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Energy Procedia 18 (2012) 807 – 816

Energy Procedia

Refrigerants and their environmental impact Substitution of hydro chlorofluorocarbon HCFC and HFC hydro fluorocarbon. Search for an adequate refrigerant

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Abstract

Globally, the production of cold housing is seen as a major energy challenge of this new century. The economic development of developing countries, submitted their majority in hot climates, will lead to a growing demand chilling requirements. Yet currently, the production of cold solutions is mainly based on refrigeration systems major consumers of electrical energy.

It is then necessary to prepare socio-economically acceptable solutions tailored to meet those needs without compromising future international commitments on the protection of the environment, particularly for reducing greenhouse gas emissions and better protection of the ozone layer by use of refrigerants neutral.

For some years now, because of their impact on the environment, the use of halogenated refrigerants has been progressively subject to quotas. In this context, the use of "natural" refrigerants becomes a possible solution.

We introduce in this work the merit of redeploying these natural refrigerants as an alternative solution to replace halogenated refrigerants. The solution to the environmental impacts of refrigerant gases would therefore pass by a gas which contains no chlorine no fluorine and does not reject any CO_2 emissions in the atmosphere, in brief a green gas! The aim of our project is to contribute to the protection of our environment. Our motive being to produce cold for freezing foodstuffs and seeds, safeguarding pharmaceuticals and cooling of premises: temperature conditions, air qualities controlling and producing. This work is also concerned by a contribution to the reduction of greenhouse gases and by the replacement of the polluting cooling fluids (HCFC). It is essentially the refrigeration at low temperatures, lower than (-20°C), using the solar thermal energy, in order to improve the quality of life for many people especially in arid and semi arid regions in our country.

Keywords : refrigerants, HCFC alternatives, solar energy, conserving, seeds, cryogenic-conserving

 doi:10.1016/j.egypro.2012.05.096

1. Introduction

Could we do without heating, cooling and refrigeration? Hard to imagine!
In some areas, the temperature control is also a vital need: hospitals, laboratories, cold chain for food products, computer equipment, medical etc ... But we must also worry about the impact of lifestyle on the environment. The greenhouse effect largely determines the Earth's climate and increasing emissions of greenhouse gases associated with human activities and jeopardizes the balance current climate.

The burning of fossil fuels (coal, oil and natural gas) produces carbon dioxide (CO_2), the main gas responsible for global warming and increasing energy demand has led to a rapid increase in CO_2 emissions in the atmosphere. Heating, air conditioning and refrigeration [1] contribute significantly to this increase.

In recent decades the impact, among other, of refrigerants on the environment becomes a major issue [2]. Indeed, the presence of large leaks in the cooling system, the responsibility of these fluids in the destruction of the ozone layer and increasing the greenhouse effect is well established. Spurred on by the scientific community and international organizations, the refrigeration sector carries over 20 years to change its practices. Replacement of Hydro Chlorofluorocarbons and Chlorofluorocarbons by hydro fluorocarbons, has significantly reduced the concentration of chlorine in the atmosphere, which is responsible for the destruction of stratospheric ozone. But all these molecules turn out to be potent greenhouse gases that contribute directly to global warming.

In addition, refrigeration systems consume electricity that contribute indirectly to the emission of large amounts of CO_2. Therefore, improving the energy efficiency of refrigeration systems and the use of refrigerants with low global warming potential (GWP) are priorities that require the refrigeration sector to perform new mutations. These are the environmental tools, such as life cycle analysis, which reflect the trade-off between these two factors directly and indirectly. The objective of environmental optimization is to adapt the architecture of the refrigeration circuit properties of a fluid with low global warming potential. To satisfy these criteria, two approaches are evaluated:

- The use of new synthetic molecules with low GWP, works with the architecture of traditional cycle, which they are adapted.
- The use of natural refrigerants and adapting the architecture of the properties of the fluid.

2. History

2.1. The refrigerants used before 1929

The main gases used before 1929 during the first period of artificial cold, were:
- sulfur dioxide (SO_2),
- methyl chloride (CH_3Cl)
- carbon dioxide (CO_2),
- the chloroethane (C_2H_5Cl)
- ammonia (NH_3)

All these fluids thermodynamic properties were interesting but they all had one drawback, for example, the danger caused to humans because of their toxicity (SO_2, CH_3Cl, C_2H_5Cl, NH_3) or because they were fuels (CH_3Cl, C_2H_5Cl, NH_3) or request of the tubes and compressors particularly high pressure (CO_2).

2.2. The refrigerants used between 1929 and the Montreal Protocol

In 1929, an American scientist, Thomas Migdley and his team produced the first molecules of Dichlorodifluoromethane (CCl_2F_2) or R12. R12 and the refrigerants in the same that family have the property to be quite harmless to humans and to be interesting from the standpoint of thermodynamics.

They were produced industrially by Dupont de Nemours from 1932 (dichlorodifluoromethane - R12 and trichlorofluoromethane - R11) under the name of Freon. These refrigerants are derived from petroleum. There are a large number of refrigerants or combinations of fluids that are selected based on the operating temperatures of the refrigerant circuit [3]. We distinguish among the refrigerants, different categories:

- **Fluorinated refrigerants**

Fluorinated refrigerants are largely responsible for the destruction of the ozone layer and contribute to the increase of the greenhouse effect. The interactions between the two phenomena are real but highly complex. We distinguish several types:

- **CFCs (chlorofluorocarbons)**

They are molecules composed of carbon, chlorine and fluorine. They are stable, allowing them to reach the stratosphere without too many problems. At this stage, by transforming it contributes to the destruction of the ozone layer.

- **HCFC (hydro chlorofluorocarbon)**

They are molecules composed of carbon, chlorine, fluorine and hydrogen. They are less stable than CFCs destroy ozone and to a lesser extent. These are called transitional substances.

- **HFC (hydrofluorocarbons)**

They are molecules composed of carbon, fluorine and hydrogen. They do not contain chlorine and therefore do not participate in the destruction of the ozone layer. This is known as substitution substance. Restrictions on this family of gas are currently limited. Within the European Union, the HFC will be banned from air conditioners for cars from 2011.

- **Mixture of refrigerants**

They can be classified according to the type of fluorinated components they contain.
They are also distinguished by the fact that some mixtures are:

- Zeotropic: in a state change (condensation, evaporation), the temperature varies.
- Azeotropes: they behave like pure, with no change in temperature during the change of state.

- **Fluids down "greenhouse effect"**

They are considered less disturbing to the environment, because at once with no effect on stratospheric ozone and a low impact on the greenhouse effect [4]. They all have drawbacks, either in security, or in thermodynamics.

- **Ammonia (NH_3) or R-717**

Fluid inorganic thermodynamically is an excellent refrigerant for evaporation temperatures between -35 °C + 2 °C. But it is a fluid dangerous toxic and flammable. Despite these shortcomings, its qualities are such that it is used in industrial refrigeration**.**

- **Hydrocarbons (HC) as R-290 R-600a**

This is primarily propane (R-290), butane (R-600) and isobutene (R-600a).
These body fluids have good thermodynamic properties, but are dangerous because of their flammability. The world of the cold has always been wary of these fluids, even if they have reappeared recently in refrigerators and insulating foams. Their future use in air conditioning seems unlikely, given the cost of setting both mechanical and electrical safety.

- **Carbon dioxide (CO_2) or R-744**

Fluid inorganic, non-toxic, non flammable, but inefficient in thermodynamics. Its use would involve high pressure and special compressors. Currently, specialists in air conditioning and refrigeration are interested again by:

- its low environmental impact (ODP = 0, GWP = 1);
- the low specific volume resulting in facilities with low volume (small leak);

It has the distinction of having a low critical temperature at 31 °C at a pressure of 73.6 bars. Note that using this type of refrigerant also leads to significant constraints such as the need to work:

- at high pressures (80 or 100 bar);
- in transcritical that requires control of condensation in the gas phase (gas cooler);

- **Water (H_2O)**

Fluid inorganic, of course, without toxicity. Although its high enthalpy of vaporization is interesting, it does not lend itself to the production of cold below 0 °C. It is not suitable for compression cycle and its applications are rare.

3. Properties of refrigerants

In theory, air or nitrogen (fluid streams on our planet ...) could be used as refrigerant. In short, any fluid presents a potential for refrigeration. But in practice it is quite different. These fluids must meet the following criteria:

- The refrigerants are selected mainly for their high absorption property of heat (calories) when they spend of their liquid phase to their gas phase (the heat absorbed by the fluid during the change of state is named: latent heat of vaporization). Refrigerants are used pure or mixed in the trades of refrigeration and air conditioning.

- These fluids must respect the environment because of the potential risk of leakage into the atmosphere.
- They must be harmless to humans for the same reason as above ...
- They are also selected according to the operating temperatures of two heat exchangers of the refrigeration circuit in question (the condenser and evaporator). Indeed, the fluids used to obtain low temperatures are different fluids such as air conditioning.

Finally, their pressures (which are based on the temperatures of the exchangers mentioned above) should allow their use in a refrigeration system with a reasonable size of the pipes and compressor. Indeed, it would not be economical to use nitrogen to air conditioning; the pressure required is too great, requiring extra thick pipe and a giant compressor.

4. Restriction of use since the Montreal Protocol

Following the Montreal Protocol (1987) refrigerants CFCs (chlorofluorocarbons) were finally abandoned in 2000 and gradually replaced by HCFCs and within it providing an opportunity for the development of substitutes.

Following the EU regulations 2037/2000 and 842/2006:

- the use of HCFCs with high impact on the greenhouse effect should be permanently discontinued in 2015[5],
- the gradual replacement of HCFCs with HFCs,
- containment of refrigeration to reduce the amount of refrigerant.
- by 2015, the use of low-GWP HFCs.

In addition, it recommends to reduce and to stop production of the gases most harmful to the ozone layer and those having a significant impact on the greenhouse effect. These are the refrigerants which the molecule is rich in chlorine and whose life is great.

The conferences that followed highlighted the trend and shortened deadlines: the Copenhagen conference, it was decided to stop production of CFCs 31 December 1994 and that of HCFC 31 December 2014. CFCs are being permanently removed except for small quantities and particularly necessary (use in medicine, primarily as propellants in metered dose inhalers, Ventolin type).

Estimating future emissions of CFCs and other refrigerants according to different scenarios:

Emissions (K tons)	**CFC**	**HCFC**	**HFC**	**Others**	**Total**
2002	144	236	100	18	**499**
2015 Continuation of the activities	25	455	359	23	**861**
2015 Reduction of the activities	14	259	155	22	**451**

Table 1: According to the IPCC and TEAP, emissions of these compounds tend to decrease. The figures above show the two scenarios with continued activities or not emit these gases. The direction we are moving should normally lead to lower emissions of CFCs and HCFCs and increasing emissions of HFCs. [6]

To determine the impact of refrigerants on the ozone layer and the greenhouse effect, three main indices were defined:

- **ODP** : Ozone Depletion Potential;
- **GWP** : Global Warning Potential;
- **TEWI** : Total Equivalent Warning Impact.

ODP (Ozone Depletion Potential)

This is an index that characterizes the participation of the molecule to the depletion of the ozone layer. We calculate the value of this index compared to a reference molecule, namely either R11 or R12 that have ODP = 1.

GWP (Global Warning Potential)

This is an index that characterizes the participation of the molecule to the greenhouse effect. We calculate the value of this index compared to a reference molecule, namely CO_2, and for well-defined periods (20, 100, 500 years) (Figure 2). CO_2 has a GWP = 1.

TEWI (Total Equivalent Warning Impact)

The TEWI is a concept designed to exploit global warming during the operational life of a refrigeration system for example, using a determined refrigerant taking into account the direct effect due to refrigerant emissions and the indirect effect due to the energy required to operate the system. For more information, is given by the formula: $TEWI = (GWP \times L \times n) + (GWP \times m[1-C]) + n \times E \times \beta$

Where:

- GWP: Global Warming Potential;
- L: annual emissions of fluid in kg;
- n: the system life in years;
- m: refrigerant charge in kg;
- C: factor recovery / recycling between 0 and 1;
- E: annual energy consumption in kWh;
- β: CO_2 emissions in kg / kWh.

The table 2 is showing ODP, GWP and lifetime depending on the type of fluid:

Type of refrigerant		ODP	100-year GWP	Life cycle	
halons		3 to 10	1300 to 80 000	20 to 70 years	Prohibited ODP>0
CFC	**-11**	1	3 800	45 years	
	-12	1	8 100	100 years	
	-115	0,6	9 300	1 700 years	
Bromide of methyl		0,6	1 300	0,7 year	
HCFC		0,05	400 to 1 800	1 to 20 years	Prohibited in 2005
HFC		0	140 to 11 700	1 to 300 years	Authorized ODP=0
PFC		0	6 500 to 9 200	10 000 to 50 000 years	
SF6		0	23 900	3 200 years	
Ammonia		0	0	few days	

Table 2: A table showing ODP, GWP and lifetime depending on the type of fluid [7]

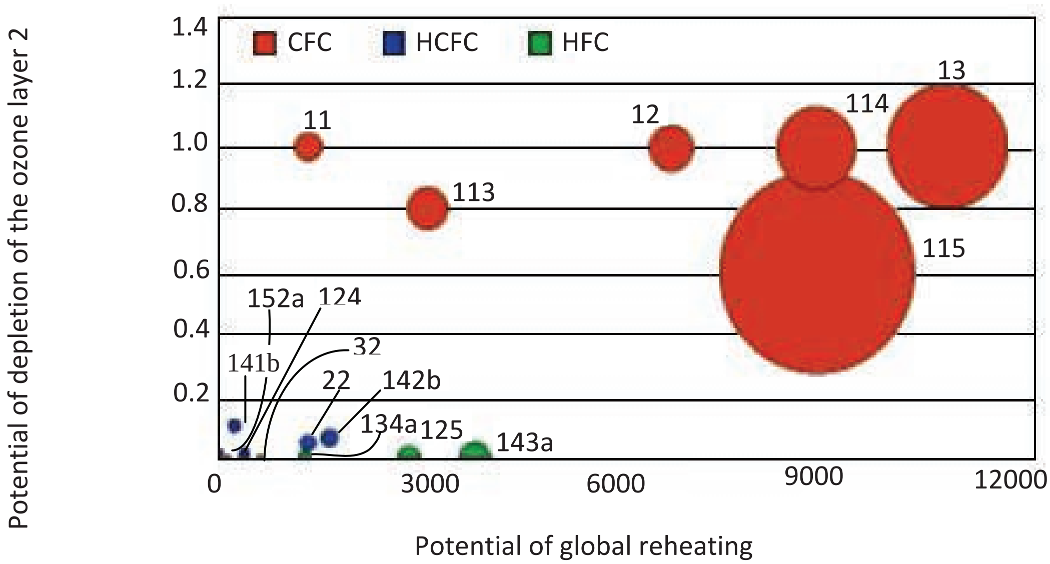

Figure 1: Highlighting the potential to deplete the ozone layer on the ordinate (ODP), the Global Warming Potential abscissa (GWP) and the lifetime of CFCs, HCFCs, HFCs (circle sizes). Number subordinating the circle corresponds to the reference compound [8]

Regulation 2037/2000 of the European Parliament and the Council of 29 June 2000 on substances that deplete the ozone layer is designed to reduce emissions of these compounds (Figure 2)

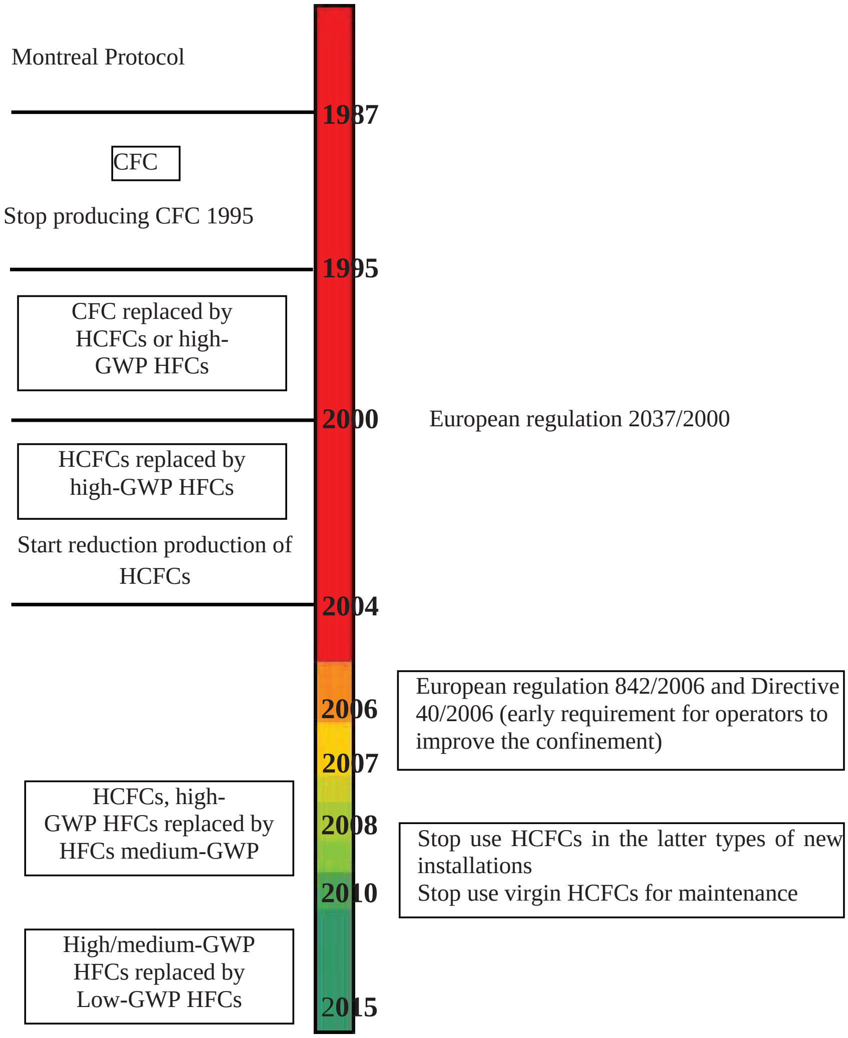

Figure 2: European regulations on the use of fluids [9]

Regulations on HCFCs

The part of the European text relative to the decrease of the quantity of HCFC-market is included below:

Deadline: Entry into force	**Regulation (EC) No 3093/94**
1/1/1995	The level of HCFC marketed or used on their own account by producers and importers does not exceed the 1989 level.
1/1/2004	35% reduction in the level of HCFC marketed based on calculated in 1995.
1/1/2007	60% reduction in the level of HCFC marketed based on calculated in 1995.
1/1/2010	80% reduction in the level of HCFC marketed based on calculated in 1995.
1/1/2013	95% reduction in the level of HCFC marketed based on calculated in 1995.
1/1/2015	Prohibition of placing on the market of virgin HCFCs.

5. Synthesis of indices of impact

The idea of the Montreal Protocol was to reduce the impact of leakage of refrigerants on the ozone layer. In the following table, we see that:

- the elimination of CFC solves the problem of the ODP that is the negative impact on the ozone layer;
- there remains the problem of the impact of HCFCs and HFCs with high GWP on the greenhouse effect.

Name	Formula and proportion of every constituent for mixtures	GWP (100 years)	ODP
CFC			
R11	$CFCl_3$	4000	1
R12	CF_2Cl_2	8500	1
HCFC			
R22	CF_2HCl	1700	0,055
R408A	R125/143a/22 (7/46/47)	(2650)	
R401A	R22/152a/124 (53/13/34)	(970)	
HFC			
R32	CH_2F_2	580	0
R125	CF_3CHF_2	3200	0
R134a	CF_3CH_2F	1300	0
R143a	CF_3CH_3	4400	0
Mixtures HFC			
R404A	R125/143a/134a (44/52/4)	3260	0
R407C	R32/125/134a (23/25/52)	1525	-
R410A	R32/125 (50/50)	1730	-
R422A	R125/134a/600a (85,1/11,5/3,4)	2535	-
R422D	R125/134a/600a (65,1/31,5/3,4)	2235	-
R427A	R32/125/143a/134a (15/25/10/50)	1830	-
R507A	R125/143a (50/50)	3300	-

Table 3: Replacement of main refrigerants [10].

6. Future

The impact of refrigeration systems and air conditioning on stratospheric ozone are mainly related to the emissions of refrigerants that deplete the ozone. The contribution of these systems in terms of global warming has its origins in the emissions of refrigerants and greenhouse gas emissions associated with energy use. Due to the fact that the component energy consumption has an impact on global warming most pronounced (significantly), the replacement of refrigerants (HFCs) in favor of less efficient solutions in terms of energy will only increase the greenhouse emissions overall.

In the absence of an ideal alternative refrigerant (pure compound or mixture), our contribution will be to make an overall assessment taking into account the ozone depletion, global warming and the lifetime in the atmosphere which provides essential information on environmental problems, security, stability, compatibility, cost and other key questions and compare the impacts of refrigerants used today with those of alternative refrigerants and chlorofluorocarbons (CFC) that were replaced.

In addition, because of problems related to the environment, the industry has a strong need for experimental data on mixtures of refrigerants in order to better evaluate the performance of refrigeration units and the Kyoto Protocol creates a new constraint that leads to development of new refrigerants. These fluids, probably mixtures in many cases, are the compromise constraints outlined above.

It may be interesting to examine the associations of halogenated refrigerants with natural refrigerants such as air, CO_2 or ammonia [11], hence the interest of our research, we are interested on the study of mixtures of a hydrocarbon with a natural refrigerant.

7. Conclusion

The ultimate solution lies in replacing these fluids by gas contribute less to increasing the greenhouse effect is the subject of much research and debate on global warming adds to the discussion the question of choice a suitable refrigerant. Hence the urgent need for substitution. Substitution is a basic rule in the prevention of chemical hazards. In the case of refrigerants, it can be a complex operation: many products are not harmful to human health, but are for the environment.

Care should be taken to choosing a refrigerant with, overall, the fewest possible hazards (health, fire, environment), which again, may have to be compatible with existing refrigeration.

The aim of our project is to contribute to the protection of our environment. Our motivation is to produce cold for different uses such as food preservation and freezing seed, saving pharmaceuticals and cooling. This work is also concerned with a contribution to preserving the environment by reducing greenhouse gas emissions and the replacement of cooling pollutants (HCFCs). This is essentially the refrigeration at low temperatures, below (-20°C), using solar thermal energy, to improve the quality of life for many people especially in arid and semi arid areas of our country.

Bibliography

[1] Jean Desmons, Aide-mémoire, Froid industriel, 2ème édition, DUNOD, 2006.
[2] 12 technologies pour l'avenir de l'environnement (Ministère de l'Industrie et du Commerce Extérieur/SRI International - 1992).
[3] Les fluides frigorigènes ED 969, Aide – Mémoire Technique, INRS – 2005.
Revue des applications électriques dans le résidentiel et le tertiaire n° 35 - Octobre 1993.
[4] Duminil, M. Frigorigènes et systèmes frigorifiques à compression : l'effet de serre équivalent total (ESET). Revue Générale du Froid. Novembre 1995, n°36.
[5] Y. Khetiba*, A.-H. Meniaib, A. Lallemand, Computer-aided design of CFC and HCFC substitutes using group contribution methods, Science Direct, 2009.
[6] Questions relatives aux hydrofluorocarbures et aux hydrocarbures perfluorés, GEIEC/GETE, 2005.
[7] Chemical and Radiative Effects of Halocarbons and Their Replacement Compounds, Intergovernmental Panel on Climate Change (IPCC), 2001.
[8] Chemical and Radiative Effects of Halocarbons and Their Replacement Compounds, Intergovernmental Panel on Climate Change (IPCC), 2001.
[9] Règlement européen CE
[10] Remplacement des principaux fluides frigorigène: www.dehon.com
[11] P. Rapin. P. Jacquard. Formulaire du froid. ISBN : 2-10-002693-3. Dunod. 1996
Bivens, D.B. and Minor, B.H. Fluoroethers and other next generation fluids. International Journal of Refrigeration Vol. 21, no. 7 pp 567-576, 1998.
Jansen, C.M.A. et al. Risk Assessment of the Use of Flammable Refrigerants (Draft interim report), EEC Contract Jou2-CT92-0060. TNO Environmental and Energy Technology., 1993.