Refrigerants and environment

O B Tsvetkov, Yu A Laptev
ITMO University, St. Petersburg, Russia
E-mail max_iar@irbt-itmo.ru

Abstract. The refrigeration and air-conditioning industries are important sectors of the economy and represent about 15% of global electricity consumptions. The chlorofluorocarbons also called CFCs are a class of refrigerants containing the halogens chlorine and/or fluorine on a carbon skeleton. Because of their environmental impact the Montreal Protocol was negotiated in 1987 to limit the production of certain CFCs and hydrochlorofluorocarbons (HCFCs) in developed and developing countries. The halogenated refrigerants are depleting the ozone layer also major contribution to the greenhouse effect. To be acceptable as a refrigerant a fluid must satisfy a variety of thermodynamic criteria and should be environment friendly with zero Ozone Depletion Potential and low Global Warming Potential. The perspective of a future phase down of HFCs is considered in this report taking into account a strategy for the phase out of HCFCs and perspective of choosing of various refrigerant followed by safety issues.

The chlorofluorocarbons also called CFC’s are a class of compounds containing the halogens chlorine and/or fluorine on a carbon skeleton. The refrigerant CFC12 was introduced in the 1930s. CFC’s replaced many of refrigerants such as NH₃, CO₂ in Refrigeration sectors. The major CFC and HCFC refrigerants are nonflammable, low toxic, extreme stable. The extreme stability of CFC refrigerants allows them to persist for many years in the upper atmosphere, where the molecule finally breaks down, releasing the chlorine which is responsible for catalyzing the destruction of stratospheric ozone [1, 2].

The first convention signed in March 1985 for the protection of the ozone layer allowed to engage researches on the CFC’s effects. But the discovery on the ozone’s hole above the Antarctic on May 1985 has only accelerated the emergency of a convention requiring to stop the use of CFC. The Protocol of Montreal was signed on September 1987 to stop progressively the production of CFC and HCFC. After Montreal 1987 the chemical industry was prepared for phasing out CFCs by providing alternatives. The main products have been the HFC-134a as an alternative for R12 and mixtures mainly non-azeotropic mixtures, based on the HFSs R32, R125, R134, R143a, R152a and R290. Non azeotropic refrigerants have exhibit temperature glide during evaporation associated with the fall in boiling point of changing mixtures of their constituents. The majority of these mixtures requires changes in the manufacture of components, new sealing materials and new lubricants. But the main problem is that in the majority of applications the efficiency is lower than with the CFC and HCFC they are to replace. Because CFC’s have long lifetimes, they accumulate in the atmosphere and their concentrations will grow even if their emissions would reduce. The major CFC refrigerants are responsible also for 15–20% of the predicted global warming trend.
The hydrofluorocarbon (HFC) refrigerants have been launched as refrigerants for the ozone depleting chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants. All halogenated refrigerants including HFC’s classified as Greenhouse gases. Emission of refrigerants contributes significantly to the Greenhouse effect in comparison with CO₂ classified as the main Greenhouse gas in the atmosphere [3–5].

Potentially could be used the next generation of refrigerants as low-GWP candidates – the fluorinated propene and ethene based HFO-working: hydrofluoroolefins (table 1) [6–8].

Table 1. Fundamental thermodynamic parameters for propene isomers

| ASHRAE designation | Structure         | \( t_0 \) (°C) | \( t_{\text{crit}} \) (°C) | \( p_{\text{crit}} \) (MPa) | \( \rho_{\text{crit}} \) (kg \cdot m⁻³) |
|--------------------|-------------------|----------------|-----------------------------|----------------------------|----------------------------------|
| R1234ye (E)        | CH₂F₂CH=CHF       | –22.0          | 106.7                       | 3.534                      | 473                              |
| R1234yf            | CF₂CF=CH₂         | –28.0          | 96.1                        | 3.435                      | 473                              |
| R1234ze (E)        | CF₂CH=CHF         | –19.0          | 111.2                       | 3.576                      | 473                              |
| R1234ze (Z)        | CF₂CH=CFH         | 9.0            | 153.6                       | 3.970                      | 473                              |
| R1243zf            | CF₂CH=CH₂         | –25.2          | 105.0                       | 3.740                      | 423                              |
| R1225ye (Z)        | CF₂CF=CFH         | –20.0          | 106.1                       | 3.355                      | 517                              |
| R1225ye (E)        | CF₂CF=CHF         | –15.0          | 113.6                       | 3.401                      | 517                              |
| R1225zc            | CF₂CH=CF₂         | –21.8          | 103.4                       | 3.312                      | 517                              |

\( (t_{\text{crit}}, p_{\text{crit}}, \rho_{\text{crit}}) \) – critical constants of refrigerants; \( t_0 \) – boiling point under atmospheric pressure

It is important to adopt any change in refrigeration industry between energy consumption and environment protection. In 1991 the overall environmental impact for any given refrigeration system has been classified as TEWI (Total Equivalent Warming Impact) calculations based on two categories of Global Warming Potentials (GWP) namely Direct GWP and Indirect GWP [2]. In 2015 additional holistic indices have been developed to measure this impact including all effects from the release of refrigerants into the atmosphere during the lifetime of the system, annual leakage and losses during the disposal of the unit, emissions from the manufacturing process, energy consumption and disposal of the system. LCCP 2015 (Life Cycle Climate Performance) is a more comprehensive than TEWI to evaluate refrigeration systems and heat pumps for various locations around the world [9].

A very important group of long term CFC, HCFC and HFC alternatives to eliminate environmental problems are natural working fluids like CO₂, ammonia, air, hydrocarbons, water. Due to the flammable and toxic nature the safety aspects are dominant in relation to the application of ammonia and hydrocarbons.

Heat pumps are regarded as an important option in the application of renewable energies and thereby in the reduction of global warming, therefore is renewed interest in the use of CO₂, for the replacement of the conventional refrigerants. [10–12].The use of CO₂ (carbon dioxide), may provide a totally safe, economical and cost-effective solution. The trans-critical CO₂ cycle is well adapted to heat pumps for hot service water production, and district heating networks. The CO₂ cycle can be considerable improved by recovering the expansion work for instance in a skrew expander, in the ejector cycle. The use carbon dioxide as a volatile secondary refrigerant may give the temperatures as low as –45 to –50 °C.

The use of propane/butane as refrigerant in home refrigerators is generally accepted. It’s realistic the application of hydrocarbons in other small equipment, in equipment like small residential heat pumps, small room air conditioners and automotive air conditioning. Heat pumps effectively utilize renewable thermal energy resources, such as natural or waste heat. In nearly all situations heat pumps will save energy and in many cases they offer other advantages as well. A high electricity price relative to gas and oil prices favors fossil fuel fired heating systems, but low electricity prices can make difficult for heat pumps to compete with electric resistance heating. A heat pump will typically require a higher investment than its alternative. Heat pumps have to be considered as an integral part.
of energy systems and refrigeration and heat pump programmers and policy measures must be part of a wide ranging energy and environmental policy.

References

[1] McLinden M O and Didion D A 1989 *Int. J. Thermophys.* **10** pp 536–76
[2] CFC’S. The day after 1994 *Proc. from IIF/IIR Conf.*
[3] Klimenko V V and Tereshin A G 1996 *Kholodilnaya Tekhnika* **5** pp 10–1
[4] World Meteorological Organization (WAC) 2011 *Greenhouse Gas Bulletin* **7**
[5] Overview of Regulations Restricting HFC Use. Focus on the EUF–Gas Regulation 2014 26th *Inform. Note on Refrigeration Technologies* (IIF/IIR) January p 7
[6] Calm J M 2008 *Int. J. Refrigeration* **31** pp 1123–33
[7] Brown J S 2009 *ASHRAE-J. August* pp 22–9
[8] McLinden M O, Brown J S, Kazakov A F and Domanski P A 2015 *Proc ICR* (Yokohama, Japan)
[9] Guideline for life cycle climate performance 2016 **1.2** (IIR Paris) p 26
[10] Kraus W E, Quack H 1994 *Kl. Lüft- und Kältetechnik* **12**. s 582–5
[11] Kalnin I M 2012 *Kholodilnaya Tekhnika* **1** pp 42–9
[12] Suhii A A and Antanenkova I S 2012 *Proc. of Conf. on the Optimization, Security and Safety of Heat and Nuclear Systems* (Moscow) pp 126–7

Acknowledgments

This work is part of the research program financially supported by the Russian Foundation of Fundamentals Research under Grant № 15–08–08503.