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EFCTC Position on HFOs- the new generation of fluorocarbons

EFCTC member companies are dedicated to providing sustainable, safe and energy-efficient solutions for refrigeration and air conditioning, and we are committed to investing in research and development to meet the needs of our customers and consumers. In response to such needs, a considerable research and development effort is being made to enable HFOs, the hydrofluoroolefins, to be considered as viable replacements for HFCs in some applications. The first significant application will be for MAC (mobile air-conditioning). While there is extensive additional work required by producers and potential users of these fluids in other applications, HFOs offer many of the key properties of existing HFCs, but with very low GWPs.

HFOs are the fourth generation of refrigerants, with each generation being a step-change improvement on the previous generation. HFOs are also expected to be used in other applications such as insulation foam, technical aerosols and solvents. There are many examples across industry of continuous or step-change improvements to meet the environmental challenges. This includes addressing climate change.

HFOs are not expected to be the only technology considered for the future, and there will be there is a continuing role for a wide range of technologies including hydrocarbons, carbon dioxide, ammonia, and indeed HFCs.

HFOs offer the potential to reduce the "bank"[1] of high GWP HFCs, whilst maintaining or improving energy efficiency, and at same time meet the necessary environmental standards for their sustainable use. HFOs may also be used in mixtures with HFCs where the properties of HFOs alone cannot achieve the required safety or performance standards. They can offer effective solutions where other fluids are not appropriate.

HFOs- What's in a name?

Although HFOs only contain hydrogen, fluorine and carbon like the HFCs, they are distinctly different. They are olefins, which means they have very short atmospheric lifetimes of a few days, leading to distinct environmental benefits, when compared to HFCs. Whatever their name, the important issue is to recognise the difference between HFCs and HFOs environmentally, particularly when framing legislation.

HFOs are subject to all the legislation that applies to the supply and use of chemicals, including REACH in the EU. Reports on toxicology are disclosed through the US EPA SNAP programme, and there is transparency in determining the safe use of HFOs, for example through the CRP-1234 consortium that thoroughly investigated the safe use of HFO-1234yf for car air-conditioning[2].

[1] It must be recalled that HFCs are used predominantly in closed systems and their emissions can be prevented through proper maintenance and design of equipment. The main concern is that this "bank" represents a potential source of emissions.

[2] SAE International Industry Evaluation of low global warming potential refrigerant HFO-1234yf, Phase 3 Final Report completed October 2009

Companies supplying HFOs have a duty of care to ensure that the guidance on their safe handling and use is rigorous.

HFOs -The fourth generation of fluorocarbons used as refrigerants

For the development and introduction of HFCs extensive toxicology and environmental studies were undertaken through industrial consortia using independent laboratories where appropriate. The global warming potential of the HFCs was well understood at that time, but the urgency in phase-out of ozone depleting substances and the speed at which it was achieved was only possible due to the massive investment in HFCs. EFCTC fully supports an ambitious global agreement on the reduction of Greenhouse Gas emissions and therefore accepts that a “Business as Usual” scenario for HFCs is not an option, given the potential for their growth particularly in emerging economies.

While HFCs continue to have a role in a range of applications, their one negative feature of high global warming potential means that a new generation of fluorocarbons that eliminates the GWP, as a concern, would be a step-change improvement.

The necessary step-change improvement has now resulted in the development of HFOs, which meet all important environmental requirements whilst maintaining the key technical and safety properties of HFCs for many applications.

HFOs –the fourth generation of refrigerants, eliminating the remaining important environmental risks

	ODP Ozone Depletion Potential	GWP Global Warming Potential	Atmospheric Lifetime	POCP Photochemical Ozone Creation Potential –Local air quality
CFCs	High	Very High	45-1700 years	No
HCFCs	Low	High	1-20 years	No
HFCs	0	High	1-52 years[3]	No
HFOs	0	~4 similar to HCs	10-12 days	Low
HCs	0	~4 – 20	~10 days	Medium - High

The main HFOs of commercial interest do break down to trifluoroacetic acid (TFA) in the atmosphere[4]. This is washed out of the atmosphere into the aqueous environmental compartment. However it has been concluded that TFA from HFOs would have negligible

[3] Excluding HFC 23 which is a by-product and not used for refrigeration in any significant quantity
[4] Luecken, D. J.; L.Waterland, R.; Papasavva, S.; Taddonio, K. N.; Hutzell, W. T.; Rugh, J. P.; Andersen, S. O., Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement. Environmental Science & Technology 2009, 44, (1), 343-348

environmental impact[5]. There are no other significant breakdown products such as high GWP HFCs or ozone-depleting substances.

TFA in the environment was investigated when HFCs were being developed since it is a breakdown product of a number of commercial refrigerants including HCFC-123 HCFC-124, HFC-134a and HFC-227ea[6].

TFA is a naturally occurring chemical. Over 200 million tonnes are present in the oceans, having apparently accumulated over many million years from chemical reactions in or around sub-sea volcanic vents.[7] However, TFA is not confined to the oceans. Samples of fog, rain, river and lake water analysed during the 1990s contained concentrations ranging from tens to tens of thousands of ng $litre^{-1}$, with a typical European level of 100 ng $litre^{-1}$ (found in German rainwater) in 1995.[8] At that time, the only man-made precursor present in the atmosphere was HFC-134a, at a concentration which would have sustained a global average concentration of TFA in precipitation of only 2 ng $litre^{-1}$. A probable global natural cycle for TFA would involve transport from the oceans in the sea-salt aerosol, subsequent evaporation (as trifluoroacetic acid) and long range transport before deposition in rainwater.

An overall environmental risk assessment has been conducted on the basis of the data generated by the TFA studies. The results were published in *Human and Ecological Risk Assessment.*[9]

Tests have shown that mammals are not affected by TFA at concentrations many thousands of times higher than expected in the environment. With humans, some fluorinated drugs break down in the human body to form trifluoroacetate, which is rapidly excreted. Tests with fish and crustaceans show these organisms are also highly resistant to TFA. Because TFA has very low affinity for lipids (fats), there is no potential for passive accumulation in fatty issues, even after long exposure at low levels.[9]

Microorganisms that have been tested do not actively concentrate TFA from the environment. TFA does not inhibit the growth of bacteria and most of the algae tested, even at high concentrations. The growth of one species of alga was inhibited by TFA at concentrations about 1000 times above those expected in rain and snow.

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[5] Hurley et al., Chem. Phys. Lett., 450, 263 (2008);

[6] WMO, Scientific Assessment of Stratospheric Ozone: 2006, World Meteorological Organization, Geneva (2007);

[7] Frank H., E.H. Christoph, O. Holm-Hansen and J.L. Bullister, "Trifluoroacetate in Ocean Waters", *Environ. Sci. Technol.*, 36, 12-15, 2002 and Scott B.F., R.W. Macdonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer and D.C.G. Muir, "Trifluoroacetate (TFA) Profiles in the Arctic, Atlantic and Pacific Oceans", *Environ. Sci. Technol.*, 39, 6555-6560, 2005

[8] see for example Berg M., Muller S.R., Muhlemann J., Wiedmer A., Schwarzenbach R.P., "Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland", *Environ. Sci. Technol.* 34(13):2675-2683, 2000 and Römpp A., O. Klemm, W. Fricke and H. Frank, "Haloacetates in Fog and Rain", *Environ. Sci. Technol.*, 35 (7), 1294 -1298, 2001

[9] Boutonnet J.-C., P. Bingham, D. Calamari, C. de Rooij, J. Franklin, T. Kawano, J.-M. Libre, A. McCulloch, G. Malinverno, J.M. Odom, G.M. Rusch, K. Smythe, I. Sobolev, R. Thompson and J. M. Tiedje, "Environmental Risk Assessment of Trifluoroacetic Acid", *Human and Ecological Risk Assessment*, 5,1, 59-124, 1999

Plants take up TFA through the roots as well as through leaf surfaces. Trifluoroacetate has no known toxicity to plants at the concentrations at which it is expected to be deposited in rain and snow. In prolonged exposure, however, at concentrations several thousands of times greater than these levels, TFA inhibits plant growth and development.

In summary TFA has been well investigated, is a natural substance with about 200 million tonnes in the oceans; the use of HFOs and the resulting concentrations of TFA do not represent an environmental concern.

Manufacture of HFOs

When selecting manufacturing routes for HFOs to meet short, medium and long term requirements, raw material availability, process efficiency and cost are important considerations in route selection. The raw materials may include substances controlled by the Montreal Protocol and that are already widely used as feedstock where they are completely converted to other substances. In addition the raw materials will include hydrogen fluoride, the fundamental building block for all fluorocarbons. All these chemicals need to be contained in well-designed chemical plants meeting appropriate local and national consents, including in the EU IPPC[10]. This is no different to any other chemical process including the manufacture of highly flammable hydrocarbons or flammable and toxic ammonia.

Safety for use of HFOs

The introduction of any new chemical substance in the EU falls under REACH[11] (Registration, Evaluation, Authorisation and Restriction of Chemicals). This sets out the toxicity and environmental testing requirements, which "should ensure a high level of protection for human health and the environment". Similarly in the USA, the EPA SNAP programme[12] requires all relevant toxicity testing data to be made available. In addition, as is true for any other industrial chemical, workplace exposure limits and guidance in Material Safety Data Sheets will enable HFOs to be handled correctly and safely.

The HFO-1234yf Cooperative Research Programs conducted over the last two years at international laboratories investigated a range of issues including:

- ✓ Safety and risk assessment
- ✓ Air-conditioning system efficiency and performance
- ✓ Material compatibility
- ✓ Flammability
- ✓ Toxicity

[10] IPPC Integrated Pollution Prevention and Control
[11] REACH Regulation 1907/2006
[12] The Significant New Alternatives Policy (SNAP) Program is EPA's program to evaluate and regulate substitutes for the ozone-depleting chemicals that are being phased out under the stratospheric ozone protection provisions of the Clean Air Act (CAA).

The extensive testing at third-party facilities did not identify significant risks for the use of HFO-1234yf in mobile air-conditioning systems.

Fluorocarbons have been safely and effectively used in a wide range of applications over the past sixty years, even though they all have the potential under certain circumstances to produce hydrogen fluoride (HF) as a thermal decomposition product. HF is a distinctly pungent acidic gas. Exposure to low concentrations of HF is irritating, but exposure to high concentrations of HF has the potential to produce severe irritation and acute toxicity.

HFC 134a has been used for over sixteen years in mobile air-conditioning. Despite its classification as a category I flammable gas under the GHS (Globally Harmonised System of classification of chemicals), HFO 1234yf in practice is very marginally flammable and the implications for safety have been investigated in detail. The CRP-1234yf concluded that, with the application of new safety standards, the specific requirements of HFO1234yf are considered to maintain the safety of the vehicle at today's level.

It is important to recognise that standards have been defined to allow the safe use of a wide range of refrigerants, including hydrocarbons and ammonia, for a wide range of applications with certain safety requirements or exclusions being applicable depending on the particular refrigerant.

Energy Efficiency of HFOs

It is known that several of the HFOs under present or recent investigation have energy efficiencies similar to HFC-134a. Although the development of technology and designs for best use of HFOs is still in an early phase, their use in existing systems designed for HFC-134a shows that the HFOs under current investigation can already deliver essentially equivalent or better energy efficiency when compared to the HFC-134a performance.

Furthermore the HFOs under active investigation will all allow the operation of subcritical vapour compression cycles for air conditioning or refrigeration even in warm climates, in contrast to CO_2 (R-744). The energy efficiency of the transcritical CO_2 cycle is very sensitive to ambient temperature: the energy efficiency of HFO based refrigerants is therefore expected to be better in warm climates than CO_2 as a consequence. With the lower GWP offered by use of HFOs, the overall carbon footprint of a/c or refrigeration equipment will be dominated by the energy efficiency of the system.[13]

In addition HFOs with their marginal flammability characteristics or in mixtures with HFCs, are expected to be used in applications where the highly flammable HCs are not appropriate.

Conclusion

HFOs deserve serious consideration as viable low GWP fluids for use in a range of applications. The safety and performance in use of these fluids and their attractive

[13] See reference 2 which reports the Life Cycle Impact of HFO-1234yf in mobile air-conditioning systems

environmental properties hold considerable promise to improve the environmental performance of air-conditioning and refrigeration systems as well as in other applications.

Even so, there are continuing roles for a wide range of technologies including hydrocarbons, carbon dioxide, ammonia, and indeed HFCs.

However, particularly in developing countries that are at the start of the accelerated phase out of HCFCs, HFOs offer an opportunity to adopt Low GWP fluids in applications where their use has been proven. HFOs may also be used in mixtures with HFCs where the properties of HFOs alone cannot achieve the required safety or performance standards.

See also: http://www.sae.org/standardsdev/tsb/cooperative/altrefrig.htm