HFO refrigerants explained

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Hydrofluoroolefin, or in short HFO, is a definition that is familiar to many of us. R1234yf, R1234ze(E) are few examples of HFOs. They are used in a number of applications today, but have been barely studied just a decade ago. This article will cover some basics about HFOs.

What are the HFOs?

Hydrofluoroolefins (HFOs) are nothing new for chemistry. Much like traditional hydrofluorocarbons (HFCs), they composed from hydrogen, fluorine and carbon. The only difference is that they are unsaturated, meaning that they have at least one double bond. Such molecules are named olefins or alkenes, hence it is correct to name such refrigerants as HFC, HFA or HFO. The later name has become the most used name to refer refrigerants with carbon-carbon double bond.

The presence of the carbon-carbon double bond is not unique for HFOs as there are other unsaturated compounds to be fond, as for example unsaturated hydrocarbons (e.g. propene). In fact, HFO-1234yf is a propene molecule that is halogenated by replacing 4 atoms of hydrogen with 4 atoms of Fluorine (see Figure 1).

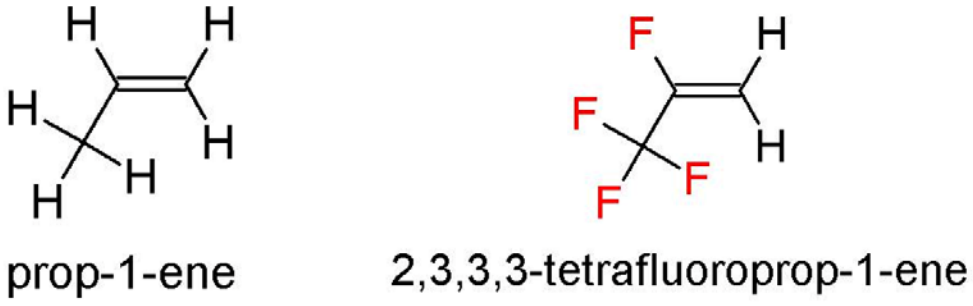

Figure 1 – Structural formula of propene (a) and HFO-1234yf (b)

HFOs are relatively stable compounds, but are more reactive than HFC due to the reactivity of the carbon–carbon bond. This also reduces their global warming potential and therefore became favorable property in light of increasing concerns on climate change.

Environmental effect

The interest to HFOs as potential refrigerants arose with the adoption of European Directive 2006/40/EC on mobile air-conditioning systems (MACs) that aimed on at reducing emissions of fluorinated greenhouse gases in the automotive air-conditioning systems. It therefore, de facto, banned the long term use of R134a refrigerant, which is itself came as an environmentally friendly replacement to R22 just a dozen years before the Directive. Fluorinated propene isomer R1234yf has become a refrigerant of a choise and many cars manufacturers have adopted new refrigerant in nearly 50 vehicle models [1].

Unlike R134a, new refrigerant has very low effect on global warming. This feature is common for other HFOs, for a number of which their integrated over 100 yr. contribution to global warming is not greater than that of CO_2 [2]. This is mainly due to their short lifetime that is within a couple of weeks for many HFOs (see Table 1)

Table 1 – Lifetime and global warming potential of some HFOs [2].

Refrigerant	**Chemical formula**	**Lifetime, days**	**GWP (100 yr.)**
HFO-1234yf	$CF_3CF=CH_2$	10.5	<1
HFO-1234ze(E)	trans-$CF_3CH=CHF$	16.4	<1
HFO-1234ze(Z)	$CF_3CH=CHF$(Z)	10.0	<1
HFO-1336mzz(Z)	$CF_3CH=CHCF_3$(Z)	22.0	2

Safety

The experience suggests that there is no single best refrigerant as, when selecting refrigerant, one normally faces trades off between different criteria. In case of HFOs the benefits on the environmental side are partly outweighed by the concerns on their safety.

The concerns on safety of HFOs were in particularly raised by Daimler AG, when the company made the decision to discontinue usage of HFO-1234yf in some of their car models [3]. The decision was followed by a number of tests that showed potential danger of flammable HFO use in MACs. The results were questioned by refrigerant manufacturer, that claims that “neither flammability nor HF formation present a significant safety concern” [4]. The potential danger of HFO-1234yf in MACs thus led a number of car manufacturer to look after alternative MAC system designs [5]. In particular, Volkswagen has already announced the use of CO_2 based systems in selected models of cars [6].

It is therefore 2 main safety issues that are related to HFOs: flammability and their potential to form dangerous acids. A number of HFOs, including HFO-1234yf, HFO-1234ze(E), are flammable, while others are not, as for instance HFO 1336mzz(Z) and HFO-1233zd(E). We have discussed the flammability issues related to different refrigerants in the previous Kyla.

Like any other the halogenated hydrocarbons, HFO is easily decomposable under the influence of high temperatures to form hydrogen fluoride - the highly soluble in water gas

that easily form acid, that would cause skin irritation, eye irritation and throat irritation and could lead to death [7]. It is quite obvious that flammable refrigerants have greater probability to get under effect of high temperatures and therefore bring greater risk of formation of dangerous substances.

VIP status of HFO

HFO, being technically HFCs, are surprisingly given special rights by many. For instance, the newly adopted EU Regulation 517/2014 on fluorinated greenhouse gases excludes HFOs from the definition of ‘‘hydrofluorocarbons’’ and, therefore, do not include them in their ambitious schedule of the reduction of the quantity of hydrofluorocarbons placed on the market. Japan adopts similar behavior and removed a number of HFOs from their “the act on rational use and proper management of fluorocarbons” that has recently came into effect [8].

Applications of HFO

As of today, HFOs found in a number of applications. In refrigeration and heat pump technology HFO-1234yf has been chosen to replace R134a in MAC systems; HFO-1234ze(E) and HFO-1233zd(E) are used in chillers [9] [10] and HFO-1336mzz has suggested for high temperature heat pumps [11].

The application of new HFOs extended when they used as a component of lower GWP refrigerant mixtures. For instance, HFO-1234yf and/or HFO-1234ze(E) are components of new refrigerant mixtures (e.g. R448A, R449A, R450A, R513A) that aim to replace traditional refrigerants with high environmental impact. These new refrigerant mixtures are already supported by leading compressor manufacturers [12] [13] with some reliability concerns due to comparatively higher compressor discharge temperatures of some of the new refrigerants [14].

HFOs are new range of synthetic refrigerants that promise to be a part of solution to the environmental problems. Still, considering ongoing investigations in regard of their safety, and looking back to the previous generations of synthetic refrigerants, it is still too early to tell whether hey represent the long term solution or not.

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