Thermodynamic assessment, screening and trade-offs in alternative working fluids selection for refrigeration, heat pumping and organic Rankine cycles

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Abstract. Global warming and ozone depletion are leading effects attaching the consideration of environmental organizations. Conversion to alternative hydrofluorocarbons (HFC) refrigerants without chlorine atoms progressed over the last two decades. However recently because of the significant global warming impact of HFCs the hydrofluoroolefins (HFOs) were proposed as new generation alternative refrigerants. This article discussed fluorinated propene based isomers, summarizes refrigerant numbering scheme, flammability, fundamental parameters and thermodynamic properties of isomers containing five-, four- and three-fluorine atoms respectively. In the present study evaluated the refrigerant performance in an idealized vapor compression refrigeration cycle. Presented HFC and HFO blends as non-flammable refrigerants with relatively low global warming potential values.

1. Introduction
The paper deals with the present uses of halocarbon refrigerants and effect due to environmental regulations. The expected impact of regulations on the halocarbon producing and using industries is discussed. A status report on alternative products in equipment design is provided.

2. Montreal environmental treaty
The halocarbons are a class of compounds containing the halogens chlorine and/or fluorine on a carbon skeleton. In the 1930s the first compound – dichlorodifluoromethane named freon-12 (R12) was introduced as a refrigerant. Halocarbons replaced refrigerants such as ammonia and sulfur dioxide and in common use and today serve as the working fluid playing on important role in refrigeration, air-conditioning, heat – pumping equipment, in many of the social, demographic and technological innovations in the world [1]. The major chlorocarbons refrigerants are characterized by their non – flammability, low toxicity, good thermal property and extreme stability. The CFC refrigerants persist for many years once emitted to the atmosphere, diffuse to the upper atmosphere where the molecules finally breaks down, releasing the chlorine which is responsible for catalyzing the destruction of stratosphere ozone [2]. In March 1988 a panel of world scientists announced conclusion of their detailed analysis of global atmosphere ozone data
collection since 1969. For the first time these scientists found reliable evidence of measurable ozone depletion in the range 1.7–3.0% in northern midlatitudes (30–64\degree). They concluded that the major contributors are most likely CFC compounds in the atmosphere. In September 1987 the Montreal meeting of the United Nations Environmental Program was attended by 55 nations. As a result 197 nations today signed the Montreal Protocol on Substances that Deplete the Ozone Layer. For the CFCs R11, R12, R113, R114, R115 freeze at 1986 level was followed by a 100% reduction in 1996. There are limited exception for the developing countries. The measures hold both for production and CFC consumption. Bulk products containing CFCs and products made using CFCs are also banned [3–5].

Much attention has been point to how compounds that may serve as alternatives. The Ozone Depletion Potential (ODP) of compounds is related to the presence of chlorine, particularly in the fully halogenated ones (CFCs). So the partially halogenated chlorofluorocarbons (HCFCs) had been considered as promising replacement fluids. Five types of refrigerant was considered for replacement R12 and R502 (R22+R115) refrigeration system: R22, HCFC blends, R134a, HFC blends, HFC azoetrope. The major problem with HCFCs is their ozone depleting potential and their scheduled phase out under the Montreal Protocol. The non–ozone depleting hydrofluorocarbons (HFCs) were seen as long term replacement. Is best known R134a acclaimed as an R12 replacement. In order to match the performance of existing CFC - refrigerants a number of HFC blends have been produced. The use of HCFC based blends is an attractive medium term solution been in the longer term HCFCs themselves are phased out, chlorine free refrigerators (HFC) are needed. R134a was found to be a relatively good substitute for R12 in high and medium temperature applications. HFC – 134a has zero ODP. It is nontoxic and nonflammable. Under the air-conditioning working conditions the coefficient of performance (COP) of HFC – 134a is slightly higher than that of HCFC – 22. But the volumetric capacity (Q\textsubscript{0v}) of R134a is only as 60% as that R22. Up to now, the binary and ternary mixtures proposed to replace R22 are R407C (R32+R125+R134a), R404A (R125+R143a+R134a), R410A (R32+R125), R32+R152a, R32+R134a, R152a+R134a+R32. The R407C look very similar to R22 in capacity and operating pressures. Known as R410A the near azeotrope of R32 and R125 is significantly different from the others in that it operate at very high pressure, approximately 50% higher than R22. While the theoretical thermodynamic efficiency of R410A is not as high as R22 the heat transfer characteristics are superior and most system test with system optimized for R410A have shown superior performance to R22.

3. Global warming

The ideal working fluid would be a volatile substance, with an appropriate pressure/temperature relationship, high latent heat, low index of compression, high acoustic velocity and high critical temperature. The ideal fluid should be non - flammable, non-toxic and miscible with readily available lubricants. The main disadvantages of the HFC – refrigerants which are being replaced is their high Potential of Global Warming (GWP) [6]. The halogenated CFC – and HFC – refrigerants are also major contributions to the greenhouse effect. Because of their long life and strong infrared absorptions the CFCs and HFCs are responsible for approximately 10–15% of the predicted global warming trend [7,8] in spite of atmospheric concentrations several orders of magnitude lower that of carbon dioxide. Refrigeration affects global warming trough energy consumption and the direct effect of refrigerants when and if they are released into the atmosphere. Global warming has provided the impetus to deal with the old problem of the exhausting of finite resources. The consequences of the increase in global warming are reported to be:

- an increase in the earth’s temperature by 0.5 K from 1860 to 1990;
- a rise in the mean level of the seas;
climate change;
harvest modification – ecosystem changes.

The problem can be approached by:

regulation on energy efficiency (energy saving);
regulations on greenhouse gases (environment protection).

The Parties to the Montreal protocol did however, decide in Kigali to decrease HFC consumption by 2036 to level of 15% from the level of refrigeration consumption at 2012–2014 years [9, 10]. The amendment to the Montreal Protocol adopted in October 2016 requires a significant reduction of the value of global warming potential of fluids used in air conditioning and refrigeration equipment. Hydrofluorocarbon (HFC) refrigerants having a high GWP will be eliminated or their use will be significantly reduce.

4. Low GWP replacement fluids

As next generation of synthetic refrigerants having zero ODP, low GWP and extremely short atmospheric lifetime have been proposed hydrofluoro - olefins (HFOs) especially ethylene and propylene isomers. Containing an unsaturated (carbon-carbon double) bond and can also be referred to as olefins or alkenes. The fluorinated isomers also can be identified with prefixe HFO (hydrofluoro-olefin) [11]. For example HFO – 1234ye, HFO – 1234ye. 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 zis – 1.2.3.3 – tetrafluoropropene (R1234ye(Z)). The hydrofluoroolefins have been proposed for example as alterative refrigerants for R134a, which has GWP of 1430. Both refrigerants have a GWP value of 2.2 and 2.3 respectively, low toxicity and mild flammability. A good alternative may offer the mixing of refrigerants cotaining CO2, R32, R125, R134a and HFOs. Such mixtures can reduce the flammability of HFOs, improve the thermodynamic performance and to be a good alternative to pure substances [12].

Table 1 provides the estimates for the fundamental thermodynamic parameters of \( t_{c} \), \( p_{c} \), \( t_{nbp} \) and for comparison parameters for current HFC – and – HCFC – refrigerants [11, 13].

| ISO designation | Parameter | \( t_{nbp} \), °C | \( t_{c} \), °C | \( p_{c} \), MPa |
|-----------------|-----------|-----------------|----------------|----------------|
| R1225ye(E)      | –15.0     | 113.6           | 3.401           |
| R1125ye(Z)      | –20.0     | 106.1           | 3.335           |
| R1234yf         | –28.0     | 96.1            | 3.435           |
| R1234ye(E)      | –22.0     | 106.7           | 3.534           |
| R1234ze(E)      | –19.0     | 111.2           | 3.576           |
| R1234ze(Z)      | 9.0       | 153.6           | 3.970           |
| R22             | –40.8     | 96.2            | 4.99            |
| R32             | –51.8     | 78.35           | 5.83            |
| R134a           | –26.1     | 101.1           | 4.06            |
| R410A           | –51.6     | 72.5            | 4.95            |

In table 1 \( t_{c} \), \( p_{c} \) are the critical pressure and the critical temperature of fluids, \( t_{nbp} \) – temperature of normal boiling point. Hydrofluoroolefins (HFOs) have been proposed particularly
by in the automobile air conditioning system, for medium and high-pressure applications, heating and refrigeration applications. 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. Some models were developed for predicting their properties [14, 15] and for the evaluation of the energy performances of vapour compression refrigeration configurations using low GWP refrigerants as working fluids haven been proposed as alternative refrigerants for current HFC and HCFC and natural working fluids [13].

Figure 1 shows the fundamental tradeoff between COP and the volumetric cooling capacity for the simple cycle at the refrigeration operating conditions of the current refrigerants R22, R134a, R125, R32, R410A, ammonia, propane, isobutene and of some hydrofluoroolefins (HFOs) [13]. Figure 1 presents also for the preliminary screening of refrigerant candidates the COP/COP$_{\text{Carnot}}$ values when the absolute COP values is referenced to the COP$_{\text{Carnot}}$ value for the Carnot cycle.

5. Conclusion
Owing to environmental problems arising from the use of working fluids various refrigerant have been banned and their phase – out deadlines established through the Montreal, Kyoto and Kigali international protocols. Since chlorofluorocarbons (CFCs) have been phased out HCFC and HFC alternative refrigerants have been searched. Recently the interest in hydrofluoroolefins (HFOs) has increased as new HFC – alternatives.

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