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The Contribution of Refrigeration Systems to Global Warming

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I. Introduction

I.1.Climate changes. Greenhouse gases

Human activities lead to the emission of greenhouse gases into the atmosphere. According to research, this increase in greenhouse gases is expected to cause climate change. Sunlight travels through the atmosphere and reaches Earth. One part of the radiation is absorbed by the soil, the other being re-emitted into the atmosphere, where it is absorbed by greenhouse gases (which leads to a warming of both the soil and the atmosphere). By absorbing infrared radiation, these gases control how natural energy penetrates through the climate system. The terrestrial greenhouse effect is a natural phenomenon extremely useful to life on Earth. Without the presence of greenhouse gases, the average temperature of the Earth would be about -20 ° C (United Nations Framework Convention on Climate Change, 2001).

It is known that the climate of a planet is determined by its mass, the distance from the Sun and the composition of the atmosphere. The earth is positioned between the planets Venus and Mars. Venus has almost the same mass as the Earth but has a denser atmosphere composed of 96%, which leads to maintaining a very high temperature of its surface of up to + 460 ° C.

In contrast, the atmosphere of Mars is much more rarefied, which led to the loss of the greenhouse effect and implicitly to the decrease of the average temperature to -50ºC. Climatic models predict that the temperature of the globe will increase by almost 1° – 3.5°C/year. This projected change is greater than in any other climate change experienced in the last 10,000 years, based on current emission trends and assumes that no efforts are being made to limit the emission of greenhouse gases. There is still much uncertainty about the scale and impact of climate change at regional level. Due to the delayed effect of the oceans, surface temperature does not respond immediately to greenhouse gas emissions, so climate change will continue for many years after atmospheric concentrations have stabilized.

Climate change, namely global warming, is likely to have a significant impact on the global environment. In general, the faster climate change, the greater the risk of environmental damage.

As a result of global warming, the main sea level is expected to rise by 15-95 cm by 2100, causing flooding in low-lying areas (the years 2004, 2005 are an example of such disasters worldwide), as well as other damage. The climate and thus the ecosystems and agricultural areas, can move to the polar regions by up to 150-550 km. Forests, deserts, other uncontrolled ecosystems will also feel climate change. As a result, some areas will become wetter and others more arid, desertifying, which will contribute to the extinction of many species in the world's flora and fauna.

Human society will face new risks and pressures. Food security is unlikely to be threatened globally, but for some regions there is this likelihood of a reduction and even a food disaster.

The presumptions are pessimistic if nothing is done. "Running water" will also be affected, as the structure of precipitation and evaporation changes around the world.

Infrastructure will suffer, especially from rising "sea levels" and "extreme weather". As a result, economic activities and human health will experience many direct and indirect effects.

GREENHOUSE GASES. A significant contribution to the variation of the terrestrial temperature is brought by the greenhouse gases. That is why scientists have dedicated countless studies and papers to them (United Nations Framework Convention on Climate Change, 2001).

The following is a summary of this particularly topical theme.

The Earth's climate is driven by a continuous flow of energy (from the Sun). This energy is mainly in the form of visible light. About 30% is immediately scattered back into space, and the remaining 70%, which is absorbed, "passes down" through the atmosphere to heat the Earth's surface. The Earth sends this energy back into space in the form of infrared radiation. As mentioned in the introductory part, "greenhouse gases" in the atmosphere block infrared radiation so as not to escape directly from the surface into space. Their levels are determined by a balance between “sources” and “destroyers”. “Sources” are processes that generate greenhouse gases; "Destroyers" are processes that destroy these gases. People are affecting greenhouse gas levels by introducing new sources or interfering with destroyers. The main greenhouse gases are: carbon dioxide, ozone, methane, nitrous oxide, chlorofluorocarbons (CFCs), water vapor and other gases. Apart from CFCs, all other gases occur naturally.

Table 1.1 exemplifies some important greenhouse gases, as well as their main characteristics.

Table 1.1

Gas type	**Chemical formula**	**Concentration 1994 ppbv**	**Life (years)**
Carbon dioxide	CO_2	358.000	variable
Methane	CH_4	1.721	12,2 ± 3
Nitrogen oxide	N_2O	311	120
CFC -12	CCl_2F_2	0,503	102
HCFC - 22	$CHClF_2$	0,105	12,1
Perflourmet	CF_4	0,070	50.000
Sulfur hexafluoride	SF_6	0,032	3.200

Additionally, the values of the Global Warming Potential (GWP) are reminded. Thus, it ranges from the value 1 for CO_2, 24.5 for CH_4, 310 for N_2O, 8,500 for CCl_2F_2, 1,700 for $CHClF_2$, 6,500 for CF_4 up to 23,900 in the case SF_6.

Carbon dioxide, responsible for more than 60% of the effects of greenhouse gases, is produced by the fuels used to generate energy, as well as from the cutting and burning of forests. In the following sub-chapter, the effect on climate change is detailed, so references are made mainly to other greenhouse gases below.

Methane represents 15-20% of the total intake of these gases and it is even increasing.

Nitrogen oxides are emitted from agricultural activities as well as from other sources and also have an important contribution.

Artificial chemicals called halocarbons (CFCs, HFCs, PFCs) and other gases, such as sulfur hexafluoride (SF_6) are emitted by industrial processes. In this sense, the Freon's used mainly in refrigeration systems (CFCs, HCFCs and HFCs) can be exemplified.

Natrium oxide protoxide, chlorofluorocarbonates and ozone contribute to the remaining 20% of the increased effects of greenhouse gases.

Together, these greenhouse gases make up less than 1% of the atmosphere. However, it is enough to produce a greenhouse effect that keeps the planet about 30oC warmer than if these gases did not exist. The levels of all major greenhouse gases (with the possible exception of water vapor) are the result of human activity.

But water vapor levels can also increase due to feedback. In this regard, water vapor plays an important role in climate change thanks to positive feedback. Warmer air retains more moisture and experimental modeling predicts that mild global warming will lead to an increase in water vapor levels. On the other hand, it is possible that certain regions may become dryer.

Due to the fact that climate modeling must also take into account clouds and torrential rains, it is particularly difficult to make accurate predictions, and the exact size of this feedback remains unknown. Sometimes the climate system needs to be corrected, by increasing the levels of these gases, in order to maintain the natural balance. In the long run, the Earth must "get rid of energy at the same level as it receives energy" from the Sun (United Nations Framework Convention on Climate Change, 2001). As long as a thicker layer of greenhouse gases helps reduce space losses, the climate must change in some way to restore the balance between incoming and outgoing energy. This correction will include a "global warming" of the Earth's surface.

Meanwhile, industrially produced "sulphate aerosols" may have a local cooling effect. This partially compensates for the heating by the greenhouse effect; however, these aerosols remain in the atmosphere for a relatively short time compared to the time the greenhouse gases remain. It should be noted that they can also cause other problems, such as acid rain, which means that you do not have to constantly resort to cooling the climate only with sulfate aerosols (as several researchers have suggested at one time).

I.2. Legislative provisions on climate change

● Rio de Janeiro Conference - Convention on Climate Change.

The First World Climate Conference recognized climate change as a serious problem and called on the governments of the world to 'foresee and prevent potential man-made changes that could be against the well-being of humanity' (United Nations Framework Convention on Climate Change, 2001). It has also put together plans to establish the World Climate Programme (WCP) under the joint responsibility of the World Meteorological Organization (WMO), the United Nations Environment Programme (UNEP) and the International Scientific Unions of the Climate (ICSU).

A large number of intergovernmental conferences, focusing their attention on climate change, took place between 1980 and 1990. With the increase in the number of scientific evidence on this issue, the participants of the international conferences, scientists with experience in the field, have expressed concern about climate change. The Intergovernmental Panel dealing with Climate Change (IPCC) prepared its first assessment in 1990. Established in 1988 by UNEP and WMO, the IPCC was given a mandate to assess existing knowledge about the climate system and climate change, the social impact of climate change and possible response strategies. The report confirms the scientific evidence on climate change. It has given the basis for serious negotiations within the framework of the Convention on Climate Change.

In December 1990, the UN General Assembly approved the start of negotiations on a treaty. Thus, the Intergovernmental Negotiating Committee for a Framework Convention on Climate Change (INC/FCCC) met and debated this issue for five sessions between February 1991 and May 1992. The importance of the "Earth Summit" in Rio in June 1992, which was attended by negotiators from 150 countries, must be stressed in this respect.

The 1992 United Nations Framework Convention on Climate Change was signed by 154 states in Rio de Janeiro. Other agreements adopted in Rio were the Rio Declaration and AGENDA 21 of the Convention on Biological Diversity and Forest Principles, documents of particular importance. The Convention entered into force on 21 March 1994.

On 21 September 1994, developed countries began proposing strategies for climate change. In the meantime, the INC continued the preparatory meeting for another six sessions, focusing on issues related to commitments, agreements on financial mechanisms, technical and financial assistance to developing countries, and institutional procedural issues. The INC was dissolved after the 11th (final) session in February 1995, with the Conference of the Parties (COP) becoming the last authority of the Convention.

The Climate Change Convention aims to stabilize the concentration of greenhouse gases in the atmosphere at a level that must prevent anthropogenic interference in the climate system. Such a level must be achieved within a sufficient framework time to enable ecosystems to adapt naturally to climate change to ensure that food production does not threaten countries to take measures aimed at returning their emissions to the level of the 1990s.

Several states can jointly adopt a common emissions target. Countries in transition to the market economy have also ensured a certain level of flexibility in the implementation of their commitments. The richest countries must provide "new and additional financial resources". The convention recognizes that the expansion to which the parties of developing countries are implementing their commitments will depend on the financial and technical aid of developed countries. The Convention continues to oblige all countries to limit their emissions, gather relevant information, develop industries to adapt to climate change, and work together on research and technology.

- **Conference of the Parties (COP).**

The Conference of the Parties is the "supreme body" in the Convention on Climate Change (United Nations Framework Convention on Climate Change, 2001).

The COP must promote and review the implementation of the Convention. In this respect, progress is largely made through the exchange of information. The mobilization of financial resources is vital for developing countries to be able to fulfil their obligations. The COP is also responsible for the entire ongoing process.

The first session of the Conference of the Parties was held in Berlin from 28 March to 7 April 1995. Delegates from 117 countries and 53 observers attended COP-1. They agreed that the commitments to developed countries contained in the Convention were inadequate and drew up the "Berlin Mandate" which includes additional commitments. Also, the specialists reviewed the first round of communications and completed many of the financial and institutional maneuvers necessary to act under the Convention in the years to come.

COP-2 was held in Geneva from 8 to 19 June 1996. The IPCC adopted its second evaluation report in December 1995. This evaluation report has been written and reviewed by nearly 2,000 scientists and specialists around the world. It has made itself known all over the world, the 'importance of human influence on the global climate.' However, the report has done much more, confirming the validity of those so-called 'no-go options' and other strategies with effective (real) costs for combating climate change. To this end, the IIPC has published a number of technical and specialist papers, ahead of the publication in 2001 of its third evaluation report.

The Kyoto Protocol was adopted at the COP-3 in December 1997. Under the Protocol, which was adopted unanimously, industrialized countries have made commitments to reduce collective greenhouse gas emissions by at least 5% by 2012 compared to 1990 levels. The Protocol entered into force 90 days after being ratified by at least 55 Parties to the Convention, including developed countries that account for at least 55% of total emissions.

The 1998 Conference in Buenos Aires adopted a two-year action plan. Held between 2 and 13 November 1998, the COP-4 set deadlines for the completion of the particularly important details of the Kyoto Protocol. In addition to the "mechanisms of the Protocol", the Action Plan provides solutions on the modalities of submission to the provisions, as well as to various measures. COP–5 took place between 15 October and 5 November 1999 in Bonn, and COP-6 was held in The Hague in 2000.

● The Kyoto Protocol.

The Kyoto Protocol to the United Nations Framework Convention on Climate Change strengthens the international response to the problem of climate change; it is based on legal commitments to stop and then change the level of growth-oriented emissions that began in industrialized countries 150 years ago. The Kyoto Protocol is the first instance in which governments have agreed to use economic instruments to implement their commitments. The development of these instruments will give more possibilities to those who understand their significance, in order to achieve maximum cost-effectiveness.

As has been mentioned before, developed countries are committed to reducing collective greenhouse gas emissions by at least 5%. This reduction in emissions is being pursued by the WMO/UNEP secretariat based in Switzerland. The European Union's main objective is to distribute different coefficients for reducing emissions of such gases among the Member States. For example, 7% USA and 6% Hungary, Japan and Poland. Russia, New Zealand and Ukraine are in the process of stabilizing their gas emissions. Norway can increase its emissions to 1%, Australia up to 8%, and Iceland up to 10%.

Each target of the gas emissions of that country must be reached, in the period from 2008 to 2012, according to the legislative provisions.

Countries will have a certain degree of flexibility in the way that they will do and measure their reductions in gas emissions. In particular, an international regime for "emissions trading" will be estimated to enable industrialized countries to buy and sell emission credits among themselves; This will allow them to purchase "emission reduction units", financing certain types of projects in other countries.

In addition, "a clear development mechanism" for promoting sustainable development plans enables industrialized countries to finance emission reduction projects in developing countries, which receive credits for the implementation of these measures.

The operational guide for these different schemes was developed under the scope of the two-year action plan finalized by cop-6 in 2000-2001.

Emission reductions in a wide range of economic sectors will be pursued. The protocol enables governments to work with each other, improve energy efficiency, optimize energy in transport sectors, promote forms of energy that can always be improved, phase out inadequate tax provisions and protect forests and other carbon-reducing 'basins'.

The Conference of the Parties to the Convention (COP) will also be used as the Meeting of the Parties to the Protocol (MOP). This is how this structure is expected to reduce costs and make it easier to conduct intergovernmental processes. Parties to the Convention who are not Parties to the Protocol shall have the opportunity to participate as observers in meetings related to the Protocol.

The new agreement will be reviewed regularly. The parties will also act appropriately on the basis of the most up-to-date scientific, technical and socio-economic information.

● **The Montreal Protocol.**

As indicated in the previous subchapter, the 1987 Montreal Protocol set targets for reducing substances that contribute to the depletion of the ozone layer. Also, the atmospheric concentrations of many CFCs are stabilized and are expected to decline further in the coming decades (the United Nations Framework Convention on Climate Change and the Ozone Secretariat of the United Nations Environment Programme, 2001).

Other halocarbons used as substitutes to protect ozone, in particular hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), contribute to global warming, so they are covered by the Kyoto Protocol (1997) and must also be reduced (a detailed analysis of the implementation of the main legislative provisions, refrigeration systems are done in the next sub-chapter).

The Protocol also covers hexafluors (SF_6) used as an electrical insulator, heat conductor and freezing refrigerant.

I.3. Regulations (EC) of the European Parliament

Regulation (EC) no. 842/2006 of the European Parliament and of the Council on certain fluorinated greenhouse gases.

Regulation (EC) no. 1516/2007 refers to the standard verification requirements for leak detection for stationary refrigeration equipment, air-conditioning equipment and heat pumps containing certain fluorinated greenhouse gases.

Regulation (EC) no. 303/2008 refers to minimum requirements and conditions of mutual recognition for the certification of companies and personnel with regard to stationary refrigeration equipment, air-conditioning and heat pumps containing certain fluorinated greenhouse gases.

Regulation (EC) no. 307/2008 refers to the minimum requirements for training programs and the recognition of personnel training certificates, as regards the air-conditioning systems of certain motor vehicles containing fluorinated greenhouse gases.

Regulation (EC) no. 308/2008 is in accordance with Regulation (EC) No 842/2006 envisages training programs and certification by Member States.

I.4. Community ACQUIS and implementations of the Montreal and Kyoto protocols in the field of refrigeration and air conditioning systems

Based on the environmental *acquis* Communautaire, reference is made in this sub-chapter to the requirements raised by the Montreal Protocol and its subsequent amendments on the protection of the ozone layer and the Kyoto Protocol on the greenhouse effect [22].

Refrigeration systems and heat pumps, through working agents, have a negative effect both on the ozone layer and on the heating of the Earth's atmosphere through the greenhouse effect [23]. Below are some considerations based on the latest global data in the field of refrigeration systems.

It should be noted that EU environmental legislation covers:

- production activities or processes that may have an impact on the environment or human health: construction, industrial units, transport and disposal of waste;
- protection of environmental quality: control of dangerous substances in the air, water or soil;
- the products, by means of the manufacturing process and their direct effect on the environment;
- legislation and procedural rights: such as impact assessment, access to information and public consultation.

The EU *acquis* is grouped into: **air quality, climate chang**e, horizontal legislation, waste management, water quality, nature protection, industrial pollution control and risk management, genetically modified chemicals and organisms, vehicle and mechanism noise, nuclear safety and radiation protection, civil protection, policies and international cooperation.

Of these, the first two issues refer specifically to the field of refrigeration technique and air conditioning, an area on which emphasis has been placed in this chapter.

THE IMPACT OF ALTERNATIVE REFRIGERATION TECHNOLOGIES.

Article 6 of the Montreal Protocol (1987) and the regulations that followed (London, Copenhagen, Rio de Janeiro, Vienna, Kyoto, Beijing, Bonn, etc.) refer to refrigeration systems and heat pumps.

Committees have been set up at international level to deal directly with environmental protection issues. One of these is the Technical Committee of Options, which includes 48 representative countries from Africa, Asia, Europe, South America and North America. In order to discuss the main problems faced by this area, a series of meetings took place in Denmark (Aarhus), France (Paris), the USA (Washington D.C.) in 1996 and 1997, and in India (New Delhi), Norway (Oslo) and Germany (Nuremberg) in 1998. The activity of these committees referred, among others, to the impact of refrigerants on the environment, the production and consumption of CFC and HCFC, domestic refrigeration systems, commercial refrigeration, industrial refrigeration, etc.

The economic impact of refrigeration technology is more important than one might think; in this respect, for example, the most than 300 million tons of refrigerated and frozen products are mentioned, as well as the fact that investments in refrigeration equipment exceed USD 100,000 million annually.

Production of CFC has been subject to progressive severe restrictions within the framework of the provisions contained in the Montreal protocol articles. In both developed and developing countries, HCFCs and HFCs were the first CFC substitutes.

A rational approach to phasing out the consumption of HCFCs as transitional chemicals should allow a minimum period of time to allow the industry to develop and market the alternative substances and the corresponding new equipment in order to avoid unnecessary costs. For a short time, HCFCs are still a valid option, as transitional substances, for refrigeration installations and air conditioning equipment.

However, for a long time, for both vapor and gas compression systems, other substances must be found.

The research focused on the following alternatives [22], [23]:

a) pure HFC refrigerants, their azeotropic mixtures (class 500) and zeotropic (class 400);
b) ammonia (R-717);
c) hydrocarbons and their mixtures (E.g. HC-290, HC-600, HC-600a, etc.);
d) carbon dioxide (R-744);
e) water (R-718).

None of the above refrigerants are perfect; all have both advantages and disadvantages, which must be taken into account by governments, equipment manufacturers, and ultimately their users. For example, HFCs have a relatively high global warming potential, ammonia is more toxic than other agents, and hydrocarbons can be flammable in certain situations.

Energy efficiency is directly linked to global warming and greenhouse gas emissions. Thus, it remains a very important requirement for all refrigeration technologies and it must be evaluated for the entire refrigeration system (refrigerants, equipment, operating conditions).

The five types of refrigerants above are in different stages of research, production or marketing.

• **HFCs** have a wide applicability in many sectors, but they are greenhouse gases whose emission into the atmosphere is to be severely restricted.

• **Ammonia and hydrocarbons** are increasingly used in sectors where they can be easily stored, but their clearances are also restricted firstly for reasons of toxicity, flammability and then for safety reasons.

• For some applications, the equipment with is in the development stage and the first demonstration components are already on the market. However, in all cases, account must also be taken of the contribution it makes to the phenomenon of global warming. In this respect, when assessing the total contribution to the climate warming phenomenon, which was mentioned above, (Total Equivalent Warming Impact - TEWI), both the direct and the indirect effect (through the amount of release to the production of the drive energy) must be taken into account and even optimal calculations must be made.

• The equipment that uses water as a working agent (refrigeration systems with absorption and ejection) has also developed and a certain increase can be observed in their use, but for limited applications.

Efforts shall be made by international organizations to develop standards in order to allow the use of new refrigerants.

I.5. Conclusions for Romania

The flexible policy to the Montreal Protocol agreements and its subsidiary amendments are coordinated in Romania by the Ministry of Environment (MM) (formerly the Ministry of Environment and Water Management - MMGA). He is the main creator of legislative initiatives relating to the Montreal Protocol and the other provisions at both European and global level. In this respect, MM is the sole responsible for the development of the legal framework, respecting the international environmental agreements ratified by the Romanian Government and which ensure the implementation of these agreements.

There are presented in the annexes, data from 1995 until now, particularly useful to specialists in the field of cold and air conditioning, included in the "National Program for the gradual elimination of substances that deplete the ozone layer" made available by the Ministry of Environment, the main creator and coordinator of legislative initiatives in Romania. In order to achieve the national desiderata of our country, as a result of joining the EU and for this purpose of implementing the legislative measures developed by it, in Romania it has been acted and is acting, mainly, in the following directions [22], [23]:

● Short-term solutions (rational and strict use of CFC in existing installations; prohibition of the realization of new installations operating with CFC, prevention of CFC leakages outside; recovery of CFC from existing installations) as specified above. In addition, it is recommended to continue to use ammonia, a refrigerant with great tradition in our country, at least in the industrial sector.

● Medium-term solutions (use of HFCs in new installations; use of other refrigerants - pure fluids or mixtures of synthesis fluids, natural fluids - which have ODP = 0 and low GWP; increased energy efficiency of refrigeration installations; use of other systems for the production of artificial cold such as those with absorption and ejection). The sale of imported freons must be done with great caution so that Romania does not become a warehouse of polluting fluids and therefore their import is done only for existing installations and following calculations of economic optimum.

● Long-term solutions (study of other refrigerants, pure fluids or mixtures of synthesis fluids, natural fluids, which have ODP = 0 and GWP = 0, or low; improvement of new technologies without the use of CFC, HCFC, or HFC such as air or gas cycles, use of water vaporization) to obtain artificial cold.

The production, marketing and consumption of refrigerants such as CFC, HCFCs and even HFCs, is increasingly regulated, such as the Montreal Protocol and the Kyoto Protocol. The careful supervision of the refrigeration system, in order to reduce the leaks in the atmosphere of the refrigerants, the recovery, reconversion and destruction of the CFCs and the replacement with a non-polluting substitute are increasingly common practices. However, the problem of transport and storage of refrigerants, as well as that of the storage of existing CFCs, should not be neglected, in order to reduce any impact on the environment (destruction of stratospheric ozone, heating of the earth's atmosphere) and to minimize any risk due to toxicity and flammability.

Finally, in order to implement the international legislation on the destruction of the ozone layer, but also on the one regarding the warming of the earth's atmosphere, in Romania, action must be taken both for the development of industry, education and research, with the aim of training good specialists in the field and for the continuous improvement of the national legislation.

II. Usual refrigerants

II.1. General presentation

The operation of the refrigeration machine involves the existence and interaction of three bodies:

- the warm one (for example the environment);
- the cold one (the object whose temperature must be lowered or kept below that of the environment);
- the one circulating in the refrigeration plant or machine, transporting the heat in the opposite direction to its normal tendency (i.e. from "cold" to "hot").

It is called a refrigerant and it goes through a series of physical states periodically returning to the original state in which the refrigeration machine consumes thermal, mechanical or electrical energy.

Thus, it can be concluded, in the language of specialists in the field of cold and air conditioning, that the role of the refrigerant is to take the heat from the environment to be cooled (for example in the evaporator) and to give it to a high temperature to the environment (for example by means of the condenser).

Refrigeration systems can be:

1) with direct vaporization (when the evaporator is placed at the consumer's own cold – for example, cooling the air in a room by vaporizing a refrigerant in the evaporator placed in it);

2) with indirect vaporization (when an intermediate agent is recirculated between the evaporator and the cold consumer – e.g. cooling of technological spaces in a laboratory).

The following are presented the main provisions at national and international level regarding the refrigerants indicated in SR ISO 5149/98, SR EN 378-1/2002 standards and in ASHRAE Standard, [18], [19]. Refrigerants shall be classified in terms of characteristics in the three groups listed below.

Group 1: *Non-flammable refrigerants which are not substantially harmful to human health.*

According to the above standards this group comprises refrigerants which are non-flammable and may be used in systems where the total load, in sufficient quantity to cool the spaces concerned, may be released into the atmosphere close to the spaces occupied by persons, without exceeding the limits indicated in Table 1.2.

Table 1.2

Usual limits for Group 1 refrigerant concentrations [18]

Nr. refrigerant R	**Chemical name**	**Chemical formula**	**Usual limits [kg/m^3]**
11	Trichlorofluoromethane	CCl_3F	0,3
12	Dichlorodifluoromethane	CCl_2F_2	0,5
12B1	Bromochlorodifluoromethane	$CBrClF_2$	0,2
13	Chlorotrifluoromethane	$CClF_3$	0,5
13B1	Bromotrifluoromethane	$CBr F_3$	0,6
22	Chlorodifluoromethane	$CHCl F_2$	0,3
23	Trifluoromethanesulonic	$CH F_3$	0,3
113	In trichlorotrifluoro	$CCl_2FCCl F_2$	0,4
114	In dichlorotetrafluoroides	$CCl F_2CCl F_2$	0,7
500	R12(73.8%) + + R152a(26.2%)	CCl_2F_2/ CH_3CHF_2	0,4
502	R22(48.8%) + + R115(51.2%)	CHCl $F_3/CClF_2CF_3$	0,4
503	R23(40.1%) + + R13 (59.9%)	CCl_3F/ $CH F_3$	0,4
744	Carbon dioxide	CO_2	0,1

The use of the direct cooling system in a space occupied by people is an important security issue. Direct systems are limited according to the provisions set out in SR ISO 5149/98, to specific quantities of refrigerant, for reasons of toxicity or risk of asphyxiation. The contact of these agents with flames or hot surfaces may result in toxic decomposition products under certain conditions. The main breakdown products of Group 1 refrigerants, with the exception of carbon dioxide, are hydrochloric acid and hydrofluoric acid. Although toxic, their presence is easily detectable due to the excessively irritating odor, even at low concentrations.

The maximum load shall be determined by means of Table 1.2, which refers to the smallest space occupied by persons, using as a criterion the total volume of all rooms cooled by air from an air circulation system, provided that the air supply in each room is not reduced to less than 25 % of the total air supply to that room. This limits the concentration that could form if there were refrigerant leaks. A system containing a quantity of refrigerant in Group 1 larger than that permitted in Table 1.2 must be of an indirect type and all parts containing refrigerant, with the exception of piping, must be installed in a machinery room or outside the building.

It should be taken into account to avoid the formation of stagnant cold agent bags heavier than low air and it is recommended each time to take measures to minimize discharges of refrigerant into the atmosphere [18].

Group 2: *Toxic or corrosive refrigerants whose lower explosion limit is equal to or greater than 3.5% by volume when they form a mixture with air.*

This group comprises refrigerants whose dominant characteristic is toxicity. Some of the refrigerants in this group are flammable, but with a lower explosion limit equal to or greater than 3.5% by volume, which imposes appropriate additional restrictions [18]. Ammonia is the only refrigerant of this group widely used. It has the advantage of being easily detectable in case of leaks, due to the characteristic odor even at concentrations much lower than the dangerous concentrations. Ammonia is flammable only for a very limited range of concentration increased to a high flammability temperature. All other refrigerants in this group are rarely used and are of theoretical interest only.

Group 3: *Refrigerants whose lower explosion limit is less than 3.5% by volume when they form a mixture with air.*

This group comprises refrigerants whose dominant characteristics are explosion power and flammability, with a lower explosion limit at concentrations below 3.5 % by volume. These agents are generally of poor toxicity. It should be noted that for refrigeration systems where refrigerants of different groups are used, the rules specific to each group, contained in the abovementioned standards, shall apply. Table 1.3 shows the main physical characteristics of these refrigerants according to SR ISO 5149/98 [18]. The provisions of European standard EN 378-1:2000 [19], simplify the grouping of refrigerants as set out below:

1) Refrigerants shall be classified in terms of flammability:

- *Group 1*: Non-refrigerants in any concentration in the air.
- *Group 2*: Refrigerants whose lower flammability limit is equal to or greater than 3,5 % by volume when they form a mixture with air
- *Group 3*: Refrigerants whose lower flammability limit is less than 3,5 % by volume when they form a mixture with air.

2) Classification in terms of toxicity:

- Group A: Refrigerants which are not substantially harmful to the health of working-class staff who are exposed 8 hours a day respectively for 40 hours a week, at a concentration value equal to or greater than 400 ml/m3 (400 ppm(V/V));

Table 1.3

Physical characteristics of refrigerants [18]

Number refrigerant R	Group refrigerant	Chemical name	Chemical formula
11	1	Trichlorofluoromethane	CCl_3F
12		Dichlorodifluoromethane	CCl_2F_2
12B1		Bromochlorodifluoromethane	$CBrClF_2$
13		Chlorotrifluoromethane	$CClF_3$
13B1		Bromotrifluoromethane	$CBr\ F_3$
22		Chlorodifluoromethane	$CHCl\ F_2$
23		Trifluoromethanesulonic	$CH\ F_3$
113		In trichlorotrifluoro	$CCl_2FCCl\ F_2$
114		In dichlorotetrafluoroides	$CCl\ F_2CCl\ F_2$
115		In chloropentafluorides	$CCl\ F_2C\ F_3$
500		R12(73,8%) + R152a(26,2%)	CCl_2F_2/CH_3CHF_2
502		R22(48,8%) + R115(51,2%)	$F_3/CClF_2CF_3$
744		Carbon dioxide	CO_2
30	2	Methylene chloride	CH_2Cl_2
40		Methyl chloride	CH_3Cl
160		Ethyl chloride	CH_3CH_2Cl
611		Methyl formate	$C_2H_4O_2$
717		Ammonia	NH_3
764		Sulphur dioxide	SO_2
1130		Dichloroethylene	CHCl-CHCl
170	3	Ethan	$CH_3\ CH_3$
290		PROPANE	$CH_3\ CH_2\ CH_3$
600		Butane	$CH_3CH_2CH_2CH_3$
600a		Isobutane	$CH(CH_3)_3$
1150		Ethylene	$CH_2 - CH_2$
1270		Propylene	C_3H_6

Table 1.3 (continued)

Number refrigerant R	Table molecular relative	Constant gas	Point of boiling to 101 kPa	Point freezing	Temperature critically
		J/(kg K)	°C	°C	°C
11	137,4	60,5	23,8	-111	196
12	120,9	68,64	-29,8	-158	112
12B1	165,4		-4		
13	104,5	79,64	-81,5	-181	28,8
13B1	148,9	55,9	-58	-168	67
22	86,5	96,2	-40,8	-160	96
23	70		-82		
113	187,4	44,44	47,7	-35	214,1
114	170,9	48,64	3,5	-94	145,7
115	154,5	53,84	-38,7	-106	80
500	99,29	83,75	-28	-159	105
502	112	74,52	-45,6		90
744	44	189	-78,5	-56,6	31
30	84,9	976,6	40,1	-96,7	250
40	50,5	164,7	-24	-97,6	143
160	64,5	128,9	12,5	-138,7	187,2
611	60	138,6	31,2	-104,4	214
717	17	488,3	-33,3	-77,9	132,4
764	64	129.8	-10	-75,5	157,5
1130	96,9	65,6	48,5	-56,7	243
170	30	276,5	-88,6	-183	32,1
290	44	188,6	-42,8	-188	96,8
600	58,1	143,2	0,5	-135	152,8
600a	58,1	143,2	-10,2	-145	133,7
1150	28	296,1	-103,7	-169,4	9,5
1270	42,1	197,7	-48	-185	91,5

Table 1.3 (continued)

Number refrigerant R	Pressure critically absolutely	Temperature of ignition	Combustibility Concentration range in the air that gives mixtures explosive	
	bar	°C	limit lower % (V/V)	limit upper % (V/V)
11	43,7			
12	41,2			
12B1				
13	38,6			
13B1	39,6			
22	49,3			
23				
113	34,1			
114	32,8			
115	31,2			
500	43,4			
502	42,7			
744	73,8			
30	46,1			
40	66,8	625	7,1	18,5
160	52,7	510	3,6	14,8
611	60	458	4,5	20
717	113	630	15	28
764	78,8	-	-	-
1130	53,3	458	6,2	16
170	49	515	3	15,5
290	42,6	470	2,1	9,5
600	35,5	365	1,5	8,5
600a	37	460	1,8	8,5
1150	50,6	425	2,7	34
1270	46	497	2	11,4

● *Group B*: Refrigerants which are not substantially harmful to the health of the working staff who are exposed 8 hours a day respectively for 40 hours a week at a value of less than 400 ml/m3 (400 ppm(V/V)).

Taking into account the degree of flammability and toxicity, the grouping shown in Table 1.4 was achieved.

Table 1.4

Safety groups

Strongly flammable	A3	B3
Weakly flammable	A2	B2
Nonflammable	A1	B1
Toxicity	low	enhanced

The provisions of the European standard EN 378-1: 2000 indicate the grouping of refrigerants into three groups marked with:

L1 = A1;
L2 = A2, B1, B2;
L3 = A3, B3.

As an observation, the L1 group corresponds to the least harmful refrigerants (non-flammable and low toxicity), and the L3 group corresponds to the most harmful from the same points of view.

The choice of refrigerant is made [8] under the conditions of thermodynamic, thermophysical, technological, economic, ecological and safety properties.

Among the most important thermodynamic requirements are:

- normal vaporization temperature as low as possible;
- ensuring an operation at a higher pressure than the atmospheric one;
- the saturation pressure corresponding to the condensing pressure to be in the usual technical field;
- latent heat of vaporization as high as possible;
- the specific volume of the vapors inlet by the compressor to be as small as possible;
- the overheating temperature of the vapors discharged by the compressor must be as low as possible;
- the compression ratio as low as possible to ensure the efficiency of the installation;
- ensuring a use over a wide range of temperatures.

The main *thermophysical and technological properties* that refrigerants must fulfill are:

- high heat transfer conduction and convection coefficients;
- low dynamic viscosity in order to ensure the lowest load losses and therefore low energy consumption;
- the chemical appropriate behavior of the refrigerant in contact with various materials from which the equipment in the construction of the refrigeration plant can be made.

Regarding to environmental and safety requirements, refrigerants must make as little contribution as possible to stratospheric ozone layer depletion and to global warming (through the greenhouse effect).

The main criteria for assessing refrigerants in terms of their impact on the environment are [8]:

- ODP [Ozone Depletion Potential] - degradation potential on the ozone layer which can be defined as: “ozone depletion potential, calculated in a stable mode for 1 kg of gas emitted annually into the atmosphere, compared to the achieved effect of 1 kg R11refrigerant”.

- GWP [Global Warming Potential] - the direct effect on global warming, defined as follows: 'the contribution of the refrigerant in question to the greenhouse effect, summed up for a given time of one kg of gas, relative to one kg of CO2”.

The ODP and GWP values for the main refrigerants are detailed in Table 1.5 according to SR EN 378-1 / 2002.

- TEWI [Total Equivalent Warming Impact] - the measure on the heating effect caused both by the greenhouse effect produced by the refrigerant leaks (direct effect) but also by the carbon dioxide resulting from the systems for the production of electricity necessary to operate the refrigeration systems (indirect effect).

II.2. Global warming and the TEWI factor

As mentioned above, a calculation method [19] has been developed that can assess the influence of the operation of individual refrigeration systems on the effect of global warming (TEWI). All "halo carbonate" refrigerants (including HFCs) belong to the category of "greenhouse gases". The emission of these substances contributes to global warming. The influence is much greater anyway compared to CO2 which is the main greenhouse gas in the atmosphere.

For example, over a period of 100 years, the emission of a 1 kg of R134a refrigerant is the equivalent of 1300 kg of CO_2 ($GWP_{100} = 1300$).

For this reason, the main problem for the future is to reduce refrigerant losses. On the other hand, the major contribution of refrigeration systems to the effect of global warming is the indirect emission of CO_2 caused by energy production.

Thus in Europe, the average CO_2 emitted is around 0.6 kg / kWh of electricity. Of course, the significant greenhouse effect occurs after a longer period of operation of the plant.

Globally have already been developed, with great effort legal regulations to reduce greenhouse gases. In the EU, Regulation no. 842/2006 also known as "F-gases" [56].

Method for calculating the global warming potential (GWP) for a mixture of substances.

GWP for a mixture of substances is the weighted average, derived from the sum of the mass fractions of each substance multiplied by their global warming potential.

$$\sum \mathbf{(Substanta\ X\% \cdot GWP) + (Substanta\ Y\% \cdot GWP) + ...(Substa\ ntaN\% \cdot GWP\,)}$$

where% is a weight tolerance factor with weight tolerance +/- 1%.

For example: applying the formula to a theoretical gas mixture consisting of 23% HFC-32; 25% HFC-125 and HFC-134a result:

$$\sum (\mathbf{23\%} \cdot 550) + (\mathbf{25\%} \cdot \mathbf{3200}) + (\mathbf{52\%} \cdot \mathbf{1300})$$

Total GWP = 1602.5

The impact of total global warming (TEWI) [19] is a pathway to assessing global warming by combining the direct contribution of refrigerant emissions into the atmosphere with an indirect contribution of carbon dioxide emissions, resulting from the need to energy consumption for the operation of the refrigeration system.

TEWI = [GWP x L x n] + [GWP x m (1-recovery)] + [n x E annual x b]

GWP - is the global warming potential,

L - losses, in kg / year

n - service life (system operating time), in years

m - loading of AF (refrigerant), in kg

$\alpha_{recovery}$ - the recovery / recycling factor from 0 to 1

E_{annual} - energy consumed in kWh per year

β - is the CO_2 emission, in kg / kWh

[GWP x m (1-recovery)] - the impact of losses on direct effect recovery

[GWP x L x n] - the impact of losses due to leaks

[n x E annually x b] - impact of energy consumption indirect effect

The calculation relationship for TEWI is presented in detail in SR EN 378-1 / 2002 and takes into account the quantity of refrigerant in the systems, the quantity of expandable refrigerant in the insulations, the quantity of CO_2 escaped into the atmosphere when producing the drive energy unit of the refrigeration system, the energy consumed to actuate the refrigeration systems during its operation, the efficiency as well as the tightness of the refrigeration systems, the way of producing the electricity to drive the refrigeration systems, the lifetime of the refrigerant.

In conclusion, from an ecological point of view, the refrigerant must be chosen so that, according to the regulations of the current legislation, it has zero ODP and GWP and TEWI as small as possible.

Regarding the safety requirements that refrigerants must meet, they are provided by standards both national and international level and refer to: flammability, explosion hazard, toxicity, danger of biological contamination and the effects they may have on the products to be cooled.

It should also be taken into account the location of the refrigeration installation (houses, public places, industrial areas) as well as the quantity of refrigerant contained in the systems.

Regarding the economic requirements, the price of the refrigerant must be taken into account, ensuring the lowest possible operating expenses as well as the possibility of production in the country. In any case, the choice of refrigerant must be made following rigorous technical and economic analyzes in order to have a plant as efficient and environmentally friendly as possible.

Table 1.5

Information on the effect of refrigerants on the environment [19]

Refrigerant	Group L	Group of safety	GWP	ODP
1	2	3	4	5
R-11	1	A1	3800	1
R-12	1	A1	8100	1
R12B1	1	A1	1300	3
R-13	1	A1	14000	1
R-13B1	1	A1	5400	10
R-22	1	A1	1500	0,055
R-23	1	A1	11700	0
R-113	1	A1	4800	0,8
R-114	1	A1	9800	1
R-115	1	A1	7200	0,6
R-124	1	A1	470	0,022
R-125	1	A1	2800	0
R-134a	1	A1	1300	0
R-218	1	A1	7000	0
R-C318	1	A1	8700	0
R-500	1	A1	6000	0,74
R-501	1	A1	3150	0,29
R-502	1	A1	4400	0,33
R-503	1	A1	13100	0,6
R507A	1	A1	3300	0
R-508A	1	A1	11860	0
R-509	1	A1	4580	0,024
R-718	1	A1	0	0
R-744	1	A1	1	0
R-401A	1	A1/A1	970	0,037
R-401B	1	A1/A1	1060	0,040
R-401C	1	A1/A1	760	0,030
R-402A	1	A1/A1	2250	0,021
R-402B	1	A1/A1	1960	0,033
R-403A	1	A1/A1	2520	0,041
R-403B	1	A1/A1	3570	0,031
R-404A	1	A1/A1	3260	0
R-405A	1	A1/A1	4480	0,028
R-407A	1	A1/A1	1770	0
R-407B	1	A1/A1	2280	0
R-407C	1	A1/A1	1520	0
R-408A	1	A1/A1	2650	0,026

R-409A	1	A1/A1	1290	0,048
R-409B	1	A1/A1	1270	0,048
R-410A	1	A1/A1	1720	0
R-410B	1	A1/A1	1830	0
R-508B	1	A1/A1	11850	0
R-406A	2	A1/A2	1560	0,057
R-411A	2	A1/A2	1330	0,048
R-411B	2	A1/A2	1410	0,052
R-412A	2	A1/A2	1850	0,055
R-32	2	A2	650	0
R-50	2	A2	21	0
R-141b	2	A2	600	0,11
R-142b	2	A2	1800	0,065
R-143a	2	A2	3800	0
R-152a	2	A2	140	0
R-160	2	A2	*	0
R-123	2	B1	90	0,02
R-764	2	B1	*	0
R-30	2	B2	9	0
R-40	2	B2	*	0
R-611	2	B2	*	0
R-717	2	B2	0	0
R-1130	2	B2	*	0
R-170	3	A3	3	0
R290	3	A3	3	0
R-600	3	A3	3	0
R-600a	3	A3	3	0
R-1150	3	A3	3	0
R-1270	3	A3	3	0
E170DME	3	A3	*	0

Note:

(*) - unknown values;

[1] Table 2.5 does not have a complete list of substances that are used as refrigerants.

[2] R – numbers are in accordance with ISO 817.

[3] The values of the GWP are taken from the "Intergovernmental Panel on Climate Change: 1994, The IPCC Scientific Assessment".

[4] The values of the ODP are those listed in the “Official Journal of the European Communities L 333, volume 37, 22 December 1994”.

[5] DME- Dimethyl ether

II.3. Eco-Efficiency

As mentioned earlier, when choosing a refrigerant or designing a refrigeration, air conditioning or heat pump, the TEWI factor (calculation of the effect of global warming during operation) is evaluated.

In this way, all economic aspects are not taken into account. But when the technological assessment is done and the investment decisions are made, in addition to the environmental aspects, the economic aspects become objectively, extremely important.

As far as refrigeration systems are concerned, reducing the impact on the environment frequently involves high costs.

Thus, in many companies, discussions about minimizing environmental issues are often overlooked (as investment costs are decisive).

In order to take into account both the ecological and the economic factor, as a result of a German study done in 2005 [69], using as an example a refrigeration system for the supermarket, the term "Eco-Efficiency" was defined.

It was based on the relationship between added value (economic value) and environmental impact (ecological value).

With this assessment, the entire life cycle of a system by two terms is taken into account (Fig. 1):

❑environmental performance according to the life cycle assessment (according to ISO 14040) - LCA (Fig. 1);

❑economic performance, through a cost-cycle analysis (Lyfe Cycle Cost Analysis) -LCCA (Fig. 1).

FIG. 1. The concept of "Eco-Efficiency"

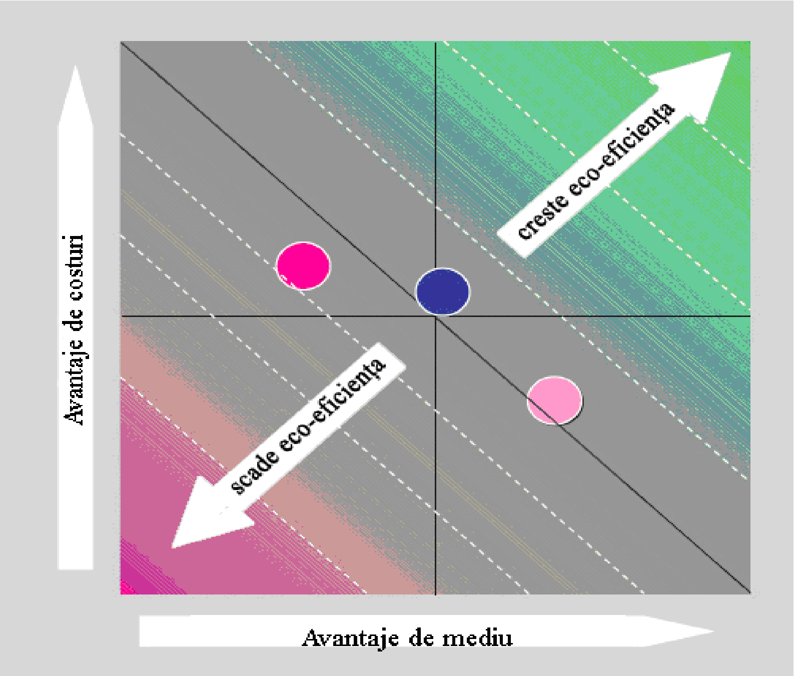
This means that an overall approach to environmental impact includes direct and indirect emissions, as well as investment costs, operating costs and capital costs.

The study also confirmed that an increase of "Eco-Efficiency" can be achieved by investing in optimizing the equipment of the plant (minimizing operating costs).

Thus, the choice of refrigerant associated with the technological system plays an important role.

"Eco-Efficiency" can be illustrated by the graphical representation in Figure 2:

Y "cost advantage"



X “environmental benefits”

Fig. 2. Example of evaluating “Eco-Efficiency”

Thus, the results of assessing the environmental advantages are displayed on the OX axis and the results of the life cycle cost analysis are presented on the OY axis. This representation clearly shows that the highest "Eco – Efficiency" is found in the upper right part of the dial and the smallest at the bottom left.

II.4. The principal refrigerants

In this subchapter are presented the main natural refrigerants used worldwide, and in the next chapter are provided data on new and prospective refrigerants.

II.4.1. Ammonia (NH_3-R717) [8]

In industrial plants, the most widely used refrigerant both globally and nationally is and it seems that ammonia will remain. This is a colorless gas with a characteristic odor.

● The main **advantages** of this refrigerant from the point of view of ensuring the four requirements presented are:

- it has good thermodynamic and heat transfer properties. Normal vaporization temperature t_{ON} = - 33.4 0C, condensing pressure does not exceed 14 - 16 bar for temperate climatic conditions, high latent heat of vaporization around 1,200 kJ / kg (300 kcal / kg), mass volume of vapors v "(0 ^{0}C) = 289 l / kg, thermal conductivity λ and convection coefficient α, high;

- the easy of detecting refrigerant leaks due to the strong pungent odor at about 5 ppm;

- it is an environmentally friendly refrigerant. Thus, it has zero ODP (not containing chlorine or bromine does not attack stratospheric ozone); has zero GWP (it is not a greenhouse gas because it does not absorb infrared radiation);

- the liquid refrigerant leaks evaporate instantly without contaminating the soil or the groundwater. Being about twice as light as the air, the ammonia vapors escaping from the refrigeration systems rises into the atmosphere with a short lifespan, of a few days, they decompose;

- it is a cheap refrigerant produced in our country and with a long tradition;

- is inert to steel, plastics and immiscible with oil having a low sensitivity in contact with humid air or water in the refrigeration system;

- compared to refrigerants, they require lower primary energy for the same refrigerating power.

● From the **disadvantages** we mention:

- it is toxic, explosive and flammable at volume concentrations in the air of 15… 28% or at even lower concentrations if oil vapors are present in the mixture;

- causes deadly or very serious injuries, in a few minutes, at a concentration of 0.5… 1.0% (the deadly dose is 30,000 ppm, the suffocating effect on humans appearing at 25 ppm);

- in contact with the eyes, mouth, respiratory tract causes irritation;

- in the presence of water, it attacks zinc, copper and their alloys (brass, bronze, etc.), so for industrial ammonia systems are used pipes and steel equipment;

- it has a high adiabatic exponent, which leads to high overheating temperatures of compressed vapors and a high compression power.

II.4.2. Refrigerants (Rxyz) [8]

● They are refrigerants widely used in the refrigeration technique due to the **advantages** presented below:

- from a thermodynamic point of view they have convenient temperatures and pressures (e.g. t_{ON} = - 40.8 0C, p_C (+ 35^{0}C) = 13.54 bar for R22);

- have lower mass volumes than ammonia, which leads to smaller pipe sizes [e.g. for R22 v" (0^0 C) = 47.15 l/kg];

- have a small adiabatic exponent, which causes a low temperature of overheating of compressed vapors;

- are odorless, those without chlorine (HFC), are not toxic, and those without hydrogen (CFC) are not flammable or explosive;

- are chemically neutral to steel, copper and plastics.

● The principal **disadvantages** of refrigerants are:

- low latent heat of vaporization compared to ammonia around 200 kJ/kg [e.g. for R22, l_V = 205 kJ / kg, and for R134, l_V (0 ^{0}C) = 198, 4 kJ / kg];

- most (except R22) are miscible with lubricating oil;

- there are no ecological refrigerants; so they all have a greenhouse effect and the vast majority attack the ozone layer. Table 1.5 presents the values of ODP, GWP's and the strategy for their use for the coming years.

Based from these major disadvantages, the legislative provisions (the Montreal Protocol and the Kyoto Protocol with the related amendments) of recent years have led to the limitation and even prohibition of the use of some refrigerants. Thus, at the beginning, CFCs, then HCFCs were restricted, and now the use of HFC refrigerants was also limited.

Also in the next chapter is presented an analysis of the perspective refrigerants, which are recommended to be as natural fluids as possible;

- they have an inappropriate behavior in contact with water: the refrigerants without hydrogen (CFC) do not allow the water to dissolve in them so that it can freeze in the plant producing blockages and even cracks of the pipes;

- refrigerants with hydrogen HCFCs and HFCs decompose chemically in contact with water at over 25 mg / kg, leading to the formation of highly corrosive acids (HCl and HF);

- have a viscosity higher than ammonia;

- they are not produced in our country and are expensive (especially the ecological ones).

Taking into account the importance given to these refrigerants, especially in the last 10 to 20 years, the main physical-chemical characteristics and other important data are presented below. Thus refrigerants are halogenated derivatives of saturated hydrocarbons obtained by replacing hydrogen refrigerants with chlorine, bromine or flour atoms.

The general chemical formula of hydrocarbons is: C_pH_{2p+2}, obtained for p = 1 methane (CH_4), p = 2 ethane (C_2H_6), p = 3 propane (C_3H_8), p = 4 butane (C_4H_{10}) etc.

The symbolization of the refrigerants will be done with the letter R (from the abbreviation of the word "Refrigerant" which is designated in standards established by ASHRAE in the USA - see table 1.5) followed by a group of two or three digits as follows:

R x y z,

where: $x = p - 1$; $y = 1 +$ number of hydrogen atoms; $z =$ number of atoms (F) of flour in the formula of the respective refrigerant.

The number of bromine atoms is especially highlighted and the isomers are differentiated by a letter a, b (R134a, R142b).

Some examples are given: R 11 ($C Cl_3 F$); R 12 ($C Cl_2 F_2$); R 22 ($CH Cl F_2$).

The refrigerant's scoring system was developed by Dupont in (1956) and for example for R134a:

- The first digit on the right represents the number of fluorine atoms.
- The second digit on the right represents the number of hydrogen atoms PLUS ONE.
- The third digit on the right represents the number of carbon atoms MINUS ONE.

By mixing pure freon's, mixture refrigerants with ecological advantages are obtained.

If these mixtures behave corresponding to a pure substance (the phase change flows isobaric and isothermal) they are called azeotropic mixtures and are denoted by R5. If the mixtures show a temperature difference during the phase change they are called zeotropic and are denoted by R4. As shown in Table 1.5 these substances have zero ODP and very low GWP.

Depending on the influence it has on the stratospheric ozone, refrigerants are classified into three types:

1) CFCs: Chlorofluorocarbons - which have the most destructive effect on ozone due to the presence of chlorine and fluorine and have been practically banned internationally. For example: R-11 / CFC11; R-12 / CFC12; R-115 / CFC115 (Not used as a pure substance, but as a mixture, also known as R502); R-502 / CFC502.

For "special" applications in the refrigeration industry, several refrigerants are used. These are generally CFCs or mixtures of CFCs such as: R-114 / CFC114; R-500 / CFC500; R-13 / CFC13; R-13B1 / CFC13B1; R-503 / CFC503.

With the reduction and then the banning of CFCs, transition alternatives (HCFCs) as well as medium and long-term (HFCs) presented below have been found.

2) HCFCs: Hydrochlorofluorocarbons - which have a lower depletion action due to the presence of hydrogen in molecules, considered as transition refrigerants. For example: R-22 / HCFC22; R-123 / HCFC123 replacing R-11.

3) HFCs: Hydrofluorocarbons - which are harmless to ozone having neither Cl nor Br but which nevertheless have a greenhouse effect, are considered medium and long - term refrigerants. The most important, as well as the possibility of replacement, are:

R-134a / HFC 134a - replaces R12
R404A / HFC404A - replaces R502
R407C / HFC407C - replaces R22
R507C / HFC507C - replaces R-502 (very similar to HFC404A)
R410A / HFC410A - replaces R22 in new equipment

II.4.3. CO_2 refrigerant

It is being used more and more due to the main advantages it has [43]:

- environmentally friendly (GWP, ODP);
- does not contribute to environmental pollution;
- is not aggressive in case of losses;
- small quantity;
- efficient;
- economic;
- very good heat transfer in vaporizers;
- vaporization temperature by 2-3 K higher for the same temperature of the exhaust air from the evaporator;
- increased compressor efficiency by approx. 15% (shorter operating time, better COP);
- more efficient cooling of products;
- low electric power of the pumps;
- lower electricity consumption comparable to other intermediate refrigerant systems;
- much lower price compared to R404a or other intermediates refrigerant;
- the quality of cooled products;
- lower temperature of the air from the evaporator at the same vaporization temperature, means product with a lower temperature, so better quality;
- after defrosting, the operating temperature is quickly reached without the danger of damaging the product;
- no danger to the products (non-toxic, odorless, colorless);
- lower price for pipelines and for plant due to the smaller dimensions;
- lower price for control elements, shut-off valves, electromagnetic valves, e.g. due to their smaller size.

II.5. Intermediary refrigerants

The intermediate refrigerants take the heat from cooled environments and transfer it to the refrigerant. This type of refrigerant is used in plants where the contact of the refrigerant with the product to be cooled may have undesirable effects or if certain leaks of the refrigerant may be toxic to operating personnel [14]. Thus, a new circuit appears between the cooled medium and the evaporator, called the *secondary circuit* or *intermediate refrigerant circuit*.

In addition to water and air, there are two major groups of intermediate refrigerants: solutions of mineral salts in water and alcohols in water.

● The main **brines** (salt solutions with water) are: sodium chloride, calcium, magnesium and potassium. The physical properties of brines depend on their concentration ζ defined as:

$$\zeta = \frac{\text{masa de sare}}{\text{masa de apa + masa de sare}} = \frac{M_S}{M_a + M_S} \cdot 100\%$$

The basic quality of brines is that they freeze temperatures at much lower than water. Depending on the chemical composition and concentration, the physical properties of the brines vary: density, mass heat, viscosity, etc.

An important issue is the choice of the concentration of intermediate refrigerants. This must be done in accordance with the operating requirements of the refrigeration system.

If in order to ensure your temperature in a cooled space, it is necessary for the brine (the intermediate refrigerant circulating through the equipment) to have a temperature (t_{sar}) lower by 5 - 8 °C, i.e.:

$$t_{sar} = t_a - (\ 5 \text{ --- } 8\ )°C$$

The refrigerant must also vaporize at a lower temperature:

$$t_0 = t_{sar} - (\ 8 \text{ ---} 10\ )\ °C$$

In order to avoid the freezing of the brine to an accidental decrease of t_0, the concentration must be chosen so that for solidification (t_{solid}) it is 8 --- 10 °C lower:

$$t_{solid} = t_0 - (\ 8 \text{ --- } 10\ )\ °C$$

Having the t_{sar} temperature determined, from the tables and diagrams, the corresponding concentration of the solution is found. Also, the brine in a refrigeration plant must have a slightly alkaline reaction with p_H = 8.5 --- 9.5.

● Regarding the **alcoholic solutions** used as intermediate refrigerants, the most common are the solutions of ethylene-glycol and propylene-glycol in water. They are very much used in installations that produce cold in the technological spaces of the food industry. Under the general name of ethylene-glycol, two substances are used: mono and diethylene-glycol, but only the first one has applicability as an intermediate refrigerant. Monoethylene glycol corrodes the steel. Thus an inhibitor such as sodium tetraborate 2 --- 3% to the mass of the solution is applied. When using copper pipes, the recommended inhibitor is 2.4% triethanolamine phosphate or 0.7% orthophosphoric acid relative to the mass of the solution.

Practically, all intermediate refrigerants must meet the following requirements: low freezing temperature, low viscosity, high specific heat, low corrosive action in relation to the materials of which refrigeration equipment is made, chemical stability, low toxicity, non-flammability and no danger of explosion.

II.6. Alternatives to refrigerants

The depletion of stratospheric ozone and the atmospheric greenhouse effect due to the emissions of refrigerants led to drastic changes in frigotehnics and air conditioning technology since the early 1990s. This is especially true in the field of commercial refrigeration and A / C factories with a wide scope of application. Until recently, the main refrigerants used for these systems were ozone depleting destroyers, namely R12, R22 and R502; for special applications were used refrigerants R114, R12B1, R13B1, R13 and R503.

With the exception of R22, the use of these substances is no longer allowed in many industrialized countries. In the European Union, however, there are recent regulations for the elimination of R22, which will be carried out step by step due to the enormous consequences resulting for all refrigeration and air conditioning equipment. Although HFCs (R134a, R404A, R507A, R407C, R410A) are chlorine-free refrigerants, they have a significant impact on global warming (high GWP).

The recommended alternatives are natural refrigerants those with zero ODP and zero or low GWP (NH_3, CO_2, water, hydrocarbons, etc.).

The results of several studies confirm that refrigeration systems with mechanical vapor compression normally used in the commercial field are much superior to all other processes for cooling spaces down to - 40 °C.

The selection of an alternative refrigerant is of great importance in the design of the plant. As specified, the recommended alternatives are refrigerants with zero ODP (ozone depletion potential) and zero or low GWP (global warming potential).

A calculation method for the evaluation of the installation has also been developed, which allows an analysis of the total influence on the greenhouse effect expressed by the TEWI factor (in which both a direct and an indirect effect are taken into account), defined and explained in detail. in SR EN 378.

Another more extensive method of evaluation has since been developed in terms of eco-efficiency. In this way, economic and ecological criteria were taken into account. Thus, they remain, in the future, the main criteria for assessing refrigerants, regarding the protection of the environment.

As alternatives to replace CFCs, HCFCs and even HFCs, the centralized data in Tables 1.6, 1.7 and 1.8 can be traced. For example, in the case of R12, the substitute R134a is relatively favorable, as for R502 with R404A and R507A. From the category of HFCs, refrigerants R32, R152a, R134a are seen as direct substitutes. They can be used very well as pure substances; due to the specific characteristics they have. The most important criteria to consider are flammability, thermodynamic properties and global warming potential. These substances are much more suitable to be components of optimal mixtures.

Apart from HFC refrigerants, both NH_3 and hydrocarbons are considered viable alternatives (their use for commercial applications is, however, limited by strict safety requirements). CO_2 is becoming more important as an alternative refrigerant and also as a secondary fluid. Due to the specific features, there are restrictions on general applications.

Figure 3 shows the strategy for replacing refrigerants in the short, medium and long term [69].

Data on refrigerants definitions, classification, TEWI factor, choice, e.g. are found in SR EN 378-1 (Annexes A, B, C, D, E, F, G, ZA, ZB) and **REGULATION (EC) No. 842/2006 F-Gas.**

SHORT, MEDIUM AND LONG TERM REFRIGERANTS

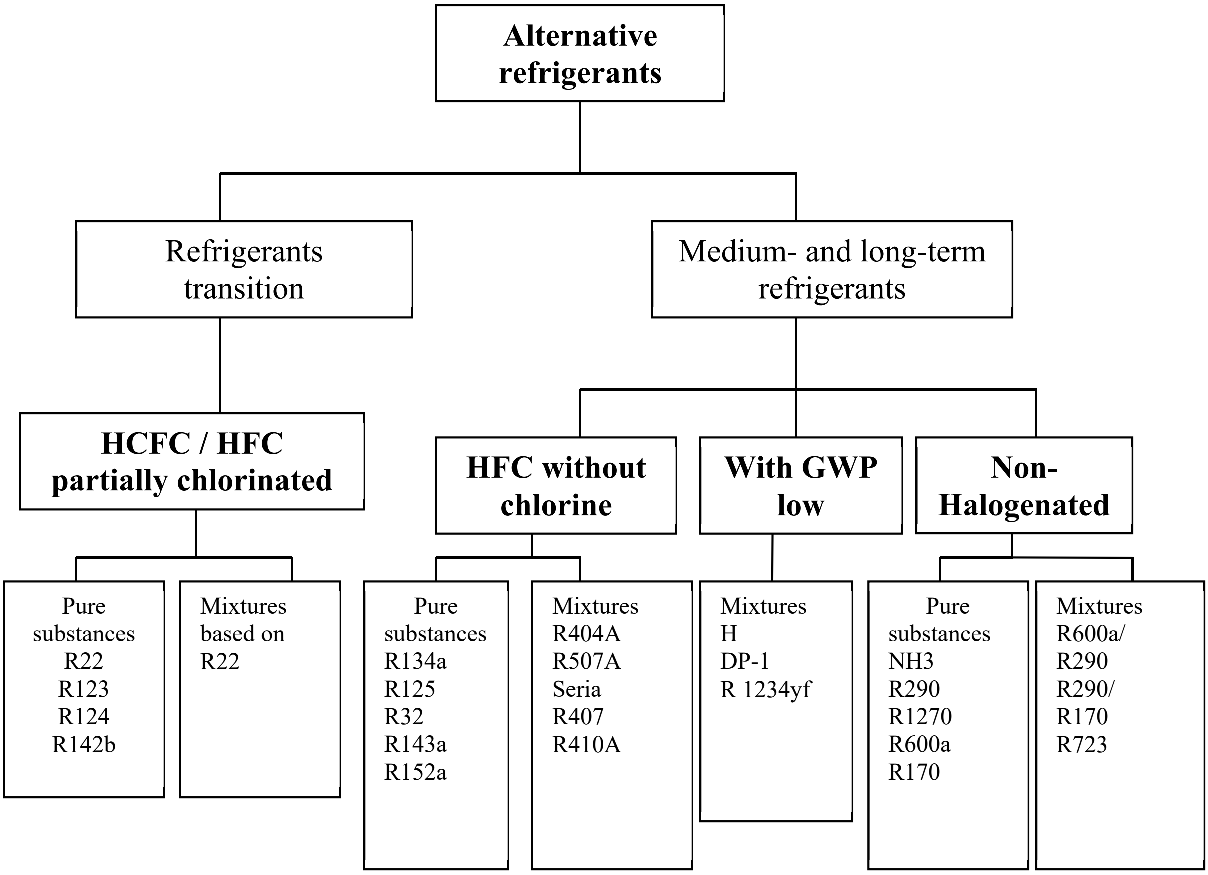


Figure 3

Table 1.6

Transitional refrigerants

Previous refrigerants	Alternative	Trade name	Composition
R12	R401 A	MP39	R22/152a/124
(R500)	R401 B	MP66	R22/152a/124
	R409A	FX56	R22/124/142b
	R413A	ISCEON M049	R134a/218/600a
R502	R22	-	-
	R402A	HP8O	R22/125/290
	R402B	HP81	R22/125/290
	R403A	-	R22/218/290
	R408A	FX10	R22/143a/125
R114	R124		
R12B1	R142b		
R13B1	v. tabelul 3.2		
R13			
R503			

Table 1. 7

Chlorine-free refrigerants (HFCs) and mixtures (long-term alternatives)

Previous refrigerants	Alternative	Trade name	Composition (With mixtures)
R12	R134a		
R500	R152a		
R502/	R404A	Variate	R143a/R125/R134a
R22	R507A		R143a/125
	R422A	ISCEON M079	R125/134a/600a
R22	R407C	Variate	R32/125/134a
	R410A	Variate	R32/125
	R417A	ISCEON	R125/134a/600
	R422D	M059	R125/134a/600a
	R427A	ISCEON	R125/32/134a/143a
		M029 FX100	
R114	R236fa	-	
R12B1	R227ea	-	
R13B1	R410A		R32/125
			R125/218/290
R13	R23		
R503	R508A	KLEA508A	R23/116
	R508B	Suva 95	R23/116

Table 1.8

Non-halogenated refrigerants (Long-term alternatives)

Refrigerants	Alternative	Formula
R1 2	R290/600a	C_3H_8/C_4H_{10}
(R500)	R600a	C_4H_{10}
R502	R717	NH_3
	R290	C_3H_8
	R1270	C_3H_6
R22	R717	NH_3
	R723	NH_3 + *DME*
	R290	C_3H_8
	R1270	C_3H_6
R114 R12B1	R600a	C_4H_{10}
R13B1	There are no direct alternatives	
R13 R503	R170	C_2H_6
Various	R744	CO_2

III. Practical examples

III. 1. Case study - AIR-WATER heat pump

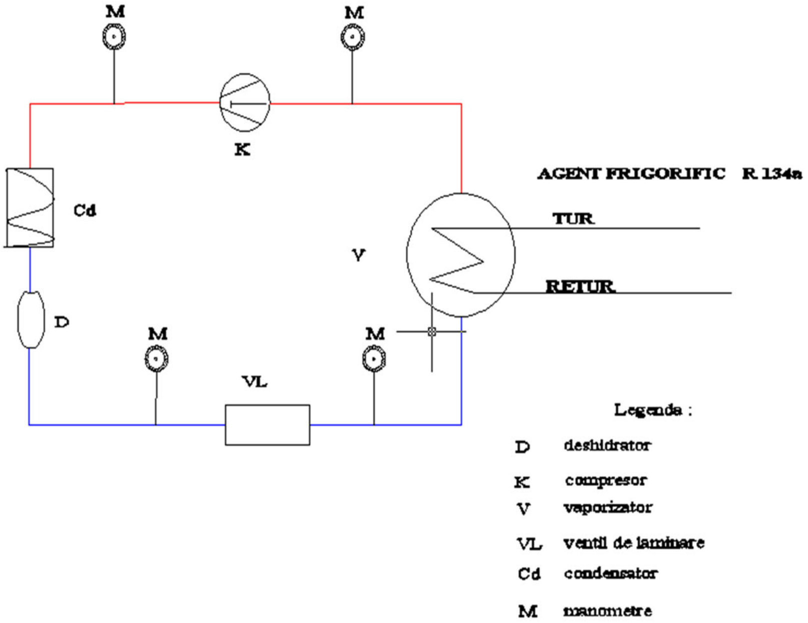


Fig. 4. The scheme of the installation.

The air / water heat pump contains:

- *- hermetic compressor with piston;*
- *- aluminum spiral condenser in a double housing*
- *- evaporator with bladed pipe (Cu / Al)*
- *- thermostatic lamination valve*
- *- fan (2 steps)*
- *- double enameled steel boiler with a volume of 270 dm3*
- *- air inlet / outlet up-up or sideways*

The environmentally friendly refrigerant used by the heat pump is R134a, and its range of application is from + 6 ° C to + 35 ° C.

The working pressure is between 6 ÷ 12bar and the maximum working temperature is 55 ° C.

TEWI FACTOR CALCULATION

Hypotheses:

- the calculation of the total equivalent impact of the global warming was made for the air-water heat pump that works with the R134a refrigerant but also with the possible ecological alternative HFO-1234yf, having the refrigerant charge of 0.78kg.
- we assume that the installation will operate for 13 hours a day
- the electric power consumed by the pump will be 0.54kW
- in one year the installation will operate for 261 days
- the refrigerant leakage will be 8% of the mass of refrigerant, while the recovery factor will be considered 0.9
- the operating time of the system will be 15 years
- CO_2 emission will be 0.6 kg / kWh
- GWP = 1300- for refrigerant R134a
- GWP = 4 - for the refrigerant HFO 1234yf

The refrigerant	**R-134a**	**HFO 1234yf**
GWP	1300	4
L [kg/an]	0.0624	0,0564
n [years]	15	15
m [kg]	0.780	0.705
$\alpha_{recovery}$	0.9	0.9
E_{annual} [kWh /an]	1832.22	1832.22
β [kg/kWh de CO_2]	0.6	0.6

The refrigerant	**R-134a**	**HFO 1234yf**
GWP x Lx n	1216.8	3.384
GWP x m(1 - $\alpha_{recovery}$)	101.4	0.282
n x E_{annual} x β	16489.98	16489.98
TEWI in kg CO_2	17808.18	16493.646
TEWI in tons CO_2	17.808	16.493

In conclusion, from an environmental point of view, the refrigerant HFO-1234yf must be chosen according to the EU Regulations, for its excellent properties in terms of environmental protection, but the flammability and toxicity tests are still continued and are not yet on the market.

This global warming potential is evaluated against CO_2 and researched over a period of 100 years.

III. 2. Comparisons

In the applications presented below, the comparisons for 3 types of refrigerants are centralized in 30 possibilities (depending on the mass and the electrical power consumed). Basically, it was calculated the total equivalent warming impact of an air-water heat pump that works with R134a, R407C, R410A refrigerants having the refrigerant charge of 0.5 kg …… 25 kg. The plant was considered to operate for 13 hours a day, 261 days a year, the electrical power consumed (Pc) varying between 0.5…..5kW. The refrigerant leakage was in all cases 8% of the mass of the refrigerant, the recovery factor was considered 0.75, the operating time of the system was 15 years, and the CO_2 emission was 0.6 kg / kWh.

(1) $TEWI=[GWP \times L \times n] + [GWP \times m(1-\alpha_{recovery})] + [n \times E_{annual} \times \beta]$

Where:

- GWP - is the global warming potential
- L - leakage, in kg / year
- n - service life (system operating time), in years
- m - charge of AF (refrigerant), in kg
- $\alpha_{recovery}$ - the recovery / recycling factor from 0 to 1
- E_{annual} - energy consumed in kWh per year
- β - is the CO_2 emission, in kg / kWh- 0.6 kg CO2 / kWh

[GWP x m (1-recovery)] - impact of losses on recovery - **DIRECT EFFECT**

[GWP x L x n] - impact of losses due to leaks - **DIRECT EFFECT**

[n x E annually x b] - impact of energy consumption - **INDIRECT EFFECT**

CASE 1 (m= 0,5; P_e=0,5kW)

	R-134a	**R407C**	**R410A**
GWP	1300	1520	1720
L	0,04	0,04	0,04
n	15	15	15
m	0,5	0,5	0,5
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	1696,5	1696,5	1696,5
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	780	912	1032

DIRECT EFFECT **GWP x m(1 - $\alpha_{recovery}$)**	162,5	190	215
INDIRECT EFFECT **n x E_{annual} x β**	15268,5	15268,5	15268,5
TEWI in kg CO_2	**16211**	**16370,5**	**16515,5**
TEWI in tons CO_2	**16,211**	**16,370**	**16,515**

CASE 2 (m= 0,78; P_e=0,54kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,0624**	**0,0624**	**0,0624**
n	**15**	**15**	**15**
m	**0,78**	**0,78**	**0,78**
$\alpha_{recovery}$	**0,9**	**0,9**	**0,9**
E_{annual}	**1832,22**	**1832,22**	**1832,22**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT **GWPx Lx n**	**1216,8**	**1422,72**	**1609,92**
DIRECT EFFECT **GWP x m(1 - $\alpha_{recovery}$)**	**101,4**	**118,56**	**134,16**
INDIRECT EFFECT **n x E_{annual} x β**	**16489,98**	**16489,98**	**16489,98**
TEWI in kg CO_2	**17808,18**	**18031,26**	**18234,06**
TEWI in tons CO_2	**17,808**	**18,031**	**18,234**

CASE 3 (m= 1,2; Pe=0,7kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,096**	**0,096**	**0,096**
n	**15**	**15**	**15**
m	**1,2**	**1,2**	**1,2**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**2375,1**	**2375,1**	**2375,1**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT **GWPx Lx n**	**1872**	**2188,8**	**2476,8**
DIRECT EFFECT **GWP x m(1 - $\alpha_{recovery}$)**	**390**	**456**	**516**
INDIRECT EFFECT **n x E_{annual} x β**	**21375,9**	**21375,9**	**21375,9**
TEWI in kg CO_2	**23637,9**	**24020,7**	**24368,7**
TEWI in tons CO_2	**23,637**	**24,020**	**24,368**

CASE 4 (m= 1,38; P_e=0,78kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**

L	**0,1104**	**0,1104**	**0,1104**
n	**15**	**15**	**15**
m	**1,38**	**1,38**	**1,38**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**2646,54**	**2646,54**	**2646,54**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT GWPx Lx n	**2185,92**	**2517,12**	**2848,32**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$**)**	**448,5**	**524,4**	**593,4**
INDIRECT EFFECT n x E_{annual} **x** β	**23818,86**	**23818,86**	**23818,86**
TEWI in kg CO_2	**26453,28**	**26860,38**	**27260,58**
TEWI in tons CO_2	**26,453**	**26,860**	**27,260**

CASE 5 (m= 1,70; P_e=0,85kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,136**	**0,136**	**0,136**
n	**15**	**15**	**15**
m	**1,70**	**1,70**	**1,70**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**2884,05**	**2884,05**	**2884,05**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT GWPx Lx n	**2652**	**3100,8**	**3508,8**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$**)**	**552,5**	**646**	**731**
INDIRECT EFFECT n x E_{annual} **x** β	**25956,45**	**25956,45**	**25956,45**
TEWI in kg CO_2	**29160,95**	**29703,25**	**30196,25**
TEWI in tons CO_2	**29,160**	**29,703**	**30,196,25**

CASE 6 (m= 23,5; P_e=4,8kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**1,88**	**1,88**	**1,88**
n	**15**	**15**	**15**
m	**23,5**	**23,5**	**23,5**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**16286,4**	**16286,4**	**16286,4**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT GWPx Lx n	**36660**	**42864**	**48504**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$**)**	**7637,5**	**8930**	**10105**

INDIRECT EFFECT **n x E_{annual} x β**	**146577,6**	**146577,6**	**146577,6**
TEWI in kg CO_2	**190875,1**	**198371,6**	**205186,6**
TEWI in tons CO_2	**190,875**	**198,371**	**205,186**

CASE 7 (m= 2,5; P_e=0,98kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,2**	**0,2**	**0,2**
n	**15**	**15**	**15**
m	**2,5**	**2,5**	**2,5**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**3325,14**	**3325,14**	**3325,14**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT **GWPx Lx n**	**3900**	**4560**	**5160**
DIRECT EFFECT **GWP x m(1 - $\alpha_{recovery}$)**	**812,5**	**950**	**1075**
INDIRECT EFFECT **n x E_{annual} x β**	**29926,26**	**29926,26**	**29926,26**
TEWI in kg CO_2	**34638,76**	**35436,26**	**36161,26**
TEWI in tons CO_2	**34,638**	**35,436**	**36,161**

CASE 8 (m= 3,2; P_e=1,2kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,256**	**0,256**	**0,256**
n	**15**	**15**	**15**
m	**3,2**	**3,2**	**3,2**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**4071,6**	**4071,6**	**4071,6**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT **GWPx Lx n**	**4992**	**5836,8**	**6604,8**
DIRECT EFFECT **GWP x m(1 - $\alpha_{recovery}$)**	**1040**	**1216**	**1376**
INDIRECT EFFECT **n x E_{annual} x β**	**36644,4**	**36644,4**	**36644,4**
TEWI in kg CO_2	**42676,4**	**43697,2**	**44625,2**
TEWI in tons CO_2	**42,676**	**43,697**	**44,625**

CASE 9 (m= 3,8; P_e=1,4kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,304**	**0,304**	**0,304**
n	**15**	**15**	**15**

m	3,8	3,8	3,8
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	4750,2	4750,2	4750,2
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	5928	6931,2	7843,2
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	1235	1444	1634
INDIRECT EFFECT n x E_{annual} x β	42751,8	42751,8	42751,8
TEWI in kg CO_2	49914,8	51127	52229
TEWI in tons CO_2	49,914,8	51,127	52,229

CASE 10 (m= 4,3; P_e=1,65kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,344	0,344	0,344
n	15	15	15
m	4,3	4,3	4,3
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	5598,45	5598,45	5598,45
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	6708	7843,2	8875,2
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	1397,5	1634	1849
INDIRECT EFFECT n x E_{annual} x β	50386,05	50386,05	50386,05
TEWI in kg CO_2	58491,55	59863,25	61110,25
TEWI in tons CO_2	58,491	59,863	61,110

CASE 11 (m= 4,9; P_e=1,72kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,392	0,392	0,392
n	15	15	15
m	4,9	4,9	4,9
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	5835,96	5835,96	5835,96
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	7644	8937,6	10113,6
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	1592,5	1862	2107
INDIRECT EFFECT n x E_{annual} x β	52523,64	52523,64	52523,64

TEWI in kg CO_2	**61760,14**	**63323,24**	**64744,24**
TEWI in tons CO_2	**61,760**	**63,323**	**64,744**

CASE 12 (m= 5,4; P_e=2,2kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,432**	**0,432**	**0,432**
n	**15**	**15**	**15**
m	**5,4**	**5,4**	**5,4**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**7464,6**	**7464,6**	**7464,6**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT GWPx Lx n	**8424**	**9849,6**	**11145,6**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	**1755**	**2052**	**2322**
INDIRECT EFFECT n x E_{annual} x β	**67181,4**	**67181,4**	**67181,4**
TEWI in kg CO_2	**77360,4**	**79083**	**80649**
TEWI in tons CO_2	**77,360**	**79,083**	**80,649**

CASE 13 (m= 6,1; P_e=2,7kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,488**	**0,488**	**0,488**
n	**15**	**15**	**15**
m	**6,1**	**6,1**	**6,1**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E_{annual}	**9161,1**	**9161,1**	**9161,1**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT GWPx Lx n	**9516**	**11126,4**	**12590,4**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	**1982,5**	**2318**	**2623**
INDIRECT EFFECT n x E_{annual} x β	**82449,9**	**82449,9**	**82449,9**
TEWI in kg CO_2	**93948,4**	**95894,3**	**97663,3**
TEWI in tons CO_2	**93,948**	**95,894**	**97,663**

CASE 14 (m= 6,7; P_e=2,9kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**0,536**	**0,536**	**0,536**
n	**15**	**15**	**15**
m	**6,7**	**6,7**	**6,7**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**

E_{annual}	9839,7	9839,7	9839,7
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	10452	12220,8	13828,8
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	2177,5	2546	2881
INDIRECT EFFECT n x E_{annual} x β	88557,3	88557,3	88557,3
TEWI in kg CO_2	101186,8	103324,1	105267,1
TEWI in tons CO_2	101,186	103,324	105,267

CASE 15 (m= 7,1; P_e=3,1kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,568	0,568	0,568
n	15	15	15
m	7,1	7,1	7,1
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	10518,3	10518,3	10518,3
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	11076	12950,4	14654,4
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	2307,5	2698	3053
INDIRECT EFFECT n x E_{annual} x β	94664,7	94664,7	94664,7
TEWI in kg CO_2	108048,2	110313,1	112372,1
TEWI in tons CO_2	108,048	110,313	112,372

CASE 16 (m= 2,2; P_e=0,95kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,176	0,176	0,176
n	15	15	15
m	2,2	2,2	2,2
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	3223,35	3223,35	3223,35
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	3432	4012,8	4540,8
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	715	836	946
INDIRECT EFFECT n x E_{annual} x β	29010,15	29010,15	29010,15
TEWI in kg CO_2	33157,15	33858,95	34496,95
TEWI in tons CO_2	33,157	33,858	34,496

CASE 17 (m= 8,3; P_e=3,57kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,664	0,664	0,664
n	15	15	15
m	8,3	8,3	8,3
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	12113,01	12113,01	12113,01
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	12948	15139,2	17131,2
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	2697,5	3154	3569
INDIRECT EFFECT n x E_{annual} x β	109017,09	109017,09	109017,09
TEWI in kg CO_2	124662,59	127310,29	129717,29
TEWI in tons CO_2	124,662	127,310	129,717

CASE 18 (m= 7,9; P_e=3,4kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,632	0,632	0,632
n	15	15	15
m	7,9	7,9	7,9
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	11536,2	11536,2	11536,2
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	12324	14409,6	16305,6
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	2567,5	3002	3397
INDIRECT EFFECT n x E_{annual} x β	103825,8	103825,8	103825,8
TEWI in kg CO_2	118717,3	121237,4	123528,4
TEWI in tons CO_2	118,717	121,237	123,528

CASE 19 (m= 10,3; P_e=3,7kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,824	0,824	0,824
n	15	15	15
m	10,3	10,3	10,3
$\alpha_{recovery}$	0,75	0,75	0,75

E_{annual}	12554,1	12554,1	12554,1
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	16068	18787,2	21259,2
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	3347,5	3914	4429
INDIRECT EFFECT n x E_{annual} x β	112986,9	112986,9	112986,9
TEWI in kg CO_2	132402,4	135688,1	138675,1
TEWI in tons CO_2	132,402	135,688	138,675

CASE 20 (m= 11,2; P_e=3,85kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,896	0,896	0,896
n	15	15	15
m	11,2	11,2	11,2
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	13063,05	13063,05	13063,05
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	17472	20428,8	23116,8
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	3640	4256	4816
INDIRECT EFFECT n x E_{annual} x β	117567,45	117567,45	117567,45
TEWI in kg CO_2	138679,45	142252,25	145500,25
TEWI in tons CO_2	138,679	142,252	145,500

CASE 21 (m= 11,9; P_e=3,92kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,952	0,952	0,952
n	15	15	15
m	11,9	11,9	11,9
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	13300,56	13300,56	13300,56
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	18564	21705,6	24561,6
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	3867,5	4522	5117
INDIRECT EFFECT n x E_{annual} x β	119705,04	119705,04	119705,04
TEWI in kg CO_2	142136,54	145932,64	149383,64
TEWI in tons CO_2	142,136	145,932	149,383

CASE 22 (m= 12,4; P_e=3,95kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,992	0,992	0,992
n	15	15	15
m	12,4	12,4	12,4
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	13402,35	13402,35	13402,35
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	19344	22617,6	25593,6
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	4030	4712	5332
INDIRECT EFFECT n x E_{annual} x β	120621,15	120621,15	120621,15
TEWI in kg CO_2	143995,15	147950,75	151546,75
TEWI in tons CO_2	143,995	147,950	151,546

CASE 23 (m= 13,6; P_e=4kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	1,088	1,088	1,088
n	15	15	15
m	13,6	13,6	13,6
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	13572	13572	13572
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	21216	24806,4	28070,4
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	4420	5168	5848
INDIRECT EFFECT n x E_{annual} x β	122148	122148	122148
TEWI in kg CO_2	147784	152122,4	156066,4
TEWI in tons CO_2	147,784	152,122	156,066

CASE 24 (m= 14,6; P_e=4,1kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	1,168	1,168	1,168
n	15	15	15
m	14,6	14,6	14,6
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	13911,3	13911,3	13911,3
β	0,6	0,6	0,6

DIRECT EFFECT GWPx Lx n	**22776**	**26630,4**	**30134,4**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	**4745**	**5548**	**6278**
INDIRECT EFFECT n x E_{annual} x β	**125201,7**	**125201,7**	**125201,7**
TEWI in kg CO_2	**152722,7**	**157380,1**	**161614,1**
TEWI in tons CO_2	**152,722**	**157,380**	**161,614**

CASE 25 (m= 9,1; P_e=3,6kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	0,728	0,728	0,728
n	15	15	15
m	9,1	9,1	9,1
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	12214,8	12214,8	12214,8
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	14196	16598,4	18782,4
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	2957,5	3458	3913
INDIRECT EFFECT n x E_{annual} x β	109933,2	109933,2	109933,2
TEWI in kg CO_2	127086,7	129989,6	132628,6
TEWI in tons CO_2	127,086	129,989	132,628

CASE 26 (m= 15,4; P_e=4,15kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	1,232	1,232	1,232
n	15	15	15
m	15,4	15,4	15,4
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	14080,95	14080,95	14080,95
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	24024	28089,6	31785,6
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	5005	5852	6622
INDIRECT EFFECT n x E_{annual} x β	126728,55	126728,55	126728,55
TEWI inn kg CO_2	155757,55	160670,15	165136,15
TEWI in tons CO_2	155,757	160,670	165,136

CASE 27 (m= 16,3; P_e=4,22kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	1,304	1,304	1,304
n	15	15	15
m	16,3	16,3	16,3
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	14318,46	14318,46	14318,46
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	25428	29731,2	33643,2
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	5297,5	6194	7009
INDIRECT EFFECT n x E_{annual} x β	128866,14	128866,14	128866,14
TEWI in kg CO_2	159591,64	164791,34	169518,34
TEWI in tons CO_2	159,591	164,791	169,518

CASE 28 (m= 18; P_e=4,3kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	1,44	1,44	1,44
n	15	15	15
m	18	18	18
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	14589,9	14589,9	14589,9
β	0,6	0,6	0,6
DIRECT EFFECT GWPx Lx n	28080	32832	37152
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	5850	6840	7740
INDIRECT EFFECT n x E_{annual} x β	131309,1	131309,1	131309,1
TEWI in kg CO_2	165239,1	170981,1	176201,1
TEWI in tons CO_2	165,239	170,981	176,201

CASE 29 (m= 19,4; P_e=4,4kW)

	R-134a	R407C	R410A
GWP	1300	1520	1720
L	1,552	1,552	1,552
n	15	15	15
m	19,4	19,4	19,4
$\alpha_{recovery}$	0,75	0,75	0,75
E_{annual}	14929,2	14929,2	14929,2
β	0,6	0,6	0,6
DIRECT EFFECT	30264	35385,6	40041,6

GWPx Lx n			
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	**6305**	**7372**	**8342**
INDIRECT EFFECT n x E_{annual} x β	**131309,1**	**131309,1**	**131309,1**
TEWI in kg CO_2	**167878,1**	**174066,7**	**179692,7**
TEWI in tons CO_2	**167,878**	**174,066**	**179,692**

CASE 30 (m= 25; P_e=5kW)

	R-134a	**R407C**	**R410A**
GWP	**1300**	**1520**	**1720**
L	**2**	**2**	**2**
n	**15**	**15**	**15**
m	**25**	**25**	**25**
$\alpha_{recovery}$	**0,75**	**0,75**	**0,75**
E $_{annual}$	**16965**	**16965**	**16965**
β	**0,6**	**0,6**	**0,6**
DIRECT EFFECT GWPx Lx n	**39000**	**45600**	**51600**
DIRECT EFFECT GWP x m(1 - $\alpha_{recovery}$)	**8125**	**9500**	**10750**
INDIRECT EFFECT n x E_{annual} x β	**152685**	**152685**	**152685**
TEWI in kg CO_2	**199810**	**207785**	**215035**
TEWI in tons CO_2	**199,810**	**207,785**	**215,035**

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