The voice of the heating, cooling and refrigeration industry

# Q&A on HFOs and HCFOs

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## 1. What are HFOs? What are halo-olefins?

Hydrofluoroolefins (HFOs) and hydrochlorofluoro-olefins (HCFOs) are unsaturated short-chain halo-olefins, which have been introduced as alternatives to saturated hydrofluorocarbons (HFCs) as refrigerants, due to their ultra-low GWP (Global Warming Potential).

Some products from both categories are listed in the Annex 2 of the EU F-Gas Regulation 517/2014, which requires reporting but does not set any restrictions for use.

## 2. What is the difference between HFOs and HCFOs?

HCFOs contain one chlorine atom in their molecule whereas HFOs don't (see also section 10). Nevertheless, colloquially HCFOs are usually included in the group of HFOs as they both contain fluorine and are unsaturated.

Therefore, in the following, this questionnaire will refer to the generic term HFOs even though from a strictly chemical perspective, HCFOs are different from HFOs.

## 3. How are HFOs different from HFCs?

Like HFCs (hydrofluorocarbons), HFOs (hydrofluoro-olefins) are fluorine-based substances that can be used as refrigerants. They have a slightly different molecular structure than HFCs, but this difference is important: they are unsaturated, meaning that they contain a carbon-carbon double bond. This makes the HFOs chemically less stable in the atmosphere than their HFC counterparts with similar physical properties (in terms of pressure level and capacity). In other words: HFOs have a very short atmospheric life-time and ultra-low GWP (Global Warming Potential) values – typically below 10 (i.e. significantly reduced compared to conventional (saturated) HFCs).

## 4. Are all HFOs the same?

No. Like HFCs, each specific substance has its own molecular structure and physical properties based on the basic atoms of hydrogen, fluorine, chlorine and carbon. However, they have in common to be Very Short Lived Substances (VSLS).
Today, manufacturers of these substances have commercialized five pure compounds for refrigeration, air conditioning, chillers and heat pumps:

- three HFO refrigerants:
  R-1234yf, R-1234ze(E) and R-1336mzz(Z)
- two HCFO refrigerants :
  (R-1233zd(E) and R-1224yd(Z)

Note that in addition to the above-mentioned refrigerants (HFOs / HCFOs), there is the product group of hydrochloroolefins (HCOs) to which belong the refrigerants R-1130(E) and R-1130(Z).

## 5. Are HFOs flammable?

There are different categories of flammability. The classification from the ISO 817 standard is used to identify these categories: 1 (non-flammable), 2L (lower flammability), 2 (flammable), 3 (higher flammability). "Medium pressure" HFOs such as R-1234yf and R-1234ze(E) are generally classified as 2L refrigerants. "Low pressure" HFOs such as R1336mzz(Z) and the HCFOs R-1233zd(E) and R-1224yd(Z) are class 1 (non-flammable) refrigerants.
There are several main parameters that characterize the level of flammability (1, 2L, 2, 3) of a refrigerant including the burning velocity, the upper and lower flammability limit (UFL and LFL), the minimum ignition energy (MIE) and the heat of combustion (HOC). These parameters have an impact on the way the refrigerant can be used. Note that flammable refrigerants are not suitable for retrofitting existing equipment.

EXAMPLE:
For a class 3 refrigerant such as R-290, the LFL (in $kg/m^3$) is significantly lower and its burning velocity is much higher than for a class 2L gas. In practical terms it means that for example in occupied spaces far higher charge sizes are possible with class 2L refrigerants than with class 3 gases.

## 6. What is the impact of HFOs on environment and safety?

The environmental impact of a refrigerant can be assessed from a number of perspectives, especially:

- Its GWP (Global Warming Potential);
- Its ODP (Ozone Depleting Potential);
- Its energy efficiency when used as refrigerant.

The safety is generally assessed in view of flammability, toxicity[1] and operating pressure.

HFOs have ultra-low GWP (Global Warming Potential) values such as 4 for R-1234yf, 7 for R-1234ze(E) and 4.5 for R-1233zd(E) according to the 4th Assessment Report (AR4) of the Intergovernmental Panel for Climate Change (IPCC). Their GWP values have even been revised to below 1 according to the 5th Assessment Report (AR5) of the IPCC.

HFOs being fluorinated substances, they can have similar environmental impacts as HFCs when they react with hydroxyl radicals in the air after release. When such oxidized substances react with water in the environment, they can form TFA (see section 7). Scientists have concluded that such impact from HFOs is negligible.

Although HFOs are not classified as toxic under REACH and CLP, they can – as HFCs – decompose to form hydrogen fluoride (HF) or carbon difluoride ($COF_2$). The decomposition rate depends on temperature and concentration and can be accelerated by certain factors such as ultra-violet light. High decomposition rates only occur in extreme conditions, for example when exposed to open flames or very high temperatures (e.g. fire or very hot surfaces).
Like all refrigerants, HFOs need to be handled according to instructions, and by appropriately qualified technicians. Existing HFCs can also create HF and COF2, when exposed to flames. Industry has long experience in dealing with these issues through use of CFCs, HCFCs and HFCs.

## 7. What is TFA and do HFOs cause it?

Trifluoroacetic acid (TFA) is a naturally occurring substance, found in seawater, rainwater and soil.

It can also be a breakdown product of many different chemical substances including some fluorocarbons (some HCFCs, some HFCs and some HFOs) as a result of oxidation in the atmosphere followed by reaction with water. Concern has been raised of possible impact on the environment by growing amounts of TFA.

Due to these concerns, studies have been conducted to assess the risk of TFA due to fluorocarbon emissions. In June 2015, the UNEP Technological and Economic Advisory Panel (TEAP) concluded that based on studies[2], the additional impact coming from current and future uses of fluorocarbons "will add only fractionally (estimated to be less than 0.1%) to amounts already present from natural sources such as undersea vents and volcanic activity".

Additionally, not all fluorocarbons or fluoroolefins break down completely into TFA, or the breakdown product is only to small extent TFA.

For example, R-1234ze(E) is estimated to break down into TFA at less than 10%, whereas R-1234yf will break down into TFA at 100%[3]. Furthermore R-1234ze(E) and R-1234yf are often used in low GWP blends together with traditional HFCs developed for use in refrigeration, air conditioning and heat-pumps. R-1233zd(E) does not break down into TFA due to its different molecular structure.

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[1] ISO 817 introduces categories for refrigerants. Flammability is classified as 1, 2L, 2 and 3 where 1 is non-flammable and 3 is highly flammable; Toxicity is classified as A and B where B has the highest level of toxicity.

[2] For example 'Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with changing climate: implications for human and environmental health' in Photochemical & Photobiological Sciences 14 (2015) by S.Madronich, M.Shao, S.Wilson, K.R.Solomon, J.D.Longstreth, X.Y.Tang.

[3] "Environmental Impacts of HFO-1234yf and other HFOs" by S.Henne, D.E.Shallcross, S.Reimann, P.Xiao, S.Boulos, A.C.Gerecke, D.Brunner – ASHRAE 2012.

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## 8. What is HF and how likely is it to be released?

Hydrogen fluoride (HF) is a thermal or combustion decomposition product of fluorinated refrigerants (HFOs, as well as HFCs) and is a highly toxic substance. Formation of HF occurs as a result of decomposition of an HFO or an HFC and several factors are involved in the decomposition process. The decomposition rate depends on temperature, nature of combustion, humidity and the specific refrigerant.

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## 9. What is ODP and do HFOs have an impact on the ozone layer?

Ozone Depleting Potential (ODP) is a metric to show the potential for stratospheric loss of ozone that a refrigerant may cause when released into the atmosphere. This metric has been used since it was discovered that commonly used refrigerants like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) caused such a loss of ozone. This led to the Montreal Protocol and ultimately the complete phase-out of CFCs and HCFCs.

The ODP reference value of 1 is based on the Ozone Depleting Potential of dichlorofluoromethane (R-11). Other CFCs usually have ODP values of around 1, and HCFCs usually have ODP values between 0,005 and 0.2. The most widely used HCFC R-22 had an ODP value of 0.055.

Like HFCs, HFOs do not include chlorine atoms, and therefore have an ODP value of zero and no impact on the ozone layer. For HCFOs, please see section 10.

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## 10. How do HCFOs impact the ozone layer?

HCFOs might, in theory, contribute to local stratospheric ozone depletion, but the magnitude of this contribution will be extremely small due to their short atmospheric life-time. These substances do not accumulate in the atmosphere and the ozone depleting potential (ODP) of HCFOs is ultra-low, such as for example 0,00034 for R-1233zd(E)[4]. Scientists have concluded that the concentrations likely to be emitted by HCFOs are not likely to affect stratospheric ozone[5].

Tetrafluorochloropropene R-1224yd(Z) and chlorotrifluoropropene R-1233zd(E) are oxidised rapidly in the lower atmosphere with atmospheric lifetimes of 21 days[6] and 26 days[7], respectively; hence they are very short-lived substance (VSLS)[8] that, in view of their minimal effect on stratospheric ozone, are not listed as Ozone Depleting Substances in the Montreal Protocol.

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## 11. What are the applications of HFOs?

Pure HFOs are typically used in some chiller types (screw compressor, centrifugal type), certain larger size heat pumps as well as in commercial and industrial refrigeration for "medium temperature" applications (down to -10°C) and in mobile air-conditioning.

HFOs are also mixed with HFCs in a variety of blends proposed as alternatives to R-22, R-134a, R-404A and R-410A for many industrial, commercial, and transport refrigeration applications as well as in air-conditioning and heat pump applications.

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[4] Article in Chemosphere 129 (2015): "Atmospheric chemistry of short-chain haloolefins: Photochemical ozone creation potentials (POCPs), global warming potentials (GWPs) and ozone depletion potentials (ODPs)" by T.J.Wallington, M.P.Sulbaek Andersen, O.J. Nielsen. Abstract at https://www.ncbi.nlm.nih.gov/pubmed/25070769.

[5] "Atmospheric lifetimes and ozone depletion potentials of trans-1-chloro-3,3,3-trifluoropropylene and trans-1,2-dichloroethylene in a three-dimensional model" by K.O.Patten, D.J.Wuebbels (2010)

[6] Measured by the National Institute of Advanced Industrial Science and Technology, Japan (AIST); GWP calculated according to the IPCC AR5 method.

[7] Myhre, G., D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura and H. Zhang, 2013: Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[8] Ko M.K.W. and 32 others, Very Short-Lived Halogen and Sulphur Substances, Chapter 2 of Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - Report No. 47, World Meteorological Organization, Geneva, 2002.

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# ABOUT EPEE

The European Partnership for Energy and the Environment (EPEE) represents the refrigeration, air-conditioning and heat pump industry in Europe. Founded in the year 2000, EPEE's membership is composed of 48 member companies, national and international associations from Europe, Asia and North America.

EPEE member companies realize a turnover of over 30 billion Euros, employ more than 200,000 people in Europe and also create indirect employment through a vast network of small and medium-sized enterprises such as contractors who install, service and maintain equipment.

EPEE member companies have manufacturing sites and research and development facilities across the EU, which innovate for the global market.

As an expert association, EPEE is supporting safe, environmentally and economically viable technologies with the objective of promoting a better understanding of the sector in the EU and contributing to the development of effective European policies. Please see our website (www.epeeglobal.org) for further information.

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## ANY OTHER QUESTIONS?


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