Energy and environment options of working fluid alternative for different refrigeration configurations

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Abstract. Hydrofluorocarbons, currently used as refrigerants, in air-conditioning systems, for high-temperature heat pump systems in industrial applications are potent greenhouse gases. Their contribution to climate change is to increase. Future use of the hydrofluorocarbons as the hydrochlorofluorocarbons will be phased down. There are very different options to replace them and only a few pure fluids possess the combination of chemical, environmental, thermodynamic, and safety properties necessary for a working fluid. Low global warming potential refrigerants are anticipated to be the refrigerants of choice in industrial applications.

1. Introduction
Refrigeration is an essential technology for our present-day life. It is used in air-conditioning, manufacturing of different materials, medical applications freezing, cooling, food processing and preservation. The amount of energy used for refrigerant engineering is a substantial part of the total energy consumption in the modern world. The refrigeration industry today is in a state of intensive challenge to meet various mandatory regulations and deadlines. Early refrigerants were toxic, flammable, or both.

2. Chlorofluoro- (CFC) and hydrochlorofluorocarbons (HCFC)
The use of chlorofluorocarbons as refrigerants was proposed in 1930. As refrigerants, the CFCs have important advantages: high molecular mass, nonflammability and extremely stability. Since 1930 they were manufactured using large-scale production processes. These refrigerants have changed the world of refrigeration. Later HCFCs substances were developed. During the following 50 years, the CFCs and HCFCs refrigerants used CO$_2$ and ammonia in large-scale applications.

The chlorofluorocarbons are a class of compounds containing the halogens chlorine and/or fluorine on a carbon skeleton. For many years once emitted in the atmosphere the CFC and HCFC refrigerants persist for many years in the atmosphere. Diffusing to the upper atmosphere the molecule finally breaks down releasing the chlorine, which is responsible for catalyzing the destruction of stratospheric ozone. Stratospheric chlorine from CFCs and HCFCs is believed at least partly responsible for peak ozone concentrations occurring in the stratosphere and an ozone deficit at the poles [1]. Manufacture or import of CFCs has been ceased. A phase out date of 2030 was established for HCFCs.

Nowadays, the environmental problems associated with refrigerants in the light of their impact on the environment are the ozone depletion potentials (ODP) and global warming potential (GWP) [2]. The ozone depletion potential (ODP) is the ration of ozone destroyed by 1 kg of the substance emitted...
to the atmosphere that is destroyed by 1 kg of dichlorodifluoromethane (CFC-12). The global warming potential due to 1 kg of substance emitted instantaneously to the atmosphere from 1 kg of carbon dioxide. Table 1 gives some values.

Table 1. ODP and GWP potentials of CFCs and HCFCs refrigerants to be phased down by Montreal Protocol

| Refrigerant | Molecular formula | ODP | GWP  | Flammability |
|-------------|-------------------|-----|------|--------------|
| R11         | CCl\textsubscript{1}F | 1   | 4750 | A1           |
| R12         | CCl\textsubscript{2}F\textsubscript{2} | 1   | 10890 | A1           |
| R113        | C\textsubscript{2}Cl\textsubscript{1}F\textsubscript{3} | 1   | 6130 | A1           |
| R502        | R22/R115          | 0.25 | 4700 | A1           |
| R22         | CHCl\textsubscript{2}F | 0.055 | 1760 | A1           |
| R142b       | C\textsubscript{2}H\textsubscript{3}Cl\textsubscript{2}F | 0.07 | 2310 | A2           |

According to the internationally agreed amendments, the HFC refrigerants such as HFC-134a, HFC-410A, HFC-407C and HFC-404A, entirely harmless to the ozone layer, are considered as alternative refrigerants to replace CFC and HCFCs. The criteria often applied to the assessment of alternative refrigerants in the light of their impact of the environment have been the ODP and GWP. However, one should consider both for the direct contribution of the alternatives as greenhouse gases and the indirect contribution of the CO\textsubscript{2} emissions resulting from the energy required to operate the refrigeration system. It should be noted that among the chlorine-free halocarbons to be considered from the environmental viewpoint, there is no single possibility to replace HCFC-22 as well as CFC-502.

The chlorine-free alternatives offered by the chemical industry are HFC-134a as a pure fluid instead of CFC-12, and mainly non-azeotropic mixtures are based on the HFC-32, HFC-125, HFC-134a and HFC-143a. It is well known that these mixtures require changes in the manufacture of components, new sealing materials, new lubricants and decomposition problems of the non-azeotropic mixtures. One of the major disadvantages of zeotropes concerned by the industry is a problem of fractionation of the mixtures during the charging and leaking situations. It is clear that the composition of the refrigerant mixture can change dramatically if a leak occurs in the system under a vapor-liquid coexistence and is recharged with the original composition a number of times. In accord with an urgent demand, an attention was paid to zeotropes named as near-azeotropes or zeotrope-like blends, which exhibit minimal temperature and composition changes or «glides» during the vapor-liquid phase change. Table II summarizes some examples of HFC-mixture alternatives being proposed. The chlorine free alternatives offered by the chemical industry are HFCs as pure fluids and mainly non-azeotropic mixtures based on the HFCs as HFC-32, HFC-125, HFC-134a and HFC-143a. However, one of the major disadvantages of zeotropes is a problem of a large global warming potential (GWP) of the these synthetic refrigerants.

3. Global warming impact

An amendment to the Montreal Protocol, signed in 1987 and ratified today by more than 190 countries, asked for a reduction in the consumption and production of CFCs ad HCFCs. It was adopted in October 2016 [3]. It requires a significant reduction of the weighted value of global warming potential (GWP) of fluids used in the refrigeration industry. Consequently, hydrofluorocarbon (HFC) working fluids having a high GWP will be eliminated [4].

Another choice is to change the old natural refrigerants like ammonia (R744), water (R718), the hydrocarbons propane (R290) and isobutane (R600a) or CO\textsubscript{2} (R744) [5, 6].
Ammonia is an old refrigerant, which has even survived the CFCs and HCFCs in large refrigeration plants, where ammonia has always been the first choice. Ammonia has excellent thermodynamic properties similar to those of CFCs and HCFCs working fluids. It has neither an ozone depletion nor a global warming potential. But ammonia is toxic, and its characteristic smell can cause panic. Copper is not compatible with ammonia, and open compressors are usually used.

| Working fluids | Molecular formula/ composition | ODP | GWP   | Flammability |
|----------------|-------------------------------|-----|-------|--------------|
| R134a          | C₂H₂F₄                         | -   | 1430  | A1           |
| R125           | C₂HF₃                         | -   | 3500  | A1           |
| R32            | CH₂F₂                         | -   | 674   | A2           |
| R143a          | C₂H₂F₃                         | -   | 4470  | A2           |
| R152a          | C₂H₄F₂                         | -   | 138   | A2           |
| R404A          | R125/R143a/R134a               | -   | 3900  | A1           |
| R407C          | R32/R125/R134a                 | -   | 1600  | A1           |
| R410A          | R32/R125                      | -   | 1924  | A1           |
| R507A          | R125/R143a                    | -   | 4000  | A1           |
| R438A          | R32/R125/R134a/R600/R601a     | -   | 2265  | A1           |

Hydrocarbons becomes interesting again, even although they are flammable. Hydrocarbons are non-toxic, chemically stable, low cost and widely available. Propane in contrast to the majority of HFC mixtures is presently the only alternative which has a higher efficiency than HCFC-22. Propane and mixture of propane and butane are also used especially for refrigerators. Hydrocarbons reduce the refrigerant charge of a system by about 50 % and in contrast to HCFCs and HFCs they are hardly soluble in water.

Carbon dioxide is well known for low-temperature applications in refrigeration systems. The ideal application on the trans-critical CO₂ cycle is hot water production. The main problem with CO₂ is the high pressures up to 15 MPa, but due to the high density at high pressures, the size of the equipment decreases, the diameter of the piping can be reduced, heat exchanges become more compact. Due to low pressures in the range of 1.5 to 3, compressors become more efficient. CO₂ has a lower thermodynamic cycle efficiency. Its use may thus require a total redesign of low temperature units.

4. New refrigerants
Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have a high depletion potential (ODP) and hydrofluorocarbons (HFCs) are high global warming potential (GWP) working fluids and they are considered as greenhouse gases under Kyoto Protocol 1997 [7]. Natural refrigerants were expected to replace conventional refrigerants owing to its environmental benefits: zero ODP, low GWP. However, they have severe drawbacks including toxicity, flammability and lower thermodynamic cycle efficiency. As a result hydrofluoroolefins (HFOs), especially HFO-1234yf (2,3.3.3-tetrafluoroprop-1-ene), HFO-1234ze(E) (trans 1,3.3.3-tetrafluoroprop-1-ene) and hydrochlorofluoroolefins (HCFOs) that have zero ODP, low GWP and extremely short atmospheric
lifetime, have been recently synthesized [8]. Hydrofluoroolefins (HFOs) and hydrochlorofluorocarbons (HCFOs) are unsaturated short-chain halocarbons. HCFOs contain one chlorine atom in their molecule. They have a slightly different molecular structure than HFCs, containing a carbon-carbon double bond. Four pure compounds for refrigeration and air-conditioning, chillers and heat pumps are commercialized (see Table 3); three HFO refrigerants HFO-1234yf, HFO-1234ze(E), HFO-1234ze(Z) and one HCFO refrigerant HCFO-1233zd(E). When a carbon-carbon double bond exists, stereoisomers may exist. For fluorinated propene isomers, stereoisomers exist if the second appended letter is «e». For example, HFO-1234ze has two stereoisomers referred to as «trans» (E) and «cis» (Z) isomers.

**Table 3.** Molecular mass (M), normal boiling temperature (T_b) and critical parameters of HFOs and HCFOs halosomers

| HFO     | M, kg·kmol⁻¹ | T_b, K | T_crit, K | p_crit, kPa | GWP |
|---------|--------------|--------|-----------|-------------|-----|
| R1234yf | 114.04       | 243.70 | 367.85    | 3382.2      | <1  |
| R1234ze(E) | 114.04   | 254.18 | 382.51    | 3634.9      | 6   |
| R1234ze(Z) | 114.041  | 282.90 | 423.27    | 3533.0      | 1.4 |
| R1233zd(E) | 130.50    | 291.11 | 439.60    | 3623.7      | 7   |

The first appended letter must be either «y» (refers to F-group substitution), or «z» (refers to H-group substitution). The second appended letter «d» refers to =CHCl-substitution. HFOs do not include chlorine atoms and have an ODP value of zero. HCFOs might contribute in theory to local stratospheric ozone depletion, but the magnitude of this contribution will be extremely small due to their short atmospheric life-time. Chlorotrifluoropropene (HCFO-1233zd(E)) is oxidized rapidly in the lower atmosphere with atmospheric lifetimes of 26 days. There are different categories of flammability of HFOs/HCFOs. HFOs such as HFO-1234yf and HFO-12134ze(E) are generally classified as 2L (lower flammability) refrigerants. HCFOs-1233zd(E) are class 1 (non-flammable) refrigerants. One can reasonably conjecture that as the number of hydrogen atoms in the molecule relative to the total number of hydrogen and fluorine atoms increases the flammability of the molecule will increase. Although HFOs are not classified as toxic; they can decompose to form fluoride (HF) or carbon difluoride (COF₂) [9]. HFOs are also mixed with HCFs in a variety of blends proposed as alternatives to HFC-22, HFC-134a, HFC-404A, and HFC-404A for use in refrigeration, air-conditioning and heat pump applications. The most promising mixtures are composed of HFO-1234yf or HFO-1234ze(E) with HFC or natural refrigerants (CO₂) [10, 11].

5. **Conclusions**

This paper presents an overview of the current state of the art on the promising alternative refrigerants to substitute CFCs, HCFCs and HFCs, which is being applied in refrigeration, to conventional air-conditioning heat-pumping and organic Renkine cycle systems. Special emphasis is given to the updated information about the fluorinated propene isomers that could potentially be used as low-GWP refrigerant candidates.

**References**

[1] UNEP 1987 *Montreal Protocol on Substances that Deplete the Ozon Layer* (Nairobi, Kenya, UNEP)

[2] UN 1997 *Kyoto Protocol to the UN Framework Convention on Climate Change* (NY, USA)

[3] 2017 International milestone agreement on the phase-down of HFC production and consumption in Kigali Editorial *Int. J. Refrigeration* **73** V-VI
[4] Kauffeld M 2012 Availability of low GWP alternatives to HFCs feasibility of a large phase-out of HFCs by 2020 EIA report (Environmental Investigation Agency)

[5] Ma Y, Liu Z and Tian H A 2013 Review of transcritical carbon dioxide heat pump and refrigeration cycle Energy 55 156-172

[6] Person A 2008 Refrigeration with ammonia Int. J. Refrigeration 31 545-551

[7] IPCC 2007 Climate Change 2007 (UK, Cambridge, University Press)

[8] Brown J S 2009 HFOs-new, low global warming potentials refrigerants ASHRAE-Journal August 51(8) 22-29

[9] Schuster P, Bertermann R, Rusch G M and Dekant W 2010 Biotransformation of 2,3,3,3-tetrafluoropropene (HFO-1234yf) in rabbits Toxicology and Applied Pharmacology 244 (3) 247-253

[10] Kaniaka T, Dang C and Hihara E 2013 VLE measurements for binary mixtures of R 1234yf with R32, R125 and R134a Int. J. Refrigeration 36 965-971

[11] Gremashi L, Wu X, Biswas A Decker P 2013 Experimental study of compressor operating characteristics and performance when using R32, R1234yf and two new low GWP refrigerants as drop-in replacements for R410A 8th Int. conference on Compressors (London, UK)