Alternative refrigerants with low global warming potential for refrigeration and air-conditioning industries

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Abstract. Historically the use of natural and ecologically safe refrigerants was a strategy to eliminate environmental problems and avoid uncertainties with synthetic replacement fluids. Since ammonia is toxic, carbon dioxide provide high pressure, and the hydrocarbons are flammable, the general conclusion is often drawn that natural fluids gave safety problems. This paper will describe the possibilities of application as working fluids in refrigeration, heat pumping and organic Rankine cycles of the hydrofluoroolefins (HFOs) as alternative refrigerants with low global warming potential.

1. Introduction
A large number of compounds have been proposed to substitute the high global warming potential (GWP) hydrofluorocarbons (HFCs) in refrigeration, air-conditioning and heat pumping industry. In addition to natural fluids studies have shown that there are halogenated olefins characterized by the presence of C=C double bond in the molecule that are potentially suitable for a number of relevant applications.

The use of ecologically safe working fluids is a robust strategy to eliminate environmental problems and uncertainties with synthetic replacement working fluids. Some information on the typical characteristics of hydrofluoroolefins (HFOs) as new working fluids will be presented, an outline of the early history will also be given.

2. Possibilities and tradeoffs for low-GWP refrigerants
Fluorinated greenhouse gases including CFCs, HCFCs and HFCs have a significant impact on the climate change. It was recently estimated that they accounted for 12 % of all radiative forcing of long-lived greenhouse gases, caused by increasing greenhouse-gas levels since the beginning of the industrial revolution [1–2]. Due to the phase-out of CFCs under the Montreal Protocol atmospheric concentrations of these gases are declining, while those of HCFCs and HFCs used as replacement fluids rising rapidly. HCFCs are dealt with by the various Montreal Protocol amendments and were been prohibited in new systems in the EU since 2000. HCFCs will also be banned in other countries: before 2020 in other developed countries and before 2030 in developing countries [3].

The original Montreal Protocol signed in 1987 and ratified to date by more than 190 countries asked for a reduction in the consumption and production of CFCs and halons. As a result CFCs and halons have been phased out in the developed countries by January 1996 and HCFCs were phased out over the period 1996–2020. The Montreal protocol itself does not directly address the choice for certain replacement chemicals, its only aim is to phase out ozone depleting chemicals.
A «perfect» refrigerant should be environment friendly with zero ODP (Ozone Depletion Potential) and low GWP (Global Warming Potential): it should have a medium pressure range, with evaporating pressure above atmospheric to avoid air intake into the system; it should be safe (non-toxic, non-flammable). HFC-134a was developed to be the substitute to the CFC-12. In a range of physical properties relatively close to HCFC-22 the commercially available HFCs are HFC-125, HFC-32 and HFC-143a. Each of them has prohibitive disadvantages: HFC-32 and HFC-143a are flammable, HFC-125 is not flammable, but has a very bad cycle efficiency. Some blends were developed to go below the limit of flammability. In practice HFC-125 + HFC-32 (HFC-410A) and HFC-125 + HFC-143a (HFC-507) both give nonflammable quasi azeotropes at 50/50 % concentration. The near azeotrope of HFC-32 and HFC-125 is significantly different from the others in that it operates at very high pressure, approximately 50 % higher than HCFC-22. If lower pressures are desired some HFC-134a must be added. The most common blends involving HFC-134a are: HFC-404A practically identically HFC-507 with 4 % of HFC-134a added; HFC-407C is practically some HFC-410A with 52 % HFC-134a added [4].

Global warming is a big challenge for world society today [6–7]. Emissions of HFCs today contribute around 1 % to global greenhouse gas emissions, but growing by 8–9 % annually because of rapidly increasing demand for refrigeration and air conditioning in emerging economies. As anticipated for some time, an amendment to the Montreal Protocol adopted in October 2016 requires a significant reduction of the weighted value of global warming potential (GWP) of fluids used in air-conditioning and refrigeration equipment. Consequently hydrofluorocarbon (HFC) refrigerants having a high GWP will be eliminated or their use will be significantly reduced. As a result, efforts are made in order to search alternative refrigerant for high GWP refrigerants replacement. In the search for new refrigeration a number of other criteria must also be met. These include stability, short atmospheric lifetime. Also important are thermodynamic properties, low flammability and toxicity, cost and compatibility with the materials of construction. The «optimum» refrigerant depends on the constraints of the day and as in the case today with the concern of the contribution of HFCs to anthropogenic global warming.

Taking into account various criteria particularly low toxicity, low flammability, low global warming potential (GWP) and high energy efficiency, the halogenated olefins characterized by the presence of a C=C double bond in the molecule that are potentially suitable for a number of relevant applications [8–9]. The hydrofluoroolefins are the synthetic refrigerants having zero ODP, low GWP and extremely short atmospheric lifetime. The fluorinated isomers also can be identified as for example HFO-1234ye, HFO-1234yf. When a carbon-carbon double bond exist is stereoisomers may exist. For example R1234ye has two stereoisomers trans-1,2,3,3-tetrafluoropropene (R1234ye(E)) and cis-1,2,3,3-tetrafluoropropene (R1234ye(Z)) [6].

The hydrofluoroolefins (HFOs) have been proposed as novel third generation of refrigerants, particularly to replace conventional refrigerants, for example R134a in the automobile air conditioning system which has GWP of 1430. Both refrigerants R1234ye(E) and R1234ye(Z) have a GWP value of 2.3 and 2.9 respectively. Table 1 provides estimated fundamentals parameters and thermodynamic properties for some of these isomers. In the case for the fluorinated propene and ethane isomers and stereoisomers the required inputs are the acentric factor ($\omega$), the critical state properties $T_c$, $p_c$, the normal boiling temperature $T_b$, molecular mass and GWP-index [9, 10].

| Refrigerant | $M$, [kg/kmol] | $T_c$, [K] | $p_c$, [kPa] | $T_b$, [K] | GWP | $\omega$ |
|-------------|---------------|------------|--------------|------------|-----|---------|
| R1234yf     | 114.04        | 367.85     | 3382.2       | 243.70     | <1  | 0.2760  |
| R1234ze(E)  | 114.04        | 382.51     | 3634.9       | 254.18     | 6   | 0.3120  |
| R1234ze(Z)  | 114.04        | 423.27     | 3533.0       | 282.90     | 1.4 | 0.3271  |
| R1233zd(E)  | 130.50        | 439.50     | 3623.7       | 291.41     | 7   | 0.3025  |
The fluorinate propene isomers with bases 1252 and 1261, i.e. isomers containing 4H/2F and 5H/1F respectively are most likely highly flammable. As the number of hydrogen atoms in the molecule relative to the total number of hydrogen (H) and fluorine (F) atoms increases, the flammability of the molecule will increase, which would indicate increasing flammability from the R1225 isomers to the R1243 isomers.

The use of hydrofluoroolefins (HFOs) as a pure-component refrigerant causes concern due to their mildly flammability. The mixing of two refrigerants may offer a good alternative to pure substances. Such mixtures can meet the refrigerants of high cycle efficiency, b environmentally friendly and not dangerous for human beings. The most promising mixtures are composed HFO-1234yf or HFO-1234ze(E) with either an HFC or a natural refrigerant for example with CO$_2$. Such mixtures make to reduce the flammability of HFOs.

Toxicity for the fluorinated isomers is playing an important role in the development efforts being expended of these isomers. Several of the R1225 isomers are no longer being developed because of toxicity concerns. During the past years various thermophysical properties of the HFOs such as vapor pressures, critical properties, specific heat capacities, densities and transport properties were investigated [10]. The R 1234yf is an appropriate near «drop-in» replacement for R134a in existing applications and R1234ze(Z) is appropriate as a near «drop-in» replacement for R114 in high-temperature heat pumping applications.

As alternatives for HFCs has been proposed some compositions of HFC-HFO (table 2).

| Refrigerant | Composition | GWP |
|-------------|-------------|-----|
| R450A       | R1234ze/R134a | 605 |
| R456A       | R32/R1234ze/R134a | 687 |
| R513A       | R1234yf/R134a  | 631 |
| R513B       | R1234yf/R34a   | 596 |
| R448A       | R32/R125/R1234yf/R134a/1234ze | 1386 |
| R444A       | R32/R152a/R1234ze | 92  |
| R459B       | R32/R1234yf/R1234ze | 144 |

3. Conclusion
Hydrofluoroolefins (HFOs) have been proposed as new generation alternative refrigerants with low global warming potentials to replace the hydrofluorocarbons (HFCs) – greenhouse gases mainly used as refrigerants.

References
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