Global allergens and refrigeration alarmism

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Abstract. The refrigeration, air-conditioning and heat pumping industries are essential sectors of the world economy. The list of the major synthetic refrigerants characterized by the non-flammability, low toxicity, good thermophysical properties and stability are reviewed. The HCFCs and fully halogenated CFCs refrigerants are responsible for the destruction of stratospheric ozone. The paper details the effects of two allergens – the global climate change and the depletion of stratospheric ozone due to chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons. This situation has been estimated as sufficient to cause alarm. The urgent task today is to develop harmless refrigerants with zero ozone depletion potential and a minimal greenhouse effect potential.

1. Introduction

The refrigeration, air-conditioning and heat-pump industries, organic Rankine cycles are important sectors of the world economy. Low temperature engineering has played an important role in many of the social, demographic, and technological changes and advancements that have occurred in the world only over the last thirty years [1]. About 80 % of food eaten depends of the refrigeration to prevent the growth of pathogens at some point in the production and distribution chain.

The refrigeration today is everywhere: cryogenics, space industry, medicine and health products, building and data centers, LNG, hydrogen and organic Rankine cycles in energy sectors, environment. The most important role in the social, demographic and technological changes and advancements that have occurred in the low temperature engineering over the world belongs to the working fluids (refrigerants).

Vapor-compression refrigerating systems are predominant and thus the low temperature installations need the refrigerant in the present time and will need more refrigerants in the future.

The major refrigerants today are synthetic refrigerants [2, 3]: chlorofluorocarbons (CFCs), hydrofluorochlorocarbons (HCFCs), hydrofluorocarbons (HCFs), natural refrigerants (ammonia, CO₂, hydrocarbons, water, air).

The first synthetic compound called dichlorodifluoromethane or R12 was introduced as a refrigerant in the 1930s. The CFC refrigerants replaced a quickly ammonia and sulfur dioxide thanks to their nonflammability, low toxicity, excellent thermodynamic properties and extreme stability.
In 1970 the very stable molecule of CFC-11 (CCl$_3$F) was discovered in the stratosphere. Diffusing to the upper atmosphere the molecule of CFC-11 destroys the stratospheric ozone. Because of their long life, the chlorofluorocarbons can deplete the earth’s stratospheric ozone layer. The scientific studies indicate a reduction in ozone over the 70–80s years and as a result of these findings an international agreement has been reached called the Montreal Protocol on Substances that Deplete the Ozone Layer [4], designed in September 1987. The protocol calls for the regulation of consumption of CFCs and the bromofluorocarbons (BFCs) – halons. To evaluate the health and environmental effects of ozone depletion, the World Meteorological Organization (WMO) developed so called ozone depletion potentials (ODPs) and a little later – also global warming potentials (GWPs). The last one characterizes the major contribution of fully halogenated hydrocarbons to the greenhouse effect. Because of their strong infrared absorption, the synthetic refrigerants are responsible for approximately 10–15% of the predicted global warming trend [5].

To avoid the reduction in the atmospheric ozone layer, according to the terms of the Montreal Protocol a total (for developed and developing countries) phase out for CFCs by 2010 and hydrochlorofluorocarbons (HCFCs) by 2040 in all countries has been established.

CFC alternatives refrigerants have been searched based on the main condition of no chlorine atoms because of zero ODP. However another global environmental issue is global warming for more serious concerning refrigerants. The hydrofluorocarbons (HFCs) gases became relevant in all refrigeration fields but while they are non-ozone depleting substances, they have great values of global warming potential (GWP). Therefore after being approved the Kyoto Protocol in 1997 HFC refrigerants were considered as greenhouse gases and they would be progressively removed [5, 6].

One of the key elements in F-Gas Regulations is the European Unions’ (EU) Regulation on the use of Certain Fluorinated Greenhouse Gases (2014). This EU-Regulation as the Kigali Amendment (2016) calls for a phase down of HFC-consumption (Figure1), increased leakage control for systems containing high-GWP refrigerants, as well as restrictions in service of existing plants with virgin F-gases [5]. Exceptions exist for equipment intended for application to cool products to temperature below –50°C.

To reduce the impact of global warming, research efforts in modern low temperature industry today are focused on finding non-toxic fluids with low GWP, low flammability to replace these high GWP hydrofluorocarbons used in existing vapor compression systems. In the near future HFCs with GWP=150 is the maximum allowed in Europe [7].

Efforts are made in order to search alternative refrigerant for high GWP refrigerants replacement of R134a which has a GWP of 1430, R32 with GWP=675, R404A with GWP=3922, R407A with GWP=2017. To be acceptable as a refrigerant an alternative working fluid must satisfy a variety of criteria, as examples, the requirements of a non-flammable refrigerant, of low toxicity, with low GWP and other practical properties, including cost and compatibility with the materials of construction. An amendment to the Montreal Protocol adopted in October 2016 requires a significant reduction of the GWP of all fluids used in low temperature engineering equipment.
Recently hydrofluoroolefins (HFOs) that have zero ODP low GWP, and extremely short atmospheric lifetime, have been proposed as next generation refrigerants to replace HCFs working fluids. Like HFCs hydrofluoroolefins can be used as refrigerants but they have a slightly different molecular structure than HFCs. Hydrofluoroolefins are unsaturated short-chain haloolefins containing a carbon-carbon double bond. This difference is important and is now seen to be a liability – the halogenated olefins less stable in the atmosphere than their fully halogenated halocarbons. For hydrofluoroolefins may exist stereoisomers, differing in their geometrical arrangements. The isomer is referred to as «trans» isomers designated with appended «(E)» and «cis» isomers designated with an appended «(Z)». HFOs have ultra-low GWP values such as 4 for R1234yf, 7 to R1234ze(E), and 4.5 for R1233zd(E). HFOs do not chlorine atoms therefore have an ODP value of zero and no impact on the ozone layer. Hydrofluorochloroolefins (HCFOs) contain one chlorine atom in their molecule whereas HFOs do not.

In theory HCFOs contribute to local stratospheric ozone depletion but due to their short atmospheric life-time the ozone depleting potential (ODP) of HCFOs is ultra-low such as for example 0.00034 for R1233zd(E). The concentrations likely to be emitted by HCFOs are not likely to affect stratospheric ozone. HFOs such as R1234yf and R1234ze(E) are classified by ISO 817 as 2L refrigerant (lower flammability). The HCFOs R1233zd(E) and R1224yd(Z) are class 1 by ISO 817 (nonflammable). The flammable refrigerants are not suitable for retrofitting existing equipment. Although HFOs are non-toxic, they can as HFCs decompose to form hydrogenfluoride (HF) or carbon difluoride (COF₂). It is important that HF is a highly toxic substance.

**Figure 1.** Phase down schedule of the F-gas regulation placed on the market during the 2009–2012 period
It is certainly no secret that those potentially acceptable substitutes to 2031 year are the most important hydrofluorocarbons (HFCs) - namely: R134a, R125, R404A, R410A, R407A, R32, R143a. Halogenated alkenes could replace HFCs as working fluids in a wide range of low temperature applications.

2. Results and Discussion

Therefore, it is important to understand how well the substitutes perform and what is the toxicity status of these materials. All fluorinated olefins have predicted GWP values less than ten and it is important how soon the HFOs will be commercialized. In limited commercial production they are stereo isomers of R1234: R1234yf, R1234ze(Z) and R1234ze(E). They have a safety classification of A2L, as having a flame speed less than 10 cm·s\(^{-1}\). Propene R1234zc and R1234yc contain the \(=\text{CF}_2\) group that is very toxic. The stereo isomer of R1243 (R1243zf) has low acute toxicity. Isomers R1243yc and R1243zc contain the \(=\text{CF}_2\) group and so be expected to have higher toxicity. The fluorinated ethene R1132a also known as vinylidenefluorid is toxic.

The one fluorinated butane (1,1,1,4,4,4–hexafluoro–2–butene) has low toxicity and is being commercialized as a foam-blowing agent. It may be applicable for centrifugal chillers and/or organic Rankine – cycle power systems [7].

Eight alkenes contain chlorine or bromine in addition to fluorine. The use of R1233zd(E) was approved in chiller applications. R1113 known as chlorotrifluoroethylene is commercially produced as the precursor to certain specialty fluoropolymers.

HFOs are technologically more difficult molecules to manufacture than most HFCs and costly. The prices for either of two commercialized HFOs (R1234yf and R1234ze(E)) are about (88–132)USD /kg. However the price advantage for the HFCs has been reduced in some countries by a tax levied on greenhouse gases, based on their GWP. For R134a such taxes range from approximately USD 26/kg in Denmark, to USD 30/kg Australia, to USD 44/kg in Norway [7].

3. Conclusions

It is important for low temperature engineering to study the safety and environmental issues related to the use of refrigerants in numerous technical applications. A set of hydrofluorochloroolefins has been identified as the promising fluids to replace hydrofluorocarbon working fluids.

References

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