growing refrigerants utilization in EU, CO$_2$-eq emissions significantly decrease under the predicted scenario, from 147 metric tonnes in 2010 to 124 metric tonnes in 2030, as can be seen in Figure 3, meaning a reduction of 15%. According to predicted scenario (i.e. F-Gas Scenario), the total amount of used refrigerants in EU will grow about 43% between 2010 and 2030, reaching the 900,000 metric tonnes, as can be seen in Figure 4.

Currently several scenarios to the evolution of refrigerants utilization and their respective emissions are proposed, having been presented the least favourable in Figures 3 and 4. In Figures 3 and 4 is also notable the success of the European Community Directives through reduction of use of CFCs and HCFCs refrigerants and increasing use of HFCs refrigerants. It is anticipated that HFCs refrigerants will dominate in terms of use over the next decade.
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Figure 1. Total CO₂-eq. emissions per family of refrigerants in the EU from 1990 to 2010 (Clodic & Barrault, 2011)

Figure 2. Total amount (metric tonnes) of used refrigerants per family in EU from 1990 to 2010 (Clodic & Barrault, 2011)
CHARACTERIZATION OF REFRIGERANTS

In this section are presented the main characteristics and properties of refrigerants that allow its classification, according to the respective family.

General Characteristics of a Refrigerant

During the selection process of a refrigerant to use in a refrigeration system or heat pump, its general characteristics must be considered so it can be applied the most adequate refrigerant to installation and be able to meet the desired cooling or heating conditions.

The ideal refrigerant must present the following general characteristics (Dinçer & Kanoglu, 2010):

- Environmentally friendly (does not contribute to destruction of ozone layer and increase of greenhouse effect);
- Low evaporation temperature;
- Low flow rate per unit of system capacity;
- Pressure of evaporation higher than ambient pressure;
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Figure 4. Total amount (metric tonnes) of used refrigerants per family in EU from 1990 to 2030 (Clodic & Barrault, 2011)

- High enthalpy of evaporation;
- Low flammability and toxicity;
- Do not be explosive or corrosive;
- Do not be reactive, but compatible with the compressor lubricating oils;
- Chemically stable;
- Suitable thermal and physical properties (i.e. thermal conductivity, viscosity …);
- High commercial availability;
- Easily detectable on leakage;
- Low cost;
- Recyclable.

The saturation properties of refrigerants must also be considered. To achieve a reasonable rate of thermal energy transfer, the temperature difference between the refrigerant inside the heat exchanger and the external ambient should be about 10 °C (i.e. a $\Delta \approx 10$ °C). The lower pressure obtained in the
refrigeration cycle occurs on evaporator, this pressure must be higher than atmospheric pressure to prevent any air entry into the refrigeration system. Also the temperature and pressure of refrigerant on condenser must depend on the thermodynamic and physical properties of the ambient to which the thermal energy is rejected (i.e. should be considered the amount of thermal energy that ambient can receive) (Dinçer & Kanoglu, 2010).

Properties of Refrigerants

The characterization of refrigerants is only possible through the study of their properties. The properties that allow the characterization of a refrigerant are related to safety (toxicity and flammability), environmental (ODP, GWP, TEWI, LCCP, LCA and residence time in atmosphere), compatibility with materials (e.g., metals, insulators and lubricants) and performance (efficiency, properties of thermal energy transfer and critical point). Other important properties are the physical properties such as sound speed, glide and work pressure (McLinden, 2011; McQuay, 2002).

Are now studied the properties of refrigerants described in the previous paragraph.

Toxicity and Flammability

Toxicity and flammability are the two parameters used by ASHRAE (American Society of Heating, Refrigerating and Air Conditioning Engineers) to evaluate the level of security resulting of a refrigerant using. To facilitate this classification, the ASHRAE Standard 34 (2010) has adopted a standard matrix that relates both parameters, as can be seen in Figure 5.

The toxicity of a substance is defined as its concentration in an environment to cause injury in the human body (ASHRAE, 2010). A substance that has a high stability in the atmosphere (i.e. remains in the environment with the same characteristics over a long period of time) is capable to penetrate more easily into the human body through the respiratory tract. This substance can easily reach to several organs of the human body with the same characteristics when are emitted, concentrating himself on several

Figure 5. Classification matrix of refrigerants regarding the safety of their use (ASHRAE, 2010)
organisms of the human body, thus causing more profound damages. On the other hand, a substance that is more reactive (i.e. the opposite of stable) interact violently when in contact with the human body, causing damage in its surface, namely, irritation on skin, respiratory systems and eyes (McQuay, 2002).

Acute toxicity is the term used to indicate human exposure to high concentrations of a substance for short periods of time. For example: the exposure to a leakage of refrigerant inside a closed space.

Chronic toxicity refers the repetitive human exposure to low concentrations of a substance for extended periods of time. For example: the exposure experienced by a maintenance and installer technician.

Threshold Limit Value (TLV) is the maximum concentration value of a substance present in an environment to prevent the occurrence of problems in the human health, after an exposure to chronic toxicity. TLV may vary from person to person, according to their habits (smoking, alcohol or other drugs), health status, age, medication, among others (ASHRAE, 2010).

According to the toxicity level presented by refrigerants, the ASHRAE Standard 34 (2010) classifies them into two groups, class A and B, as can be seen in Figure 5.

The flammability of a substance is defined as the ease with which it ignites and burn. Lower Flammability Limit (LFL) represents the minimum concentration value of a substance in air at the STP conditions, in a perfect homogeneous mixture, in which exist the possibility of the substance ignite, being expressed in [g/cm³]. Flame spread velocity shows the speed at which the combustion reaction occurs, being expressed in [m/s]. Heat Of Combustion (HOC) represents the thermal energy released during the combustion of a substance. This index can be expressed in the following units [kJ/kg] (ASHRAE, 2010).

According to the level of flammability presented by refrigerants, the ASHRAE Standard 34 (2010) classifies them into four groups, class 1, 2, 2L, and 3, as illustrated in Figure 5.

From study of the matrix present in Figure 5 it can be concluded that:

Class A: For refrigerants belonging to this class, there are no reported cases of intoxication in humans for concentrations less than or equal to 400 ppm by volume. This determination was based on the TVL of the respective refrigerant;

Class B: For refrigerants belonging to this class, were found cases of intoxication in humans exposed to concentrations below 400 ppm by volume. This determination was based on the TVL of the respective refrigerant;

Class 1: For refrigerants belonging to this class, the flame propagation on STP conditions is not observed;

Class 2: The refrigerants belonging to this class have a low LFL value (i.e. low flammability), above 0.17 [g/cm³], a HOC value below 18.996 [kJ/kg] and a low velocity of flame spread, below 10 [cm/s], for STP conditions;

Class 2L: The refrigerants belonging to this class have a low LFL value (i.e. low flammability), above 0.17 [g/cm³], a HOC value higher to 18.996 [kJ/kg] and a high velocity of flame spread, above 10 [cm/s], for STP conditions;

Class 3: The refrigerants belonging to this class are very flammable. These has a high LFL value, below 0.17 [g/cm³], a HOC value higher to 18.996 [kJ/kg] and a high velocity of flame spread, above 10 [cm/s] for STP conditions.

It is possible to predict some characteristics of refrigerants, including flammability, toxicity and the residence time in atmosphere, through the study of the chemical composition of substances, as can be seen in Figure 6. In table 2 is presented the flammability for several families of refrigerants.

From the analysis of Figure 6 it may be concluded that:
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Figure 6. Triangle expressing the relation between chemical constitution, flammability, toxicity and the residence time in atmosphere of organic refrigerants
(Calm & Didion, 1998)

- Refrigerants rich in hydrogen (H) are highly flammable and have a very low residence time in the atmosphere (consequence of its high reactivity). Example: the hydrocarbon compounds.
- Refrigerants rich in chlorine (Cl) and bromine (Br) are highly toxic. Example: ammonia.
- Refrigerants rich in fluorine (F) and chlorine (Cl) present a high residence time in atmosphere (consequence of its low reactivity). Examples: the family of CFCs compounds (halogenated compounds).

Efficiency

The higher the efficiency of a refrigeration system, the less the amount of electrical energy required to promote a similar cooling capacity. The efficiency of a refrigeration machine, thermal efficiency to first law or COP (Coefficient of Performance) may be defined as the ratio between the energy objective of the cycle and the amount of energy introduced into the cycle to reach the energy aim.

Carnot cycle represents the theoretical cycle completely reversible for a refrigeration system whose efficiency may be expressed only depending on temperatures of the heat sources (i.e.,

\[ COP_{MF(CARNOT)} = \frac{T_f}{T_q - T_f} \quad \text{and} \quad COP_{BC(CARNOT)} = \frac{T_q}{T_q - T_f} \]

Note that properties of refrigerants are not...
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included in this equation. So efficiency can be considered a characteristic of the refrigeration system, not a property of refrigerant. There are other parameters inherent to the refrigeration system, thus not depending on the property of refrigerants, which directly influence the efficiency of these systems. Some of these parameters are the efficiency of electric motor, compressor efficiency (at full load or partial load), design and construction of heat exchangers and operating conditions. Others properties of refrigerant that may affect the efficiency of the refrigeration system are the transfer properties (compressibility), thermal energy transfer properties and acoustic velocity, among others (McQuay, 2002). In table 2 is presented the system efficiency for several families of refrigerants.

Thermal Energy Transfer Properties

The efficiency of a refrigeration cycle is maximum, only if the refrigerant presents a high capacity to transfer thermal energy. The use of a refrigerant that presents good properties of heat transfer, property that is reflected in its heat transfer coefficient, allows the construction of more compact refrigeration systems, especially as regards the heat exchangers. Thus, the decrease in size of heat exchangers will result in a price decrease of the refrigeration system. There are several factors that influence the heat transferred by a refrigerant. Some of these factors are related with characteristics of the refrigeration system components. For example: the layout and design of piping and other elements, and flow rate (Reynolds number). Other properties of refrigerants that affect the overall heat transfer ability of the refrigeration system are dynamic viscosity ($\mu$), specific heat ($c_p$) and thermal conductivity ($k$). These properties are used to calculate the Prandtl number $Pr = \frac{\mu}{k}$, a factor widely used on the sizing and design of heat exchangers.

The objective is to use as refrigerant, a substance capable to “carry” large amounts of energy (i.e. presents a higher specific heat) and easily transfers energy (i.e. have a higher thermal conductivity). It is also desirable that substance presents a low viscosity, thus allowing the increase of turbulence on flow and reduces the mechanical power produced by the compressor to promote its movement (McQuay, 2002).

ODP (Ozone Depletion Potential)

The ODP value is the index that characterizes the participation of a refrigerant molecule in the process of ozone layer destruction. The value of this index is calculated through the comparison with the contribution to the process of ozone layer destruction of the reference molecule, the molecule of R11 or R12, both presenting a ODP = 1. This value is considered the maximum potential of ozone layer destruction (Benhadid-Dib & Benzaoui, 2012).

With the signature of the Montreal Protocol in 1989, it was agreed between the signatory countries the abolition of all refrigerants that present a value of ODP > 0. These were gradually replaced by others that do not promote the ozone layer depletion (Calm, 2008). Currently the production and commercialization of refrigerants that present a value of ODP > 0 is prohibited in the European Union, as well as the commercialization of refrigeration systems prepared to use this type of refrigerants (Benhadid-Dib & Benzaoui, 2012). It is possible to predict the contribution of refrigerants to the process of ozone layer destruction through the study of its chemical composition, as can be seen in Figure 7.
Analysing the Figure 7 it can be concluded that the ODP value of a refrigerant increases with the concentration of chlorine (Cl) or bromine (Br) in chemical constitution of substance.

Halogenated compounds (CFCs), rich in chlorine and fluorine atoms are very stable in nature. When they reach the Earth’s stratosphere, these compounds react with ozone molecules due to interaction with the incident sunlight, dissociating them according to the chemical equation

\[
(CFC + \text{UV solar radiation} + 2O_3 \rightarrow 3O_2 + Cl^+) \quad \text{— named photodissociation.}
\]

The result of this reaction is chlorine free radicals that present a high residence time in atmosphere. During his lifetime, free radicals of chlorine can destroy thousands of ozone molecules, until his combination with other substance beyond the ozone molecules.

The ozone layer destruction leads to increased entry of solar ultraviolet radiation on Earth atmosphere, which represents a high risk to public health, including the increase incidence of skin cancer and burns caused by prolonged exposure to solar radiation (Dinçer & Kanoglu, 2010). In tables 2 and 8 is presented the ODP for several families of refrigerants.

**GWP (Global Warming Potential)**

GWP value is an index that characterizes the participation of a refrigerant molecule in the greenhouse increase. The value of this index is calculated through the comparison with the contribution to the greenhouse effect of the reference molecule, a molecule of CO₂, presenting a GWP = 1.

*Figure 7. Triangle expressing the relation between chemical constitution and the ODP value of organic refrigerants (Calm & Didion, 1998)*
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This comparison can be made according to heating effect caused by a molecule of refrigerant during different time periods (20, 100 or 500 years), being the most common used the 100 years (GWP$_{100}$).

With the application of the Kyoto Protocol in 2005, it was agreed between the signatory countries, the abolishing of all refrigerants that present a high-GWP value. These were gradually replaced by others that do not promote the increased greenhouse effect (Benhadid-Dib & Benzaoui, 2012).

Recently several countries have published legislation in order to reach the targets agreed in the Kyoto Protocol. Are signatories of the Kyoto Protocol 175 countries, except the United States of America and others (UN, 2014). It is also possible to predict the contribution of refrigerants to the process of global warming through the study of its chemical composition, as can be seen in Figure 8.

Analysing the Figure 8 it can be concluded that GWP value of a refrigerant increases with the concentration of fluorine (F) atoms present in chemical constitution of substance. GWP value of a refrigerant increases with the ability of its molecules in absorb solar radiation reflected by Earth (infrared radiation) and its residence time in the atmosphere. The increase of greenhouse effect may result in: an intermediate warming of the atmosphere (estimated as 3 to 5 ºC by 2050); a rise in the level of oceans (estimated as 20 cm by 2050) and climatic effects (increases in drought, rain, snow, warming and cooling) (Dinçer & Kanoglu, 2010).

Molecules with higher GWP values are those that present chemical bonds of carbon-fluorine (C-F).

Currently, about 95% of refrigerants of the HFCs family used worldwide present a GWP value between 700 and 4000 (Kohler, 2012). TEAP (Technology & Economic Assessment Panel), technical and
research unit created by UNEP (United Nations Environment Programme - Ozone Secretariat), proposes the classification of refrigerants according its GWP value could be seen in Table 1. In tables 2 and 8 is presented the GWP for several families of refrigerants.

**TEWI (Total Equivalent Warming Impact)**

TEWI value expresses the performance ratio between the refrigeration cycle and its overall impact on the environment resulting from use of a refrigerant. Applying this parameter is possible to determine the total amount of GHG emissions related to use of a refrigerant through the accounting of direct emissions (leakages) and indirect emissions (GHG emissions resulting from electricity production that is consumed by the refrigeration system - parameter related with the refrigeration system efficiency), as can be seen in Figure 9.

The value of indirect GHG emissions (registered during the refrigerant lifespan) represents the largest share of GHG emissions related to a refrigerant use. Thus, TEWI index depends on how the electricity power is generated. Replacing a refrigerant that presents a high-GWP value by other with a lower GWP value, counting only with the value of direct GHG emissions is not the best solution. If the substitute refrigerant has worst thermophysical and thermal energy transfer properties, the replacing will result in a decreased performance of the refrigeration cycle. Thus the refrigeration systems need to consume a larger amount of electric energy to achieve an equal cooling or heating capacity.

In summary, the replacement of a refrigerant needs to be properly planned or will lead to increased costs of operating the system and increase of GHG emissions. Through this parameter is possible to evaluate more comprehensively the feasibility of replacing a refrigerant.

As weak points of this parameter, not include the GHG emissions related with production, handling and transportation of refrigerants.

The value of this parameter is obtained by applying the following equation (Benhadid-Dib & Benzaoui, 2012):

$$TEWI = GWP \left[ L \times n + m \left[ 1 - C \right] \right] + \left[ n \times E \times \beta \right]$$  \hspace{1cm} (1)

where:

**Table 1. Classification table of refrigerants according its GWP value**

<table>
<thead>
<tr>
<th>GWP&lt;sub&gt;100&lt;/sub&gt;</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>GWP &gt; 30</td>
<td>Ultra low-GWP</td>
</tr>
<tr>
<td>GWP &gt; 100</td>
<td>Very low-GWP</td>
</tr>
<tr>
<td>GWP &gt; 300</td>
<td>Low-GWP</td>
</tr>
<tr>
<td>GWP &gt; 1000</td>
<td>Moderate-GWP</td>
</tr>
<tr>
<td>GWP &gt; 3000</td>
<td>High-GWP</td>
</tr>
<tr>
<td>GWP &gt; 10 000</td>
<td>Very High-GWP</td>
</tr>
<tr>
<td>GWP &gt; 30 000</td>
<td>Ultra High-GWP</td>
</tr>
</tbody>
</table>

(Kohler, 2012)
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Figure 9. Simplified scheme to the analysis of TEWI concept (Kohler, 2012; Hwang, 2013a)

GWP – Global Warming Potential;
L – Annual amount of the refrigerant emissions (leakage) [kg];
n – Lifetime of the refrigeration system [years];
m – Refrigerant charge [kg];
C – Recovery factor/refrigerant recycling [between 0 and 1];
E – Annual energy consumption of the refrigeration system [kWh];
\[ \beta \] – Carbon dioxide emissions \( \frac{\text{kg}}{\text{kWh}} \).
LCCP (Life Cycle Climate Performance)

The LCCP is the natural broadening of the TEWI index, which focused on refrigerant during their manufacture and usable life. All the direct and indirect contribution to Global Warming is taken into account from its manufacturing to their disposal (include: recovery and final treatment), passing through their use (operation), see Figure 10.

To evaluate the global impact of a refrigerant is necessary to define its production method, how is used and wasted (Riva et al., 2006).

The value of LCCP can be obtained by adding the GWP values resulting from emissions during the refrigerant manufacturing process on the Equation 1 of TEWI, namely the GWP resulting from indirect emissions - $RIE$ (energy consumption during manufacturing) and GWP resulting from direct emissions - $FE$ (fugitive emissions during the refrigerant production), as can be seen on Equation 2.

$$TEWI = (GWP + EIR + FE) \times \left( L \times n + m \left[ 1 - C \right] \right) + (n \times E \times \beta)$$ \hspace{1cm} (2)

where:

FE – Fugitive emissions;
RIE – Refrigerant Indirect Emissions during the manufacturing process.

There are specific software applied to each area of refrigerants use to calculate the value of LCCP. This software has in its database, pre-defined data on CO$_2$-eq emissions resulting from the production and use of a refrigerant according to the climate conditions existing in the location where the refrigerant is applied. An example of this software is the GREEN-MAC, applied by the automotive industry (Hwang, 2013b).

LCA (Life Cycle Assessment – LCCO2)

LCA also known as life cycle analysis, ecobalance or cradle-to-grave analysis is the valuation of the environmental impacts of a given product or service caused by its existence. This parameter joins together

Figure 10. Simplified scheme to the analysis of LCCP concept
(Hwang, 2013a)
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with the Global Warming Impact, also the eutrophisation potential, the acidification potential and the ozone depletion potential. The advantage that LCA present in relation to LCCP is in its standardization: LCA is ruled under ISO 14000 Standards. Thus, the LCA is most accurate in calculating the GHG emissions (Rebitzer et al., 2004).

The “Carbon Footprint” is considered an output from the LCA and is considered one the most objective result of a LCA study. To calculate the “Carbon Footprint” parameter is used the LCA method (POST, 2006).

Applying the concept of “Carbon Footprint” to a refrigerant allows the calculation of the total amount of CO₂ and other GHG, emitted over the full life cycle of a refrigerant, as can be seen in Figure 11. The LCA final result is expressed in grams of CO₂-eq per kilowatt hour of generation (gCO₂-eq/kWh).

LCA is a calculation method of CO₂-eq emissions more detailed and expansive than TEWI and LCCP. When applied, LCA method allows the calculation of total direct and indirect emissions resulting from the whole lifecycle of refrigerant and the devices that supports it (i.e. the entire components of a refrigeration system), namely during (Rebitzer et al., 2004):

- Design and development of technologies;
- Row material acquisition and transformation;
- Production of system devices components and refrigerant;

Figure 11. Simplified scheme of the environmental impact of a refrigerant
(Hwang, 2013a; 2013b)
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- Process of assembly;
- Operation (includes servicing);
- Recovery, recycling or destruction of refrigerant and system devices.

LCA method also includes the CO₂-eq emissions resulting from energy consumption, transportation and solid, liquid and gaseous waist produced between all steps of a refrigerant and system devices life cycle.

Compatibility with Materials

Before the commercialization of a new refrigerant it is important to understand how it reacts when in contact with the materials constituents of the refrigeration system (copper, steel, brass, lubricants, gaskets, seals, among others). All the compatibilities between the materials and refrigerant should be studied in order to understand if will cause the degradation of thermophysical properties and decrease of thermal energy transfer by the refrigerant. The damage caused on the components of the refrigeration system due to non-compatibilities with the refrigerant will allow the refrigerant leakage to the ambient. The use of inert refrigerants, substances that present a high stability in the ambient, it would be the ideal option in terms of materials compatibility. Thus, the compatibility with materials is presented as one of the greatest benefits resulting from utilization of CFCs refrigerants. Now is analysed the compatibility between the refrigerants and some of the most sensitive materials that constitute the refrigeration systems (McQuay, 2002):

- **Electric Motor:** The hermetic compressors are the most used compressors. In these types of compressors the electric motor finds it permanently exposed to refrigerant. This is important because it allows the direct refrigeration of windings of the electric motor by the refrigerant in circulation. From interaction between the refrigerant and insulation may result the absorption of refrigerant by the isolation and extraction of polymer from insulation by the refrigerant. This may degrade the insulation and promote the occurrence of faults in the electric motor. The polymer extracted by the refrigerant may deposited on any part of the refrigeration system and obstruct the refrigerant flow. The resin used for the insulation of the electric motor windings may also be affected if is exposed to refrigerant at high temperatures. Thus, during a process of refrigerant replacement, the selection of the new refrigerant is very important, because is necessary protect the compressor existing on the facility. The new refrigerant must be compatible with the origin materials of the refrigeration system;

- **Elastomers and Plastics:** There are several materials that can be made from elastomers, namely, gaskets and rubbers (i.e. sealing materials). Refrigerants and lubricants can cause the extraction of the filler material and damage the properties of sealing materials, through their expansion or contraction. The properties of plastic materials may also be affected by the exposure to refrigerants. Its degradation decreases with the increasing concentration of fluorine atoms in the composition of the refrigerant;

- **Metals:** The reactivity between refrigerants and metals increases depending on the conditions of the system. For example, the increase of refrigerant temperature or pressure.
Lubricants

All the mechanical components that produce movement suffer abrasion, thus requiring lubrication. In the refrigeration systems case, some of the components that require lubrication are the compressor and various valves scattered throughout the system. The utilization of a good lubricant should protect these equipment against wear caused by the contact between the moving parts and increase the compressor sealing. The lubricant should also be chemically compatible with the refrigerant and the other materials present in the refrigeration system to not damage them. It is expected that the lubricant and refrigerant are chemically compatible, allowing the respective homogeneous mixture. The lubricant should be sufficient miscible in the refrigerant to minimize the negative effects on heat transfer and to ensure the oil return to compressor. The proper operation and longevity of the refrigeration system directly depend on the interaction between the lubricant and refrigerant. Lubricating oils are classified according to their origin/composition. There are the following types of lubricants: mineral oils (MO); alkylbenzenes (AB); polyol esters (POE); polyalkylene glycol (PAG); modified polyalkylene glycols and polyvinyl ethers (EVP). Mineral oil and POE lubricants are the two types of lubricants more used in air conditioning systems. Mineral oils are natural (petroleum products) whereas the POE lubricants are synthetic (alcohols). Mineral lubricants are not compatible with POE oils, although it can happen mixing these lubricants after replacing for a new refrigerant. Synthetic lubricants are more hygroscopic (i.e. have a greater ability to absorb moisture) than natural lubricants. So the synthetic lubricants should never be exposed to atmospheric moisture because its combination will cause a decrease in the refrigeration cycle performance. Refrigeration systems must be properly sealed from outside ambient to not allow the penetration of external moisture. If exists the penetration of moisture into the refrigeration system, this may chemically combine with the carbon and form carbonic acid, which will contribute to the degradation of the refrigeration system materials. In table 2 are presented the lubricants compatible with the several families of refrigerants.

Table 2. Summary containing some properties of refrigerants by family of refrigerants

<table>
<thead>
<tr>
<th>Fluid Properties</th>
<th>Synthetic</th>
<th>Natural Refrigerants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HFCs</td>
<td>HFOs</td>
</tr>
<tr>
<td>GWP</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Flammability</td>
<td>No</td>
<td>Can be ignited</td>
</tr>
<tr>
<td>Toxicity</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Price of refrigerant</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Price of system</td>
<td>Low</td>
<td>Medium to high</td>
</tr>
<tr>
<td>Theoretical system efficiency</td>
<td>Good</td>
<td>Medium</td>
</tr>
<tr>
<td>Traditional lubricants</td>
<td>Alky benzenes (AB)</td>
<td>Poly alkaline \ glycol (PAG)</td>
</tr>
<tr>
<td></td>
<td>Polyol ester (POE)</td>
<td>Poly \ alkaline \ glycol (PAG)</td>
</tr>
<tr>
<td></td>
<td>Poly \ vinyl \ ether</td>
<td>Poly \ alkaline \ glycol (PAG)</td>
</tr>
</tbody>
</table>
Critical Point

The critical point of a refrigerant is found using its (p, h) or (t, s) diagrams. This is the point where the refrigerant properties in liquid and vapour state meet and become indistinguishable. At the critical point the temperature, density and composition of refrigerant are identical in the liquid/gaseous phase. If the refrigeration cycle operates above the critical point, it is difficult to separate the gas and liquid phases of the refrigerant. Operating a refrigeration cycle below (but very close) to critical point conditions brings some benefits, namely high volumetric capacity. On the other hand, there is a decrease in system efficiency, caused by the reduction of cooling capacity.

Glide

The term Glide was introduced in the refrigerants market as response to the emerging use of blends of refrigerants (zeotropic mixtures).

Blends of refrigerants consist on a mixture of several refrigerants in the same or different proportions. Thus, the resulting refrigerant adopts the behaviour of all its components.

Glide is defined as the temperature difference between the beginning and end phase change of a refrigerant in the evaporator and condenser (see Figure 12). This happens because the refrigerants that constitute the mixture have different evaporation temperatures and the blend component that presents a lower evaporation temperature is the first to evaporate. At the moment when the first component begins to evaporate, there is a change in composition of the resulting mixture, and thus the establishment of a different average evaporation point of the mixture. The change in composition of the mixture is known as fractionation. The change on average evaporation temperature of the refrigerant mixture is called Glide.

Acoustic Velocity

The acoustic velocity is a parameter considered during the designing process of a refrigeration system. This parameter defines the maximum speed at which the refrigerant may circulate in the system. If the refrigerant circulates with a velocity higher or equal to supersonic velocity, shock waves will be produced and damage the equipment of the refrigeration system. Normally the refrigerant (gas) at the entrance of centrifugal compressors acquires a supersonic speed (Mach = 1). The acoustic velocity of a refrigerant increases with the temperature increasing and decreases with the pressure increasing.

Physical Properties

Through the study of the physical properties of refrigerants is possible to know its potentialities.

The evaporation and freezing temperatures are two practical examples of the physical properties of a refrigerant. The evaporation temperature of a refrigerant indicates the temperature levels at which the refrigeration system can operate. The freezing temperature of the coolant must be lower than minimum temperature attained in the refrigeration cycle in order to prevent the refrigerant solidification in the system.

Table 2 is a summary containing some properties of refrigerants previously studied by family of refrigerants.
After the analysis of Table 2, can be concluded:

- Natural refrigerants are abundant in nature so have a low cost;
- CO₂ presents the most theoretical low efficiency, because operates according to a transcritical cycle. Its refrigeration systems present a medium cost due to need of use special materials capable to containing the refrigerant or and compress it to a very high pressure;
- Ammonia refrigeration systems present a higher cost due to incompatibility with the materials which constitute them, in particular metals (ammonia is corrosive when mixed with moisture);
- Due to its high flammability (HCs) and high toxicity (ammonia) the amount of refrigerant used on refrigeration systems should be as smaller as possible to reduce the risk of explosion (HCs) and health problems in humans (ammonia);
- HFOs can be flammable under certain environmental conditions, thus the refrigeration systems for this family of refrigerants need some improvements in comparison to traditional systems, which makes them more expensive. How they are synthetic substances, present a high cost. This family of refrigerants is compatible with the commonly used lubricants;
• HFEs have a low applicability in refrigeration industry, being widely used as cleaning solvers for electronic equipments. There are few studies with HFEs operating as refrigerants. This family of refrigerants is compatible with the commonly used lubricants, cheaper than HFCs and present a theoretical efficiency near to CFCs compounds more used.

REFRIGERANTS AND ITS HISTORICAL EVOLUTION

As already been mentioned, the first patented refrigeration machine with the capacity to operate continuously was built by Jacob Perkins in 1834 and use ethyl ether (R610) as refrigerant. Ethyl ether (R610) was the first fluid known with good thermodynamic properties (i.e. evaporative effect). These properties were discovered by William Cullen in 1755, when obtained a little amount ice through the evaporation of ether (Melo, 2011).

Ether was also been used in many refrigeration machines built in early nineteenth century. Thus ether became the first refrigerant to be commercialized on a large scale. For being the first refrigerant to be used, ether was not the most suitable for this purpose, being its utilization dangerous due to highly flammability (Dinçer & Kanoglu, 2010).

In the following years, new refrigerants were studied, namely, ammonia (R717), carbon dioxide (R744), the monocloroetano (R160), isobutane (R600a), dichloromethane (R30), sulfur dioxide (R764) and air (R729). Between all these fluids, only three became commercial. The ammonia and sulfur dioxide have been widely used in small refrigeration units and the carbon dioxide preferably used in cold rooms of ships. All of these fluids have thermochemical interesting properties, except the components (SO2, CH3Cl, NH3 and C2H5Cl) toxic to humans, (CH3Cl, C2H5Cl and NH3) highly flammable and (CO2) which can only be used at very high pressures (Benhadid-Dib & Benzaoui, 2012). The intention was find any fluid that worked.

In early twentieth century, domestic refrigerators consisted on ice boxes. The using of ice boxes had the following disadvantages: need for a daily ice supply, water drainage from thawing and variable rate of cooling. Until then, the ice used in ice boxes was extracted from cold places in nature, for example, from Hudson River in the USA and from Lousã Mountain in Portugal.

In 1928 the Company Frigidaire asked a group of scientists led by Thomas Midgley to discover a non-toxic and non-flammable refrigerant. As a result of this investigation were introduced the first halogenated hydrocarbons compounds in refrigeration industry, the chlorofluorocarbons (CFCs), in the beginning of 30’s decade. This event leads to abandonment of natural substances and beginning of the security and durability generation. The production of CFCs compounds has revolutionized not only the refrigeration industry, because they have been also used in many other applications, including cellulosic foams, aerosols and cleaning solvents. Between all the CFCs compounds known, the most widely used as refrigerants were the dichlorodifluoromethane (R12) and trichlorofluoromethane or Freon (R11). These fluids were initially produced and marketed by DuPont and Nemours companies. Obtained from petroleum distillation (i.e. are petroleum products), CFCs are composed by atoms of carbon, chlorine and fluorine.

For about 70 years the CFCs compounds dominated the domestic and slight commercial refrigeration. This was the time required to realize that CFCs compounds do not present the characteristics which were initially determined, namely, the safety of their use and his non-aggressiveness to the ambient. Several
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accidents, including the death of people through inhalation of these gases in confined spaces had been registered. The high stability of these compounds allows their migration into the Earth stratosphere and its combination with the ozone molecules, contributes substantially to the destruction of ozone layer. This effect was discovered by Sherwood Rowland and Molina Mario, in 1974, when associated the ozone layer depletion with the release of CFCs compounds to environment. This theory was confirmed in 1985 with the discovery of a hole in the ozone layer over Antarctica (Dinçer & Kanoglu, 2010).

Thus it has become necessary to ban the CFCs compounds and look for new refrigerant replacements. In 1987, 25 countries together with the EC signed the Montreal Protocol, whose purpose would be to protect the integrity of the ozone layer through the implementation of measures to control the worldwide emissions, production and consumption of substances belonging to the CFCs family. The signing of this document is still considered a major milestone in the history of refrigeration, marking the beginning of environmental concern with the study of impact resulting from use of refrigerants (UNEP, 2000). It begins the ozone layer protection generation.

The measures and deadlines set by the Montreal Protocol have been intensified in the following years to its subscription, during the conferences of London (1990), Nairobi (1991), Copenhagen (1992), Bangkok (1993), Vienna (1995), Montreal (1997) and Beijing (1999). One year after the signature of the Montreal Protocol was created the Intergovernmental Panel on Climate Change (IPCC), a scientific intergovernmental organ under the competence of the United Nations. Its goal is the production of reports that support the United Nations Framework Convention on Climate Change (UNFCCC), which is the key international treaty to reduce global warming and cope with the consequences of climate change. The first IPCC Assessment Report was published in 1990 (IPCC, 2007a).

In Germany, was published the Regulation CFC/Halon Prohibition Ordinance (FCKW-Halon-Verbots-Verordnung) in 1991. This document outlined a time scale for the CFCs compounds phase-out, according the implications of Montreal Protocol. Later, in 2006, the Regulation CFC/Halon Prohibition Ordinance was replaced by the Regulation Chemical Ozone Layer V (ChemOzonschichtV) (Refripro, 2014). The main aims of the Regulation Chemical Ozone Layer V was the prevention of the emission of ozone depleting substances (CFCs and HCFCs) into the atmosphere, through the regular inspection activities to monitoring and maintain in good conditions the refrigeration and air conditioning plants with regard to leakages and recovery of refrigerants.

ChemOzonschichtV serves as complement to CE Regulation nº 2037/2000. This last one emerged from adaptation of the Montreal Protocol, created to regulate the emission of substances that lead to destruction of ozone layer in the European space (EU, 2000). The signature of the Montreal Protocol promoted the gradual replacement of CFCs compounds by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), less harmful compounds.

The utilization of CFCs compounds was finally abandoned in 1995, in the European Union with the interruption of its production. HCFCs compounds have a lower stability on environment, which makes them less harmful to the environment than CFCs compounds. These substances are considered refrigerants of transition, because it is predicted that its utilization be temporary until the development of new substances more environmentally friendly.

The monoclorodifluormetano (R22), the dichlorotrifluoroethane (R123), the monoclorotetrafluoretano (R124), the dicloroflouretano (R141b) and certain blends (R401A and R408A and R409A) were some of the most commonly used refrigerants of HCFCs family. Several countries have published their own laws to accelerate the phase-out of halogenated compounds (CFCs and HCFCs). For example, in 1994
was published the Regulation EC 3093/94, document that specifies the phase-out periods to HCFCs compound in the European Community, see Table 3. In USA the phase-out period of R22 (HCFCs) ends on 2020 (Copeland & Emerson, 2008).

Later in 2000 was published a rectification to EC 3093/94, the CE Regulation 2037/2000. The main measures of Regulation 2037/2000 were: continuing the gradual recovery of the CFCs and HCFCs compounds, performed during the maintenance process of refrigeration and air conditioning equipment already installed, allowing the recycling, regeneration or destruction of these compounds; and the creation of mechanisms that promote the regular inspection and maintenance of refrigeration and air conditioning equipment in order to prevent refrigerant leakage.

The molecules of hydrofluorocarbons (HFCs) are known as the replacement refrigerants. These compounds do not have chlorine atoms in its constitution, which prevents their participation in the process of ozone layer depletion. However, while not participating in the process of ozone layer destruction, HFCs compounds contribute significantly to the greenhouse effect increase (i.e. global warming).

The trifluoromethane (R23), difluoroethane (R32), pentafluoroethane (R125), tetrafluoroethane (R134a), trifluoroethane (R143a), difluoroethane (R152a) and other blends (R404A, R407C R410A, R422A, R422D, R427A and R507A), were some of the most commonly used refrigerants of HFCs family.

The signature of the Kyoto Protocol is also known as one of the most important factors in the history refrigerants. This Protocol arises as a consequence of a series of conferences whose theme was the climate changes and its main objective was the reduction of GHG emissions by 5% on the period between 2008 and 2012, with reference to GHG emissions of 1990. To accomplish this objective each signatory country was established its own goals. For example, the European Union has committed initially to reduce the GHG emissions by 8%. The polluter’s agents are, in this case, carbon dioxide, methane, nitrous oxide and fluorinated gases (UN, 1998). With the signature of the Kyoto Protocol arises the global warming generation.

Rectified and signed by 175 countries, the Kyoto Protocol was published in 2005. All countries that have signed this Protocol have committed to take strict measures to reduce the emissions of GHG, considered as anthropogenic cause of global warming and responsible for global climate changes (UN, 1998).

According to the Kyoto Protocol, the reduction of GHG can be achieved through the application of three mechanisms: the Clean Development Mechanism (CDM), the emissions trading, and Activities Implemented Jointly (AIJ) (UN, 1998).

To achieve the rectified targets imposed by the Kyoto Protocol, the European Union committed itself to complete three objectives until 2020: reduce the GHG emissions by 20%, reduce the power consumption by 20%; and increase the amount of energy produced through renewable sources for 20% of total

Table 3. Phase-out period of HCFCs in the European Union, according the Regulation EC 3093/94

<table>
<thead>
<tr>
<th>Regulation EC 3039/94</th>
<th>Deadline</th>
</tr>
</thead>
<tbody>
<tr>
<td>The level of HCFCs marketed or used by producers and importers does not exceed the 1989 level.</td>
<td>1/1/1995</td>
</tr>
<tr>
<td>35% reduction in the level of HCFCs marketed based on calculated in 1995.</td>
<td>1/1/2004</td>
</tr>
<tr>
<td>60% reduction in the level of HCFCs marketed based on calculated in 1995.</td>
<td>1/1/2007</td>
</tr>
<tr>
<td>95% reduction in the level of HCFCs marketed based on calculated in 1995.</td>
<td>1/1/2010</td>
</tr>
<tr>
<td>Prohibition of placing on the market of virgin HCFCs.</td>
<td>1/1/2015</td>
</tr>
</tbody>
</table>

(Benhadid-Dib & Benzaoui, 2012)
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primary energy consumed. Posteriorly have been defined new goals by the European Union, long-term goals, to be achieved until 2050: reduce the GHG emissions by 60%; reduce the power consumption by 40%; and increase the amount of energy produced from renewable sources to 33% of total primary energy consumed (Morais, 2011).

In January 2006 was published the CE Regulation 842/2006, concerning to the utilization of certain fluorinated gases that contribute to greenhouse effect, the F-Gases. This Regulation was created with the intent to reduce the GHG emissions in the European Union, through the abolition of some refrigerants of the HFCs family, partially halogenated compounds. In this context the most important measures were: the contention (prevention, minimization and immediate repair of refrigerant leakage); recovery of F-Gases for recycling, reclamation or destruction; reporting by manufacturers, importers and exporters of refrigerant quantities greater than one tonne per year; refrigerant container and refrigeration system properly labelled with the designation of the refrigerant used and the respective main classifications (toxicity, flammability, GWP, ODP, among others); and limiting the use of certain refrigerants, under certain operating conditions (EU, 2006a).

It was also published on May 17, 2006 the MAC Directive 2006/40/EC regarding to emissions from air conditioning systems in motor vehicles. This directive restricts the use of refrigerants with a GWP\(_{100}\) higher than 150 in automotive air conditioning systems for all new automobiles and trucks, manufactured from 1\(^{a}\) January 2017 (EU, 2006b). It should be referred that the automotive industry is responsible for 50% of worldwide sales of refrigerant R134a (Melo, 2011).

On April 16, 2014 was published the Regulation EU 517/2014 on F-Gases and repealing the Regulation EC 842/2006. This Regulation was created based on the 4\(^{th}\) Assessment Report of the Intergovernmental Panel on Climate Change of the UNFCCC, in which it was resolved that F-Gases emissions should be reduced by 72% to 73% by 2030 and by 70% to 78% by 2050, values compared to 1990 levels (EU, 2014b).

The publication of Regulation EU 517/2014 shows the continuing efforts of the European Union in promoting the use of refrigerants with a very low-GWP. This specifies the phase-out periods in the European Union to HFCs compounds that present a high and medium GWP, see Table 4.

Also, according an appropriate transitional period (not defined yet), the use of refrigerants with a very high-GWP of 2500 or more, subject to maintenance processes, with a charge size of 40 tonnes of CO\(_2\)-eq or more should be banned.

<table>
<thead>
<tr>
<th>Table 4. Phase-out period of HFCs in the European Union, according the Regulation EU 517/2014</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regulation EU 517/2014</strong></td>
</tr>
<tr>
<td>Domestic refrigerators and freezers that contain HFCs with GWP of 150 or more.</td>
</tr>
<tr>
<td>Refrigerators and freezers for commercial use (hermetically sealed equipment) that contain HFCs with GWP of 2500 or more.</td>
</tr>
<tr>
<td>Refrigerators and freezers for commercial use (hermetically sealed equipment) that contain HFCs with GWP of 150 or more.</td>
</tr>
<tr>
<td>Stationary refrigeration equipment that contains HFCs with GWP of 2500 or more. Except equipment intended for application designed to cool products to temperature below - 50 ºC.</td>
</tr>
<tr>
<td>Multipack centralised refrigeration systems for commercial use with a rated capacity of 40 kW or more, or F-Gases with GWP of 150 or more, except in the primary refrigerant circuit of cascade systems where are used F-Gases with a GWP of less than 1500 may be used.</td>
</tr>
<tr>
<td>Hermetically sealed equipment that contains HFCs with GWP of 150 or more.</td>
</tr>
<tr>
<td>Single split air conditioning systems containing less than 3 kg of F-Gas with GWP of 750 or more.</td>
</tr>
</tbody>
</table>

(EU, 2014b)
On March 7, 2014 was published a Scientific review of the research regarding the safety aspects of R1234yf use in MAC systems. This study not found evidence of serious risks related to the R1234yf use in MAC systems under normal and foreseeable conditions. The publication of this study serves as an argument to persuade the vehicle manufacturers of safety resulting from the HFOs refrigerants use (EU, 2014c).

Currently, the demand for alternative refrigerants that are less harmful to the environment is one of the research areas with most featured in the refrigeration industry. Thus, the aim is to find refrigerants which do not contribute to the destruction of ozone layer or to increase greenhouse effect. In the absence of an ideal alternative refrigerant, pure or blend, it is necessary to define priorities on the research for a refrigerant that can be more environmentally friendly, has a good energy performance, be compatible with the currently used refrigeration systems, safe and has a low cost. To try to overcome this problem some future alternatives are available in the literature, namely:

**The Study of Pure Natural Refrigerants (Ammonia, Hydrocarbons, and Carbon Dioxide)**

According to the theoretical analysis made with the refrigerants (R134a, R404A, R407C, R410A, R717, R290, R600a and R1270) in chillers units used to air conditioning, ammonia (R717) presents the highest efficiency ratio (COP) for the different temperature ranges (-10/+35 °C and +5/+45 °C), preceded by isobutene (R600a) with the second highest COP. Although having lower theoretical efficiency, R410A has a higher volumetric efficiency, which allows the construction of more compact, cheap and competitive systems (Pedersen, 2012).

The use of CO₂ (R744) in MAC systems was also been studied: due to technical and safety issues remaining unresolved by the automotive OEM industry, despite years of development and large investments, this technology cannot currently compete with systems using HFCs and HFOs compounds in terms of cost/benefit (DuPont, 2008).

Cascade cycles are currently the commonly used technology to achieve safe and economical operating costs for very low temperature conditions in the refrigerant industry. CO₂/Ammonia or CO₂/N₂O systems are considered as viable alternatives for the replacements of the typical fluids. In this study CO₂, or R41 or dimethyl ether (DME) was used in the lower cycle and R1234yf, or R1234ze or ammonia was used in upper cycle. A blend called XP10 (R1234yf with R134a) was used in the upper cycle. The results for these fluids are compared against the traditional CO₂/ammonia cycle. CO₂ cycle has the lowest COP. DME cycles in lower circuit shows the best performance (DME is highly flammable, thereby necessitating the system of different designs in comparison to traditional systems which make the installations more expansive). In the upper cycles the difference between R1234yf, R1234ze, ammonia or XP10 appears to be small. Therefore the choice of the upper circuit refrigerant is most significant and ammonia does not offer a significant advantage, due to its toxicity (Naicker, 2014).

The low critical point conditions (T = 31.1 °C) of CO₂ refrigerant when compared with more conventional refrigerants can make CO₂ refrigeration systems inefficient. Above this point, there is no phase change of the refrigerant, meaning in a lower capacity of refrigerant to reject heat, being the transcritical cycle less efficient. In climates where ambient temperatures surpass 20 – 23 °C, transcritical operation is often unavoidable and CO₂ systems do not present the same success as in colder climes. It becomes necessary another additional medium (i.e. no air) to maintain the subcritical cycle operating when
ambient temperatures are above the transcritical threshold of CO$_2$. A cooling medium can be provided by coupling the high pressure side of the CO$_2$ refrigeration system to the ground with an aqueous loop. Since ground temperatures are typically lower than ambient temperatures during summer, subcritical cycle can be realised more often and vast improvements to coefficient of performance can be achieved. According to data collected at two supermarkets, the first utilizing ground coupling and second using a typical air cooled refrigeration cycle. The results show that geo-coupling lowers condensing temperatures provides a reduction rounding 25% of energy consumption. This improves opens up opportunities for CO$_2$ using in warmer climes (Leiper et al., 2014).

Using ammonia as refrigerant has great benefits in large refrigeration units, but can be relatively expansive for small to medium sized systems. However, a new concept using ammonia has now been developed for cold store and freezer plant which draws together existing technologies and integrates these within an efficient, compact, standalone packaged unit complete with air cooled condenser and housing.

The packaged ammonia plant is present as a viable alternative to an HFC/HFC based system for small to medium sized storage or freezer plant. Traditional site installed ammonia pumped circulation system would be more costly and may introduce hazards to human being health and safety due to the higher ammonia charge. With the package ammonia plants the disadvantages commonly associated to ammonia plants for this size range can be overcome and an efficient, low refrigerant charge (i.e. more safety), environmentally responsible solution can be offer with an attractive total cost of ownership (Tomlinson, 2014).

**The Study of the HFOs Refrigerants and HFOs/HFCs Mixtures**

By presenting a comparable performance and lower GWP to R134a, the refrigerant R1234fy is currently considered the most promising substitute to R134a, especially in automobile air conditioning systems. Otherwise, the R1234fy presents a lower performance than R410A witch difficult its application in residential air conditioners. Thus, is studied the use of mixtures between R32 and R1234yf at two mass fractions (80/20 and 50/50 in mass %), in order to test their use in residential air conditioners. The refrigerant mixture R1234fy+R32 with 20% of R32 mass fraction present a less heat transfer coefficient than pure R1234fy and the mixture with 50% of R32 mass fraction has a greater heat transfer coefficient than pure R1234fy at large heat and mass fluxes. The heat transfer coefficient of mixture at two concentrations are 20 – 50% lower than that of pure R32. The effects of mass diffusion on the heat transfer of a mixture are significant. Large mass and heat fluxes can improve the heat transfer coefficient of the mixture (Li et al., 2012).

After several studies to various climate and use conditions, the Japanese Automotive Manufacturers Association (JAMA) determined that R1234yf has the potential to reduce the total LCCP, or contribution to climate change, by 20 – 30% compared to R134a or R744 systems. DuPont estimate that R1234yf adoption in all new cars by the year 2017 has de potential to save more than 2,200 million litters (590 million gallons) of fuel annually due to emissions resulting from leakages – the equivalent of take approximately 1.5 million cars off road each year. In terms of safety of R1234yf use, this present a low toxicity and despite being a bit flammable is safe for use in automotive air conditioning. R1234yf can provide a low cost transition due its compatibility with proven current R134a based automotive air conditioning technology used today (DuPont, 2008).
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Was also tested the use of R1234ze as a blend component as an alternative to R134a and R410A. In Table 5 are shown some properties of the refrigerants studied (Low & Cooper, 2014). Are also included the properties of some of the most widely used HFCs refrigerants worldwide to enable the comparison between these fluids and new blends in study.

The mixtures R444A and R445A have a similar performance to R134a. These two mixtures have been investigated with the purpose of being applied in MAC systems. R444A presents a similar flammability to R1234yf while R445A in non-flammable at ambient temperature, becoming flammable at high temperatures. A theoretical cycle calculation comparison was made for conditions typical of those

Table 5. Some properties of the refrigerants studied

<table>
<thead>
<tr>
<th>Alternative Fluids to R134a and R1234yf</th>
<th>R134a</th>
<th>R444A</th>
<th>R445A</th>
<th>R1234yf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass</td>
<td>102.03</td>
<td>96.7</td>
<td>103.1</td>
<td>114.04</td>
</tr>
<tr>
<td>GWP&lt;sub&gt;100&lt;/sub&gt;</td>
<td>1430</td>
<td>92</td>
<td>130</td>
<td>4</td>
</tr>
<tr>
<td>Critical Temperature (°C)</td>
<td>101.1</td>
<td>103.2</td>
<td>98</td>
<td>94.7</td>
</tr>
<tr>
<td>Critical pressure (MPa)</td>
<td>4.059</td>
<td>4.278</td>
<td>3.973</td>
<td>3.382</td>
</tr>
<tr>
<td>Components</td>
<td>Single</td>
<td>R32</td>
<td>R125a</td>
<td>R1234ze</td>
</tr>
<tr>
<td>Components</td>
<td></td>
<td>R125a</td>
<td>R1234ze</td>
<td></td>
</tr>
<tr>
<td>Atmospheric boiling point/range (°C)</td>
<td>-26.4</td>
<td>-34.3 to -24.3</td>
<td>-50.3 to -23.4</td>
<td>-29.4</td>
</tr>
<tr>
<td>Lower Flammable limit at 60 °C</td>
<td>None</td>
<td>6.9%</td>
<td>8%</td>
<td>5.4%</td>
</tr>
<tr>
<td>Latent heat of vaporisation at atmospheric pressure (kJ/kg)</td>
<td>217</td>
<td>232</td>
<td>237</td>
<td>180</td>
</tr>
</tbody>
</table>

Fluids for Stationary Sector Applications

<table>
<thead>
<tr>
<th>Fluid</th>
<th>AC5X</th>
<th>LTR4X</th>
<th>HPR1D</th>
<th>R407A</th>
<th>R410A</th>
<th>R32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass</td>
<td>100.87</td>
<td>85.09</td>
<td>62.98</td>
<td>90.11</td>
<td>72.58</td>
<td>52.02</td>
</tr>
<tr>
<td>GWP&lt;sub&gt;100&lt;/sub&gt;</td>
<td>620</td>
<td>1295</td>
<td>407</td>
<td>2107</td>
<td>2088</td>
<td>675</td>
</tr>
<tr>
<td>Critical Temperature (°C)</td>
<td>102.2</td>
<td>85.8</td>
<td>80.9</td>
<td>82.3</td>
<td>71.4</td>
<td>78.1</td>
</tr>
<tr>
<td>Critical pressure (MPa)</td>
<td>4.24</td>
<td>4.74</td>
<td>4.515</td>
<td>5.657</td>
<td>4.902</td>
<td>5.782</td>
</tr>
<tr>
<td>Components</td>
<td>R32</td>
<td>R134a</td>
<td>R125a</td>
<td>R134a</td>
<td>R1234ze</td>
<td>R1234ze</td>
</tr>
<tr>
<td>Atmospheric boiling point/range (°C)</td>
<td>-31.3 to -26.1</td>
<td>-45.3 to -36.8</td>
<td>-57.3 to -43.6</td>
<td>-45 to -38.6</td>
<td>-51.4</td>
<td>-51.7</td>
</tr>
<tr>
<td>Lower Flammable limit at 60 °C</td>
<td>None</td>
<td>None</td>
<td>13%</td>
<td>None</td>
<td>None</td>
<td>14%</td>
</tr>
<tr>
<td>Latent heat of vaporisation at atmospheric pressure (kJ/kg)</td>
<td>222</td>
<td>250</td>
<td>332</td>
<td>236</td>
<td>273</td>
<td>382</td>
</tr>
</tbody>
</table>

(Low & Cooper, 2014)
Current and Future Trends of Refrigerants Development

in air conditioning application (evaporator and condenser refrigerant inlet temperature - 5/55 °C). Using R134a as reference, the others refrigerants have presented a COP relative to reference of: 101.6% to R444A; 98.5% to R445A; 100.3% to AC5X and 94.5% to R1234yf.

Applying the metric LCCP witch is evaluated using the car industry-developed GREEN-MAC software is possible to predict the ambient impact of a car air conditioning system filled with R134a, R444A, R445A or R1234yf, in a range of climates. The performance of R444A and R445A are comparable to R-1234yf although their direct GWP values are somewhat higher, because their energy efficiency can be better in some operation conditions. Acceptable performance was achieved through the use of R444A and R445A in systems manufactured for R134a or R1234yf. Have also been evaluated other fluids based on R1234ze for use in stationary sector applications, as can be seen in Table 5.

The AC5X is a non-flammable drop-in alternative to R134a, LTR4X is a non-flammable alternative for R32, R407 or R404A DX applications, and HPR1D is an alternative to R410A for DX applications, this blend presents a flammable range similar to R32. The AC5X and HPR1D have been evaluated for commercial and scroll compressors used in supermarket refrigeration.

The HPR1D blend has teste as drop-in substitute in a light commercial air conditioner/heat pump unit designed for R410A. The test results shown that HPR1D presents an improved performance compared to R410A, approaching performance of R32, but operating at lower compression discharges pressures and temperature (Low & Cooper, 2014).

The Study of HFCs Refrigerants with Low-GWP

Several authors have been studying the characteristics of HFCs family of refrigerants with low-GWP to be used as replacements to current used refrigerants.

In the next study were analysed the operation parameters of a refrigeration cycle at same evaporator and condenser refrigerant inlet temperature (4/40 °C) using different refrigerants (R22 - HCFC, R134a - HFC, R410A - HFC and R407C - HFC), as can be seen in Table 6 (Jain et al., 2011).

For studied conditions, the R407C presents the highest refrigerant efficiency (%) with the highest COP and lower compression work from the HFCs family in studied. R410A refrigerant has the lowest refrigerant efficiency (%) and COP.

Table 6. Table with several parameters for a refrigeration cycle operating at same evaporator and condenser refrigerant inlet temperature with the R22, R134a, R410A and R407C refrigerants

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HCFC</th>
<th>HFCs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R22</td>
<td>R134a</td>
</tr>
<tr>
<td>COP</td>
<td>2.352</td>
<td>2.31</td>
</tr>
<tr>
<td>Compressor Work (kW)</td>
<td>28.352</td>
<td>38.921</td>
</tr>
<tr>
<td>Refrigerant efficiency %</td>
<td>47.39</td>
<td>46.64</td>
</tr>
<tr>
<td>Mass flow rate (kg/s)</td>
<td>0.475</td>
<td>0.535</td>
</tr>
<tr>
<td>Condenser pressure (MPa)</td>
<td>1.938</td>
<td>1.314</td>
</tr>
<tr>
<td>Evaporation pressure (MPa)</td>
<td>0.432</td>
<td>0.25</td>
</tr>
<tr>
<td>Heat transfer rate (kW)</td>
<td>94.36</td>
<td>98.12</td>
</tr>
</tbody>
</table>

(Jain et al., 2011)
In other work was study the performance of R152a and R32 to replace R134a in domestic refrigerators. In this study was tested a refrigerator designed and developed to work with R134a, and its performance using R152a and R32 was evaluated and compared with its performance when R134a was used. The design temperature and pull-down time set by ISO for small refrigerator were achieved earlier using refrigerant R152a and R134a than using R32. The highest COP was obtained using R152a. The average COP obtained using R152a is 4.7% higher than that of R134a, while average COP of R32 is 8.5% lower than of R134a. Discharge pressure of 152a is practically equal to R134a with average percentage reduction of 0.8%. The discharge pressure of R32 was highest with average value of 8.1 and 7.2% higher than R152a and R134a, respectively. R152a offers lower energy consumption. The compressor consumes 4% and 3.2% less energy when 152a was used than R134a and R32, respectively. Summarizing, the system presents a better performance with R152a than with both R134a and R32. Thus, R152a can be used as replacement refrigerant for R134a in domestic refrigerators (Bolaji, 2010).

The Study of HCs Refrigerants and HCs/HFCs Mixtures

The HCs, HCs mixtures and HFCs/HCs mixtures appear as alternatives to be used in domestic refrigeration. A theoretical analysis with some HCs/HFC and HCs mixtures are made to the conditions obtained using the R12 and R22 at same evaporator and condenser refrigerant inlet temperature (-10/50 ºC). In Table 7 are presented the performance of different refrigerant in study (R600a/R290, R600/R290, R1270/R290 and R152a/R290).

For the conditions studied, the pure refrigerants (R12, R22 and R134a) have a slightly increased COP of all HCs and HCs/HFCs mixtures of refrigerants. Propane (R290) systems have a heating capacity, when used as a heat pump, which is about 8% lower than R22, while the COP is 5 – 7% higher. It was also shown that the refrigeration charge of a propane system is reduced by about 50%, when compared with R22, for the same geometry. Other mixtures of refrigerants which are also identified as promising are (R600/R290/R134a) and (R290/R600/R600a). Based on the results regarding the performance, HC mixtures and R152a are found as the better substitutes for R12 and R152a in domestic refrigeration sector. R29, R1270, R290/R152a, R744 and HCs/HFCs mixtures are considered as the best long-term alternatives for R22 in air conditioning and heat pump applications (Paul et al., 2013).

The Study of HFEs Refrigerants

Currently HFE compounds are used as cleaning solvents, blowing agents, refrigerants and dry etching agents in semiconductor manufacturing. There are few HFEs to still possess some environmental hazards

Table 7. Table with the performance of different HCs refrigerants and HCs/HFCs mixtures

<table>
<thead>
<tr>
<th>Fluid Property</th>
<th>Single</th>
<th>Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R12</td>
<td>R22</td>
</tr>
<tr>
<td>COP</td>
<td>3.233</td>
<td>3.180</td>
</tr>
</tbody>
</table>

(Paul et al., 2013)
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(GWP, flammability and toxicity). Some HFEs such as HFE-7500 is considered as replacer to HCFCs, HFCs and chlorinated solvents in applications in the cleaning of electronic components, and heat transfer systems due to their relatively low-GWP, very low toxicity and non-flammability (Tsai, 2005).

A theoretical comparison between the R11 and R12 (CFCs); R123 (HCFC); R134a (HFC) and R347mcc, R245fa and R245mc (HFEs) was performed and the results are presented in Table 8. The conditions were simulated for a heat pump system operating to a temperature of 30/80 °C (evaporator/condenser) (Sekiya & Misaki, 2000).

For the conditions studied, the R245fa (HFE with the best energy performance) present a COP: 7.4% lower than R11; 13% higher than R12; 4.8% lower than R123; 22.3% higher than R134a and a heating capacity: 26.2% higher than R11; 189% lower than R12; 46.3% lower than R123; 196% higher than R134a.

In the Figure 13 is shown a scheme with the historical evolution of used refrigerants, where is synthesized the information contained in this section.

CLASSIFICATION OF REFRIGERANTS

In this section will be presented the classification of primary refrigerants, according to the five main groups (families):

- Halocarbons;
- Hydrocarbons (HCs);
- Inorganic compounds;
- Azeotropic mixtures;
- Zeotropic mixtures or non-azeotropic.

Halocarbons

Halocarbon compounds contain in their chemical constitution atoms of chlorine, fluorine or bromine. Typically designated as chlorofluorocarbons (CFCs), these compounds were widely used in the past as refrigerants, solvents and blowing agents for foams. The most commonly used refrigerants of the CFCs family were the R11 and R12 (Benhadid-Dib & Benzaouï, 2012).

After signing the Montreal Protocol in 1987, the utilization of these compounds rapidly decreased during the respective phase-out period (between 1987 and 2000) in European Union, because of its negative

Table 8. Table with the performance of some HFEs refrigerants

<table>
<thead>
<tr>
<th>Fluid Property</th>
<th>CFCs</th>
<th>HCFC</th>
<th>HFC</th>
<th>HFEs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R11</td>
<td>R12</td>
<td>R123</td>
<td>R134a</td>
</tr>
<tr>
<td>COP</td>
<td>6.08</td>
<td>5.01</td>
<td>5.93</td>
<td>4.63</td>
</tr>
<tr>
<td>Heating capacity (kJ/m³)</td>
<td>1145</td>
<td>4176</td>
<td>988</td>
<td>4277</td>
</tr>
</tbody>
</table>

(Sekiya & Misaki, 2000)
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The lubrication of refrigeration systems that use refrigerants of CFCs family is performed using mineral oils. The increase of chlorine concentration in the chemical composition of the refrigerants, allows them present better properties of lubrication. Halogenated refrigerants are very stable when exposed to metals (McQuay, 2002). CFCs compounds are odorless, non-toxic and heavier than atmospheric air, which makes them dangerous when handled inside indoor ambient. The products resulting from combustion of CFCs compounds are quite toxic if they are inhaled (Dinçer & Kanoglu, 2010). In Table 9 it is possible to see the characteristics presented by the CFCs compounds and others, allowing the comparison between several types of refrigerants.

The perfluorocarbon compounds (PFC’s) are compounds belonging to the CFCs family. These are constituted by atoms of carbon and fluorine. Analyzing the characteristics of the PFC’s compounds presented in Table 9, it can be concluded that they have a high residence time in the atmosphere and a strong participation in the greenhouse effect increase, but not contributing to the ozone layer depletion. Attending to its high-GWP value, PFC’s compounds will be banned in the European Union by the action of Regulation EU 517/2014.
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Table 9. Some of the features (ODP, GWP and life cycle) and phase-out period for some of the families of refrigerants

<table>
<thead>
<tr>
<th>Refrigerants Classification</th>
<th>ODP</th>
<th>GWP&lt;sub&gt;100&lt;/sub&gt;</th>
<th>Life Cycle in the Atmosphere (Years)</th>
<th>Phase-Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>R11</td>
<td>1</td>
<td>3 800</td>
<td>45</td>
<td>By the year 2000</td>
</tr>
<tr>
<td>R12</td>
<td>1</td>
<td>8 100</td>
<td>100</td>
<td>(ODP &gt; 0)</td>
</tr>
<tr>
<td>Bromomethane</td>
<td>0.6</td>
<td>1 300</td>
<td>0.7</td>
<td>By the year 2015</td>
</tr>
<tr>
<td>HCFC</td>
<td>0.05</td>
<td>400 to 1800</td>
<td>1 to 20</td>
<td>(in EU)</td>
</tr>
<tr>
<td>HFC</td>
<td>0</td>
<td>400 to 11700</td>
<td>1 to 300</td>
<td>By the year 2017, depending on the application (in EU)</td>
</tr>
<tr>
<td>PFC</td>
<td>0</td>
<td>6500 to 9200</td>
<td>10 000 to 50 000</td>
<td></td>
</tr>
<tr>
<td>HC</td>
<td>0</td>
<td>2 to 20</td>
<td>Days</td>
<td>Not defined</td>
</tr>
<tr>
<td>HFE</td>
<td>0</td>
<td>6 to 500</td>
<td>1 to 40</td>
<td>(ODP = 0)</td>
</tr>
<tr>
<td>HFO</td>
<td>0</td>
<td>4 to 6</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>0</td>
<td>0</td>
<td>Days</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0</td>
<td>1</td>
<td>50-200</td>
<td></td>
</tr>
</tbody>
</table>

(Duarte, 2013)

Hydrocarbons

Hydrocarbons (HCs) are compounds mainly constituted by chemical bounds between atoms of carbon and hydrogen. The methane (R50), ethane (R170), propane (R290) cyclopropane, n-butane (R600), cyclopentane and isobutane (R600a) are some of the compounds that belong to the HCs family.

This type of compounds present the following characteristics: highly flammable and explosive; low toxicity; and environmentally friendly because it does not are involved in the process of ozone layer destruction and have a very low participation in the greenhouse effect increase (Dinçer & Kanoglu, 2010). Because they are highly flammable and explosive, it becomes necessary to reduce the refrigerant charge in systems to minimize the risks of its utilization (Pedersen, 2012). No problems of compatibility are found between these compounds and all materials traditionally used in refrigeration systems (Bolaji & Huan, 2013).

HCs emerged as the most advantageous solution to be applied in small packaged air-cooled equipment, namely, propane (R290) and isobutene (R600a) in domestic refrigerators and appliances. The energy efficiency of hydrocarbon chillers in medium - large range (50 ~ 400 kW) is about 10% better than in HFCs systems and its price about 20% higher compared to HFCs systems. The typical payback time of this equipment is 1 to 2 years (Pedersen, 2012). For example, the Aarhus University Hospital, Skejby in Denmark is cooled and heated by HC chillers and heat pumps, and McDonald’s chain in Denmark has installed cascade system using HCs and CO₂ in their restaurants (Kohler, 2012).

There are several families of HCs compounds, namely: hidrobromofluorocarbonos (HBFC’s); hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs); bromomethane (CH₃Br); and methane chloroform (CH₃CCl₃). The compounds belonging to these families are synthetic derived from fossil fuels. In this work will be discussed only the most important families, the hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), the hydrofluoroether (HFEs) and hidrofluoroleofinas (HFOs) (Dinçer & Kanoglu, 2010):
1. **HCFCs Compounds**: Are constituted by hydrogen, chlorine, fluorine and carbon atoms. These were created in order to replace the CFCs compounds. By having chlorine atoms in its chemical composition these compounds participate in the ozone layer destruction process, but in much lower proportions when compared with the CFCs compounds. The HCFCs compounds have a very low ODP value, as can be seen in Table 9. This type of refrigerants can use mineral (MO) or synthetic (POE) oils. In some cases, additives are used to improve the lubricant performance (McQuay, 2002);

2. **HFCs Compounds**: Are constituted by hydrogen, fluorine and carbon atoms. These are considered as the true class of substitutes for CFCs compounds, not having in its constitution chlorine or bromine atoms, resulting in its non-participation in the process of the ozone layer destruction. However, there are several HFCs compounds that have a high-GWP value, as can be seen in Table 9. The HFCs refrigerants generally require the use of a synthetic lubricant, such as a POE or PAG lubricant (esters). Are not compatible with MO lubricants (Melo, 2011). Some metals, especially metals in which chemical constitution exist atoms of zinc show increased corrosion with ester based oils and refrigerants of this family (Bolaji & Huan, 2013). Because of their safety, efficiency and cost, this type of compounds must remain an option in many regions and applications: HFCs and blends of HFOs and HFCs can provide highly efficient non-flammable solutions for developing regions; in large commercial air-conditioning with significant charge amounts and large refrigeration applications in densely populated areas to prevent toxic emissions, or explosion or inflammation of the systems (Kohler, 2012). HFCs refrigerants are widely used on ships today, but they are being replaced by ammonia-based refrigeration systems and, in large fishing vessels, by CO₂/ammonia cascade systems. This substitution was necessary, because there is a large leakage of refrigerant from the refrigeration systems existing on ships, due to rough physical actions of sea (Pedersen, 2012). The automobile sector is responsible for 50% of global sales of R134a (Melo, 2011);

3. **HFEs Compounds**: Are constituted by hydrogen, fluorine, carbon and oxygen atoms. As this compounds does not contain chlorine, iodine or bromine, does not contribute to ozone depletion. Due to chemical arrangement of their atoms, these compounds have a very low-GWP. As they have fluorine atoms in its constitution, they are chemically stable, presenting a low reactivity (lowflammability and toxicity – being more safety). Otherwise, its OH radicals were designed to react easily in the troposphere because of the inclusion of H atoms in its chemical structure. Widely used in industrial applications as cleaning solvents and anesthetic agents, HFEs are considerate as a promisor choice to replace CFCs, HCFCs, HFCs and PFCs compounds on refrigeration industry (as refrigerants and blowing agents), once some of these compounds have physical properties similar to refrigerants commonly used. These compounds are alcohol derivatives, synthetic, presenting the next properties: colorless, odorless, tasteless and low viscosity. Depending on the molecular weight, these compounds can be gaseous or liquid at ambient conditions (Sekiya & Misaki, 2000). They dissolve slightly into the mineral oil and polyester typo oil was been tested successfully. From the experience of its utilization as cleaning solvents, these compounds are perfectly compatible with the commonly used metals, plastics and elastomers, according with 3M Novec Company (3M, 2003). The lack of studies using these fluids as refrigerants is its biggest weakness;

4. **HFOs Compounds**: Are constituted by hydrogen, fluorine and carbon atoms. These compounds do not participate in the process of the ozone layer destruction and have a very low-GWP value, as can be seen in Table 9. The most promising applications of these compounds are as refrigerants (MT and LT refrigeration systems) in AMC systems, aerosol propellant and insulation foams
Current and Future Trends of Refrigerants Development

(Dinçer & Kanoglu, 2010). As challenges to use of HFOs compounds, the production capacity of R1234yf, the persistence of safety questions and new competitive technologies, may be presented as barriers to the proliferation of these compounds (Sciance, 2013). For refrigerants of this family (and blends of these with other refrigerants) is acceptable to use PAG or POE lubricants. The reactivity between HFCs compounds and PAG lubricants varies depending on oil formulation and moisture content (Low & Cooper, 2014).

Inorganic Compounds

Currently, inorganic compounds are used as refrigerants in several types of refrigeration systems, such as, commercial, industrial and mobile refrigeration systems with big cooling powers to cooling or freezing. Examples of inorganic compounds used as refrigerants are the ammonia (R717), water (R718), air (R729), carbon dioxide (R744) and sulfur dioxide (SO2). Among all these compounds, ammonia stands out as the more utilized in industrial applications, because it presents interesting thermophysical and heat transfer properties.

Air and CO2 are the most widely used refrigerants to operate a supercritical refrigeration cycle. This happens because these two refrigerants can reject thermal energy at supercritical temperatures (McQuay, 2002).

Within the whole range of inorganic refrigerants the ammonia, carbon dioxide and air are those that present the most interesting characteristics for being used in refrigeration systems (Dinçer & Kanoglu, 2010):

1. **Ammonia:** Has excellent thermodynamic characteristics when operates in refrigeration systems whose the evaporating temperatures are between -35 and +2 ° C. As disadvantages, ammonia is highly toxic and flammable. Despite the security problems that ammonia presents, their thermophysical and heat transfer properties are so good that it became, in some countries, the most requested refrigerant to operate in industrial applications. When combined with water, ammonia can be corrosive to cooper, zinc and copper and zinc alloys. Ammonia presents a little miscibility with lubricant used in refrigeration systems. As an advantage, it becomes easier separate the two components and reduce the risk of fire. On the other hand, as a disadvantage it is needed to introduce a separate mechanism to promote the return of oil to the compressor. Due to its properties (toxicity and flammability) several countries has restricted the use of ammonia as refrigerant, especially in commercial and residential applications (Paul et al., 2013). For example, ammonia heat pumps are used to heat a district in Norway, and the Hotel Scandinavia and the connected Aarhus Congress Centre in Aarhus was installed ammonia chillers in 1996 (Kohler, 2012);

2. **Carbon Dioxide:** Is not toxic (at concentrations below 5% by volume in mixture with air), not flammable, but thermodynamically inefficient. Has a good chemical compatibility with the material constituents of a refrigeration system and with a large number of lubricant oils. Its use involves high pressures (a large energy consumption for its mechanical compression), normally operating in transcritical cycles, necessitating of the utilization of specific compressors (to achieve the high pressures of the transcritical refrigeration cycle). An advantage of its utilization is that it has an ODP = 0 and GWP = 1 (i.e. non harmful to the ambient, compared with all other used refriger-
The use of CO₂ as refrigerant was proposed in 1850 by Alexander Twining. The peak of its use took place between 20s and 30s and was completely abandoned in 1960. In 1993, G. Lorentzen reintroduced the CO₂ on refrigeration by improving the transcritical thermodynamic cycle (Melo, 2011). Currently, CO₂ used in cascade refrigeration systems (R717/R744), dry-ice production and food freezing applications. For example, in Denmark several centralized refrigeration systems using CO₂ as refrigerant were built and tested. Today this technology is standard and hundreds of systems are installed presenting good performance, energy efficiency and economy (Pedersen, 2012);

3. Air: Was used for many years in cold-air refrigeration systems to cool passenger cabins in airplanes. When air is compressed a simple joule process is used to remove heat from air to the surrounding ambient. Afterwards, the air is expanded in a turbine, where it becomes cold. In Germany, a cold-air refrigeration system has been developed for trains (Pedersen, 2012). The coefficient of performance (COP) associated to the utilization of air as refrigerant is low due to its low specific weight, thus resulting in the transfer of small thermal energy quantities. Thus, air used as refrigerant is not energy efficient, but the lightness of the system components is the main advantage of its use. This makes the cold-air refrigeration systems interesting to be used in mobile transport applications. In some factories air is used as refrigerant to promote a quick freezing of the food.

Mixtures or Blends

Mixtures or blends are constituted by multiple substances. Currently, the future options of refrigerants are slim, if researchers only focus in pure natural refrigerants. Thus, the use of mixtures of refrigerants increases the possibilities of choice as well, the chances of replacement in older installations by “new” refrigerants. As advantages, this type of refrigerants takes advantage of existing technology, allowing the creation and optimization of “new” refrigerants (McQuay, 2002). There are two types of mixed refrigerants, the azeotropic mixtures and zeotropic mixtures (Dinçer & Kanoglu, 2010):

1. Azeotropic Mixtures: Consist of two or more substances with different chemical and physical properties, but behaving as a single substance. In azeotropic mixture is not possible to separate the two components using the distillation process, because these substances present the same evaporation temperature to the same ambient conditions.
2. Zeotropic Mixtures or Non-Azeotropic: Are constituted by multiple substances with different volatilities (i.e. different evaporation temperatures). When they are used as refrigerants, change their composition during the processes of evaporation and condensation. The application of these compounds as refrigerants was proposed in the early twentieth century. Recently, a great interest has been shown by the zeotropic mixtures, especially for operation as the refrigerant in heat pumps due its adaptive chemical composition during heating and cooling process, providing conditions that allow the development of new heat exchangers designs.

In Table 10 is presented a synthesis of the information relative to several refrigerants, namely the main applications and properties collected in date cheats of companies that commercialize them, including the DuPont, National Refrigerants, Linde, Forane, Honeywell, and the Report of UNEP (2010).
Current and Future Trends of Refrigerants Development

REPLACEMENT OF REFRIGERANTS

In this section are presented the existing approaches to the process of refrigerants replacement. It follows the exposure of the alternative refrigerants that present better characteristics (to short and long terms) to replace the CFCs and HCFCs compounds, according the characteristics of refrigeration system and the respective practical application.

Table 10. Physical, safety and environmental features of some refrigerants. The features were collected from data cheats of refrigerants commercialized by the companies

<table>
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<tbody>
<tr>
<td>CFC</td>
<td>R11</td>
<td>Single</td>
<td>1.00</td>
<td>4000</td>
<td>45</td>
<td>23.7</td>
<td>197.78</td>
<td>4.41</td>
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<td>Industrial refrigeration units that use centrifugal compressors, operating at LP, LT and VLT.</td>
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<tr>
<td></td>
<td>R12</td>
<td>Single</td>
<td>1.00</td>
<td>2400</td>
<td>100</td>
<td>-29.8</td>
<td>112.22</td>
<td>4.12</td>
<td>A1</td>
<td>Small refrigeration systems that utilizes reciprocating compressors at MT.</td>
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<tr>
<td></td>
<td>R13</td>
<td>Single</td>
<td>1.00</td>
<td>14400</td>
<td>640</td>
<td>-81.5</td>
<td>28.89</td>
<td>3.87</td>
<td>A1</td>
<td>Used in VLT applications in medicine, laboratory analysis, electronics and equipment testing.</td>
</tr>
<tr>
<td></td>
<td>R502</td>
<td>R22 (48.8) R115 (51.2)</td>
<td>0.311</td>
<td>4600</td>
<td>-</td>
<td>-45.3</td>
<td>81.5</td>
<td>4.07</td>
<td>A1</td>
<td>Used in LT applications in commercial refrigeration systems.</td>
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<td>HCFC</td>
<td>R22</td>
<td>Single</td>
<td>0.055</td>
<td>1700</td>
<td>11.9</td>
<td>-40.8</td>
<td>96.11</td>
<td>4.98</td>
<td>A1</td>
<td>Air conditioning systems and heat pumps used in homes. Refrigeration systems that operate at MT.</td>
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<td></td>
<td>R123</td>
<td>Single</td>
<td>0.02</td>
<td>77</td>
<td>1.3</td>
<td>27.8</td>
<td>183.89</td>
<td>3.67</td>
<td>B1</td>
<td>Systems operating LP compressors (substitute for R11).</td>
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<tr>
<td></td>
<td>R124</td>
<td>Single</td>
<td>0.07</td>
<td>620</td>
<td>5.9</td>
<td>-12</td>
<td>122.2</td>
<td>3.614</td>
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<td>Cooling systems that use centrifugal compressors.</td>
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<td>R401A</td>
<td>R22 (53) R152a (13) R124a (28)</td>
<td>0.037</td>
<td>1200</td>
<td>-</td>
<td>-32.9</td>
<td>105</td>
<td>4.61</td>
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<td>Refrigeration systems that operate at low and MT. Applied in supermarket freezers, equipped with reciprocating compressors (replacement for R12).</td>
</tr>
<tr>
<td></td>
<td>R408A</td>
<td>R125 (7) R134a (46) R22 (47)</td>
<td>0.026</td>
<td>3152</td>
<td>-</td>
<td>-44.6</td>
<td>83.17</td>
<td>4.283</td>
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<td>Refrigeration systems that operate at MT and LT. Applied in supermarket freezers (substitute for R502).</td>
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<td></td>
<td>R409A</td>
<td>R22 (53) R124 (13) R142b (28)</td>
<td>0.005</td>
<td>1585</td>
<td>-</td>
<td>-34.4</td>
<td>109.28</td>
<td>4.605</td>
<td>A1</td>
<td>Systems operating at MT and LT. Applied in supermarket freezers, equipped with reciprocating compressors (replacement for R12).</td>
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<td>HFC</td>
<td>R23</td>
<td>Single</td>
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<td>5700</td>
<td>222</td>
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<td>Systems operating at VLT (substitute for R13 and R503).</td>
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<td>Refrigeration systems that operate at VLT. Air conditioning and industrial applications.</td>
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<td>3400</td>
<td>28.2</td>
<td>48.1</td>
<td>66.015</td>
<td>3.629</td>
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<td>Air conditioning, industrial refrigeration and cooling units of water.</td>
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<td>R134a</td>
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<td>0</td>
<td>1300</td>
<td>13.4</td>
<td>-26.1</td>
<td>101.1</td>
<td>4.06</td>
<td>A1</td>
<td>Automotive and household air conditioning and heat pumps (replacement for R12). Also used as a blowing agent of foams.</td>
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<tr>
<td></td>
<td>R143a</td>
<td>Single</td>
<td>0</td>
<td>3800</td>
<td>8.2</td>
<td>-47.2</td>
<td>72.707</td>
<td>3.761</td>
<td>A2</td>
<td>Air conditioning, industrial refrigeration and cooling units of water. Refrigeration systems that operate at MT.</td>
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<td></td>
<td>R152a</td>
<td>Single</td>
<td>0</td>
<td>120</td>
<td>1.5</td>
<td>-24</td>
<td>113.26</td>
<td>4.52</td>
<td>A2</td>
<td>Automotive and housing air conditioning systems (replacement for R134a). Domestic and commercial freezers.</td>
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<td>R404A</td>
<td>R125 (44) R134a (4) R143a (52)</td>
<td>0.04</td>
<td>3300</td>
<td>-</td>
<td>-46.2</td>
<td>72.1</td>
<td>3.74</td>
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<td>Refrigeration systems that operate at MT and LT.</td>
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<td>R407C</td>
<td>R32 (23) R125 (25) R134a (52)</td>
<td>0</td>
<td>1610</td>
<td>-</td>
<td>-43.6</td>
<td>86.2</td>
<td>4.62</td>
<td>A1</td>
<td>Systems with reciprocal compressors in air conditioners and heat pumps to MT (substitute R22). Freezes systems that operate at MT and LT.</td>
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<td>R410A</td>
<td>R32 (50) R125 (50)</td>
<td>0</td>
<td>1890</td>
<td>-</td>
<td>-51.4</td>
<td>72.22</td>
<td>4.76</td>
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<td>Air conditioning and heat pump systems (replacement for R22). Refrigeration systems that operate at MT.</td>
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<tr>
<td></td>
<td>R422D</td>
<td>R125 (65.1) R134a (15) R600a</td>
<td>0</td>
<td>2700</td>
<td>-</td>
<td>-43.2</td>
<td>79.6</td>
<td>3.9</td>
<td>A1</td>
<td>Used in LT and MT applications in chillers, domestic, commercial and industrial refrigeration systems.</td>
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<tr>
<td></td>
<td>R437A</td>
<td>R125 (19.5) R134a (78.5) R600 (1.4) R601 (0.6)</td>
<td>0</td>
<td>1684</td>
<td>-</td>
<td>-32.9</td>
<td>96</td>
<td>4.096</td>
<td>A1</td>
<td>Air conditioning systems (including automotive). MT freezers, processing and storage of foods (replacement for R12).</td>
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<td>R507A</td>
<td>R125 (50) R134a (50)</td>
<td>0</td>
<td>3800</td>
<td>-</td>
<td>-46.7</td>
<td>70.9</td>
<td>3.79</td>
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<td>Refrigeration systems that operate at MT and LT.</td>
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<td>PFC</td>
<td>R508B</td>
<td>R23 (46) R116 (54)</td>
<td>0</td>
<td>10350</td>
<td>-</td>
<td>-87.6</td>
<td>13.7</td>
<td>3.935</td>
<td>A1</td>
<td>Refrigeration systems that operate at VLT (ex: refrigeration systems used in medical applications).</td>
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<td>656</td>
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<td>R245mc</td>
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<td>0</td>
<td>697</td>
<td>4.7</td>
<td>6</td>
<td>133.7</td>
<td>2.89</td>
<td>-</td>
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<td>R347mcc</td>
<td>Single</td>
<td>0</td>
<td>575</td>
<td>4.8</td>
<td>4.8</td>
<td>164.5</td>
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<td>-</td>
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<td>R356mff</td>
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<td>0</td>
<td>39</td>
<td>0.3</td>
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<td>-</td>
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<td>450</td>
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<td>164.6</td>
<td>2.48</td>
<td>-</td>
<td>Refrigerant and cleaning solvent.</td>
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<td>R1234yf</td>
<td>Single</td>
<td>0</td>
<td>4</td>
<td>0.029</td>
<td>-29.5</td>
<td>94.7</td>
<td>3.382</td>
<td>A2L</td>
<td>Automotive and housing air conditioning systems to (replacement for R134a). Domestic and commercial freezers.</td>
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<td>R1234ze</td>
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<td>0</td>
<td>6</td>
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<td>3.635</td>
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<td>Blowing agent of foams.</td>
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<td>R1270</td>
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<td>&lt; 0.02</td>
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<td>100</td>
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<td>R744</td>
<td>(CO&lt;sub&gt;2&lt;/sub&gt;)</td>
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<td>1</td>
<td>&gt; 50</td>
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</tr>
<tr>
<td>Cryogenic</td>
<td>R729</td>
<td>(Air)</td>
<td>Single</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-194.2</td>
<td>-</td>
<td>-</td>
<td>A1</td>
</tr>
</tbody>
</table>

(Duarte, 2013; UNEP, 2010; IPCC, 2007b)
Different Approaches to the Replacement Process

The refrigerants replacement process can be performed through two distinct approaches: retrofit type and drop-in type replacement’s (Melo, 2011). A replacement process of retrofit type requires a modification (i.e. upgrade) of some components of the refrigeration system. The retrofit term is used in engineering to describe the process of an equipment modernization. Normally the process of substitution by a blend happens according to retrofit process type, because is usual the lubricant substitution, thus as some equipment of the refrigeration system. This is due to incompatibility issues between the new refrigerant and the refrigeration systems equipment. On the other hand, a replacement process of drop-in type allows the direct substitution of refrigerants, without exists any incompatibility issues between the lubricant and each refrigerant (substitute and substituted) or any other components of the refrigeration system due to incompatibility of materials.

Most Common Refrigerant Replacements

The refrigerant replacement should only happen in two circumstances. The first, to comply the tight legislation applied to use of refrigerants, if the refrigerant present in the refrigeration system is dismissed or obsolete. The second, to increase the efficiency of the refrigeration cycle replacement with a new refrigerant that presents better thermophysical and thermal energy transfer properties, or also, if the new refrigerant fits best to the refrigeration system and its operation conditions. In this case, the replacement reflects the necessity for companies in reduce the operation costs related, in this case, with the cold production. Moreover, the acquisition of refrigerants more “recent” or less commercial, that exhibit improved properties, has the disadvantage of the high initial investment.

According to DuPont (American Company), the acquisition of refrigerants of low quality causes damage on compressors. The deposition of salts in the pipes and other components will decrease the system efficiency and increase the periods of maintenance and refrigerant leakages (i.e. increase costs). This happens, usually due to excess impurities and existence of moisture in refrigerants. In Table 11 is possible to see the alternatives that present better characteristics (to short and long terms) for replacement the more used CFCs, HCFCs and HFCs with high-GWP compounds. To facilitate the analysis, the refrigerants are grouped according to the type of refrigeration system (refrigeration, air conditioning and freezing) and applications (residential, commercial, industrial and automotive).

The CFCs and HCFCs refrigerants most used and whose replacement is required due to non-compliance with the current legislation are the R12 (CFC), R409A (HCFC), R502 (CFC), R11 (CFC) and R22 (HCFC). Currently, the CFCs refrigerants are discontinued, having its phase-out period occurred to 2000. Besides, the HCFCs refrigerants are currently in the phase-out period, to 2015 (target imposed by the Regulation EC 3039/94). According to the Regulation EU 517/2014 the HFCs with a GWP value higher than 150, must be discontinued until 2017 (depending on the application). This is the reason because the replacement options to long-term are present.

As options of replacement to short-term, the HFCs with high-GWP refrigerants were chosen. This family of refrigerants presents characteristics of compatibility of materials identical to the refrigerants replaced, allowing an approach to substitution of drop-in type, do not being necessary the changing of the system components or lubricating (with the exception of R134a refrigerant). The refrigerants chosen to the short-term replacement, result of the orientation obtained through the guidelines to the
Table 11. Table presenting the alternative refrigerants (to short and long term) that presents the best features to replace the CFCs, HCFCs and HFCs with high-GWP compounds, taking into account the characteristics of the refrigerating systems and its respective practical application

<table>
<thead>
<tr>
<th>System</th>
<th>Applications</th>
<th>Replaced Refrigerants (CFCs e HCFCs)</th>
<th>Replacement Options to Short-Term (HFCs) Drop-In</th>
<th>Replacement Options to Long-Term (HFCs, HFOs e Naturals) Retrofit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refrigeration</td>
<td>Housing (domestic)</td>
<td>• R12</td>
<td>• R134a*</td>
<td>• R152a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• R409A</td>
<td>• R437A</td>
<td>• R600a</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>• R290</td>
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<td></td>
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<td></td>
<td>• R1234yf</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Blends of HC/low-GWP HFCs</td>
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<td></td>
<td></td>
<td>Blend of HFO/low-GWP HFCs</td>
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<td></td>
<td></td>
<td></td>
<td>Blends of HC/low-GWP HFCs</td>
</tr>
<tr>
<td>Commercial</td>
<td>• R502</td>
<td>• R407C</td>
<td>• R32</td>
<td>• R123</td>
</tr>
<tr>
<td></td>
<td>• R22</td>
<td>• R422D</td>
<td>• R152a</td>
<td>• R717</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• R410A</td>
<td>• R600a</td>
<td>• R744</td>
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<td></td>
<td></td>
<td></td>
<td>• R290</td>
<td>Cascade systems (R717/R744)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>• R1234yf</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Blends of HFO/low-GWP HFCs</td>
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<td></td>
<td></td>
<td></td>
<td>Blends of HC/low-GWP HFCs</td>
<td></td>
</tr>
<tr>
<td>Industrial</td>
<td>• R11</td>
<td>• R123</td>
<td>• R123</td>
<td>• R123</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>• R717</td>
<td>• R717/R744</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>• R744</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Cascade systems (R717/R744)</td>
<td></td>
</tr>
<tr>
<td>Air conditioning</td>
<td>Residential and</td>
<td>• R22</td>
<td>• R407C</td>
<td>• R32</td>
</tr>
<tr>
<td></td>
<td>commercial</td>
<td></td>
<td>• R422D</td>
<td>• R152a</td>
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<td></td>
<td></td>
<td>• R410A</td>
<td>• R290</td>
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<td>• R600a</td>
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<td></td>
<td>• R1234yf</td>
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<td></td>
<td>Blend of HFO/low-GWP HFCs</td>
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<td></td>
<td></td>
<td></td>
<td>Blends of HC/low-GWP HFCs</td>
</tr>
<tr>
<td>Automotive</td>
<td>• R12</td>
<td>• R134a*</td>
<td>• R152a</td>
<td>• R123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• R437A</td>
<td>• R1234yf</td>
<td>• R717</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• R744</td>
<td>Cascade systems (R717/R744)</td>
</tr>
</tbody>
</table>

(Duarte, 2013)

* In the case of R134a, the replacement process needs the change of lubricant and expansion device, being this substitution a Retrofit, according with the data provided by the DuPont company.

replacement of refrigerants proposed by the DuPont Company. It is intended with the analysis of the short-term replacement, a quick response to the replacement of refrigerants in the refrigeration systems (air conditioning, refrigeration and freezing), present in companies, public and private buildings, shopping centers and automobiles, so that the current legislation that regulates its utilization can be followed.

It can be seen in Table 11, that in the group of options to short and long-term replacement, the R123 refrigerant is underlined. This happens because it belongs to the HCFCs family and not the HFCs family. This happens because the R123 refrigerant as a low value of GWP and ODP, see Table 10, and excellent thermodynamic properties when operate at very low temperatures. Thus, this refrigerant remains pointed
by investigators as a refrigerant with high potential to long-term when applied in industrial refrigeration systems. In cases where the replacement is performed by the R134a refrigerant, the replacement process requires the exchange of lubricant and an expansion device (i.e. a replacement of the retrofit type), as related in the orientation documents provided by the company DuPont (2011). In systems that operate with the R12 refrigerant is recommended to use lubricants of types AB (alkylbenzenes) and OM (mineral oils) and in systems that operate with R143a refrigerant is recommended to use the lubricants of type POE (polyol esters).

As long-term replacement options, were chosen the HFCs with low-GWP, HFOs, natural refrigerants and mixtures (HCs/HFCs and HFOs/HFCs) refrigerants. These refrigerants have a lower level of pollution (ODP and GWP), and for this reason are considered the future refrigerants. The choice of these refrigerants, such as long-term replacement options is based on experimental studies performed by several authors referred in this chapter. The refrigerants to be used as long-term replacement options are only possibilities of use.

The necessity to perform profound modifications on the installation/components of the refrigeration system is the disadvantage to perform a replacement by a refrigerant belonging to the long-term group, on an existing installation (i.e. a replacement of retrofit type). In this type of replacement, the characteristics of the refrigerant substitutes are not compatible with the installation features, may requiring the implementation of a new system, capable to operate the required conditions set by the new refrigerant. For example, it is not possible to use the CO₂ as a substitute refrigerant on systems which operates the refrigerant R11. Buying a new system or installation is too expensive.

The use of a refrigerant substitute may still result in a loss of performance of the refrigeration system, caused by improper adjustment of refrigeration systems that are not properly qualified to receive these new refrigerants. The increased reactivity of the used refrigerants as replacement choice to a long-term with the materials that compose the refrigeration system may result in a faster degradation of these components and increase of refrigerant leakage.

From observation of Table 11, it can be concluded that:

- In domestic refrigeration applications the refrigerants R12 and R409A are replaced. As replacement options to short-term are proposed the refrigerants R134a and R437A. As replacement options to long-term are proposed the refrigerants R152a, R600a, R290, R1234yf and blends of (HCs/low-GWP HFCs and HFOs/low-GWP HFCs);
- In commercial refrigeration applications the refrigerants R502 and R22 are replaced. As replacement options to short-term are proposed the refrigerants R422D, R407C and R410S. As replacement options to long-term are proposed the refrigerants R32, R152a, R600a, R290, cascade systems (R717/R744) and blends of (HCs/low-GWP HFCs and HFOs/low-GWP HFCs);
- In industrial refrigeration applications the refrigerant R11 is replaced. As replacement options to short-term are proposed the refrigerants R123. As replacement options to long-term are proposed the refrigerants R123, R717, cascade systems (R717/R744) and R744;
- In residential and commercial air conditioning applications the refrigerant R22 is replaced. As replacement options to short-term are proposed the refrigerants R407C, R422D and R410A. As replacement options to long-term are proposed the refrigerants R32, R600a, R290, R1234yf and blends of (HCs/low-GWP HFCs and HFOs/low-GWP HFCs);
Current and Future Trends of Refrigerants Development

- In automotive air conditioning applications the refrigerant R12 is replaced. As replacement options to short-term are proposed the refrigerants R134a and R437A. As replacement options to long-term are proposed the refrigerants R152a, R744, R1234yf and blends of HFOs/low-GWP HFCs;
- In industrial freezing applications the refrigerant R11 is replaced. As replacement options to short-term are proposed the refrigerants R123. As replacement options to long-term are proposed the refrigerants R123, R744, R717 and cascade systems (R717/R744).

REFRIGERANT RECOVERY, RECYCLING, RECLAMATION, AND DISPOSAL

The creation of the concepts of refrigerant recovery, recycling, reclamation and disposal, was one of the Montreal Protocol guidelines. This was the first document referencing the introduction of these concepts on the politics of environment preservation. These concepts were defined with the objective to promote the creation of incentives that allows the reduction of halogenated compounds (F-Gases) into the atmosphere, and thus, mitigate the resulting consequences by the emission of these compounds. However, only after a few years of the signature of the Montreal Protocol, the concern of world governments to adopt legislation to regulate this issue arises.

The Heat Pump Centre has a project which the objective focuses on data collection and analysis related to the recovery, recycling and reclamation R/R/R of refrigerants, to facilitate the planning of strategies that encourage the practice these practices (Bouma, 2003). The overall objective of this program is the documentation of practices and policies implemented for refrigerant recovery and recycling in major world markets of refrigerants use, namely, Asia, Europe and North America. This would allow the quantification of the impact of reducing emissions of refrigerants and comparing the effectiveness of different policy approaches. Some of the planned actions in course of this program are the development of standards and regulations with the competent authorities (i.e. in this case the U.S. Environment Protection Agency), promoting the creation of mandatory procedures for refrigerant R/R/R and the assessment of economic costs/benefits of leakage reduction, recovery, recycling and reutilization of refrigerants.

Currently, already exists legislation published in different countries that encourages the practice of refrigerants R/R/R and application of good practice rules, starting by the companies that selling refrigerants. For example, in Brazil, the National Plan for Elimination of CFCs refrigerants - PNC plans to install 114 decentralized units for the recovery and recycling of CFCs, HCFCs and HFCs refrigerants. All centrals will be fitted with recycling equipment and will operate on all the Brazilian nation territory, as stated in the Decree Nº 462 of December 22 of 2009 (LB, 2009).

In Portugal, Regulation EC 842/2006 presents the guide lines to R/R/R of certain fluorinated greenhouse gases (F-Gases). This Regulation obliges operators of a number of installations to follow a restricted plane for the proper recovery of F-Gases by certified personnel, to ensure the adequate R/R/R, disposal or destruction of these gases. According the Regulation EC 842/2006 (EPEE, 2014):

- Recovery means removal, collection and storage of gas or fluids from equipment into a closed vessel, appropriately identified with the designation of the collected fluid;
- Recycling means reuse of a recovered gas or fluid in the same system after having performed a basic cleaning process;
Reclamation means cleaning or reprocessing of gas or fluid to meet official specifications and to be used like virgin material;
Disposal or destruction means transformation or decomposition of gas or fluid in one or more substances which are not fluorinated greenhouse gases anymore.

The minimum requirements and conditions for mutual recognition for training and certification of personal and companies involved in installation, maintenance or servicing of refrigeration, air conditioning and heat pump equipment are also defined in the Regulation EC 842/2006 (EPEE, 2014).

To be an authorized installer (i.e. certified) is necessary to complete successfully a theoretical and practical examination by the competent authorities. The installer must also be responsible to recover from systems the F-Gases in process of decommissioning in cases of maintenance work require the removal of the refrigerant charge. The companies involved in installation, maintenance, servicing, leakage checking and recovery should be required to be certified to perform these activities and to obtain a certificate, a company should present to competent authorities the number of certified staff members per category, and an indication of the expected volume of activity and a document with the necessary tools and equipment available to the personnel engaged in activities subject to certification.

Also according the Regulation EC 842/2006 in installations containing 3 kg of F-Gases or more is required the presence of an operator responsible for the installation to keep accurate the records of all activities performed on the system. The producers, importers and exporters of F-Gases must report their transactions annually to the European Commission and the national authorities if the transitioned amount of refrigerant is greater than one tonne per year. In this context, the company that performs the operation of substitution is responsible for collection and storage of the refrigerant. As there are no facilities in Portugal to promote the regeneration of refrigerants, these are sent by the companies who execute the replacement to other countries were exist plants in which the refrigerants can be recycled or destroyed.

CONCLUSION

In this chapter of the general characteristics and properties of refrigerants were presented. As characteristics, the ideal refrigerant should be harmless to the environment, presents good heat transfer and thermophysical properties, be safe (low toxicity, low flammability and non-explosive), highly applicable, available, with low cost and recyclable.

Historical evolution of refrigerants was boosted by environmental concerns and constructive features of the refrigeration systems. Thus, the historical evolution of refrigerants can be divided into four generations: 1º any refrigerant that work; 2º security and durability; 3º ozone layer protection; 4º global warming.

The signature of the Montreal Protocol in 1987 and Kyoto Protocol in 2005 are known as the main events that marked the historic evolution of refrigerants, actions that lead to global rise of environmental concerns.

Refrigerants composed by chemical bounds of (C-Cl) have the ability to absorb light radiation in the ultraviolet range and have a long residence time in the atmosphere, thus intervening in the process of destruction of the ozone layer.

Refrigerants composed by chemical bounds of (C-F) have the ability to absorb light radiation in the infrared range and have a long residence time in the atmosphere, thus intervening in the process of destruction of the ozone layer. Because they block the infrared radiation emitted by the Earth to space and converting it into heat.
These two effects are responsible for climate change and consequent destruction of ecosystems. Thus it became necessary to take measures to reverse this trend, so emerged the Protocols above mentioned. There is currently a wide variety of data compiled from studies in which low-GWP refrigerants features are compared with the traditional refrigerants (i.e. the refrigerants commonly used currently).

The use of new refrigerants may require modified refrigeration cycles and expensive system components. The determination of indexes as the TEWI, LCCP and LCA to refrigerants before promote a replacement process is presented as an asset.

In refrigeration systems of the 2nd generation the indirect effect of GHGs emissions accounted for 80% of TEWI value. In 3rd generation, this value increased to approximately 98%. This value depends strongly on the energy matrix of the country under review, i.e. if electricity is or not produced from renewable or fossil fuels. From the 3rd generation of refrigerant, the direct impact of GHGs emissions related to a refrigerant on TEWI become marginal. Currently, the energy consumption by refrigeration systems becomes much more relevant. Thus, must be sought the improvement of thermal efficiency and heat transfer of refrigerants.

The European Union stands out as the group that more effort has demonstrated in searching and applying alternative refrigerants more environmentally friendly. This is visible through the amount of Directives and Regulations that have published in the last two decades on this field.

From the literature, the refrigerants with a more promising future: in terms of industrial and commercial applications are the natural refrigerants (ammonia and CO₂) and some blends of HFCs/HCs; in terms of automotive applications are the HFOs refrigerants and blends of HFCs/HFOs; in terms of domestic applications are the HCs and HFOs refrigerants, and blends of HFCs/HFO and HFCs/HCs.

During the next years the evolution on the field of refrigerants will be large, namely with respect to the control and use of HCs, ammonia and CO₂ as a refrigerant (technologies and equipment which enable a reduction in price, size and charge of the systems) and HFOs family (as the future of automotive air conditioning).

Finally it was introduced the concepts of refrigerant recovery, recycling, reclamation R/R/R, having these concepts as goal the reduction of refrigerants emissions into the atmosphere, thus promoting the environmental sustainability of the Planet.

REFERENCES


Current and Future Trends of Refrigerants Development


Current and Future Trends of Refrigerants Development


KEY TERMS AND DEFINITIONS

**Coefficient of Performance**: Expresses the ratio between the energetic objective of the refrigeration cycle and the quantity of energy provided to the system to comply the energetic objective of the cycle.

**Drop-In Replacement**: The refrigerant replacement does not require modifications (upgrade) in the refrigeration system components. The replacement could be direct, because does not exist incompatibilities between the new refrigerant and the installation materials.

**Flammability of a Refrigerant**: Ease with which a refrigerant comes into combustion.

**Global Warming Potential**: Index that characterizes the participation of one molecule of refrigerant to the increase of global warming. This index is determined through the comparison with the molecule of CO₂ (R744) =1, the molecule of reference.

**Residence Time in the Atmosphere**: Residence time of a refrigerant in the atmosphere.
Lubricant: It is a substance, such as grease or oil, which reduces friction when applied as a surface coating to moving parts. In other words, lubricants reduce the mechanical wear between moving parts.

Mixtures: Two or more substances which have been combined such that each substance retains its own chemical identity.

Ozone Depletion Potential: Index that characterizes the participation of one molecule of refrigerant in the process of ozone layer destruction. This index is determined through the comparison with the molecule of R12 (CFC) = 1, the maximum potential value of ozone layer destruction.

Refrigerant: Are all the fluids with a high capacity to “absorb” large amounts of thermal energy during the evaporation process at low temperature, characteristic that makes it ideal for use in refrigeration systems operating by a refrigeration vapour compression cycle.

Retrofit Replacement: The refrigerant replacement require modifications (upgrade) of some components of the refrigeration system.

Toxicity of a Refrigerant: Capability of a refrigerant to poison or do damage on the health of a person.

Vapour Compression Cycle: Thermodynamic cycle widely used in refrigeration systems to transfer heat from an environment to another. A fluid is used (refrigerant) in a closed cycle, and submitted to processes of compression, cooling with condensation, expansion and heating with evaporation.
APPENDIX: ABBREVIATION LIST

ASHRAE = American Society of Heating, Refrigerating and Air Conditioning Engineers;
EC = European Community;
COP = Coefficient of Performance;
EU = European Union;
GHG = Greenhouse Gas;
GWP = Global Warming Potential;
HOC = Heat Of Combustion;
IPCC = Intergovernmental Panel on Climate Change;
JAMA = Japanese Automotive Manufacturers Association
LCA = Life Cycle Assessment;
LCCP = Life Cycle Climate Performance;
LFL = Lower Flammability Limit;
LP = Low pressure;
LT = Low temperature;
MAC = Mobile Air Conditioning;
MT = Medium temperature;
ODP = Ozone Depletion Potential;
OEM = Original Equipment Manufacturer;
TEAP = Technology & Economic Assessment Panel;
TEWI = Total Equivalent Warming Impact;
TLV = Threshold Limit Value;
UNEP = United Nations Environment Programme;
VLT = Very low temperature;
EPA = US Environmental Protection Agency.