

30 September 2019

EFCTC Response to recent Articles about HFO-1234yf-SUMMARY

EFCTC has, through its newsletter and website¹, already commented in the past on all the points raised in recent articles “Refrigerant R1234yf again in criticism”² and an article about HFOs in the September issue of Accelerate magazine³. In this summary EFCTC provides important conclusions about the 4 main issues raised.

The detailed paper issued in the October 2019 newsletter provides more information and references to the information sources. Before commenting on each of the 4 main issues raised here is some extracts from the 2018 Scientific Assessment of Ozone Depletion. It concluded that **“There is increased confidence that trifluoroacetic acid (TFA) produced from degradation of HFCs, HCFCs, and HFOs will not harm the environment over the next few decades.** This assessment is based on the current estimates of future use of hydrofluorocarbons, HCFCs, and HFOs. Periodic re-evaluation is prudent, given the uncertainties in the sources and sinks of TFA and because of its persistence in the environment. The large body of published field measurements, toxicological studies, modelling studies, and environmental assessments point to a clear conclusion: **The current and estimated future concentrations of TFA and its salts resulting from degradation of HCFCs, HFCs, and HFOs do not pose any known significant risk to human or ecosystem health.”**

EFCTC members continue to have full confidence in the use of R-1234yf as a refrigerant for mobile air-conditioning and other applications. EFCTC supports good science and thorough investigation of the properties of all fluorochemicals produced by our member companies, including HFOs. We fully endorse emission reduction strategies during use along with best practice measures that help ensure efficient capturing of HFOs during recycling operations. We should not lose sight of their good balance of safety and performance properties and their insignificant impact on the climate because they degrade rapidly in the atmosphere.

Fire Safety and Combustion Products

All fluorocarbon refrigerants have the potential to form dangerous combustion products and this has been known for over 50 years since the use of CFCs and HFCs, with technical advice and safety guidance provided. In respect of R-1234yf, the EU Joint Research Centre was asked, in 2013, to provide an in-depth analysis of the report elaborated by KBA (Kraftfahrt Bundesamt, German authority responsible for market surveillance and product safety for road vehicles), in order to ascertain whether the results stemming from the tests are well founded and supported by a rigorous and scientific methodology. **The level 1 and level 2 testing showed no ignition of refrigerant R1234yf and no release of hydrogen fluoride (HF) despite the very high temperatures in the engine compartment. Consequently, the results as such with the vehicles tested under the conditions as described for**

¹ See EFCTC LEARN ABOUT TFA For a wide range of information about Trifluoroacetic acid/acetate as a breakdown product of some HFCs and some HFOs [here](#).

² Springer Professional Germany [source](#) and in the DKV online news

³ Accelerate Magazine [source](#)

level 1 and level 2 testing provided no evidence of a serious risk. Therefore, drawing of conclusions from level 3 tests, further than the ones already drawn from level 1 and level 2 tests regarding the safe operation of the refrigerant R-1234yf in MAC systems, is not appropriate, considering the definition of "safe product" in the General Product Safety Directive 2001/95/EC.

Atmospheric Concentrations

Substances having short atmospheric lifetimes (typically measured in days) are transported to some extent in the atmosphere as they breakdown. **The detection of HFOs in the atmosphere, with lifetimes of about 10 to 40 days, is no different to the detection of other very short lifetime substances such as propane, isobutane, pentane (non-methane hydrocarbons NMHCs, a sub-set of non-methane volatile organic compounds NMVOCs).** These hydrocarbons also have similar atmospheric lifetimes (for example 13 days for propane). The much wider sources of the NMHCs typically lead to substantially higher atmospheric concentrations that can be in the ppb (parts per billion, about 1000 times greater than the HFOs) range, particularly in urban areas. In general terms the HFCs [and HFOs such as R-1234yf] have very low Photochemical Ozone Creation Potential (POCP) values and take no part in ground-level ozone formation (commonly known as "smog"). In contrast, the alkanes (ethane, propane and isobutane) and alkenes (ethylene and propylene) exhibit steadily increasing reactivities from ethane, which is unreactive, to propylene, which is highly reactive. Now that HFOs are becoming more widely used in the EU, very low atmospheric concentrations (typically below 1 ppt parts per trillion) can be detected. **Background concentrations at end of 2017 for 3 HFOs/HCFOs are less than 0.1 ppt. To put this in context, 1 part per trillion is about the same as 1cm² compared to the area of Paris (105.4 sq. km).**

Environmental Safety

Over 200 million tonnes of trifluoroacetic acid (TFA as its salts) are present in the oceans, both coastal and deep-ocean seawater, having apparently accumulated over many million years from chemical reactions in or around sub-sea volcanic vents. More than 95% of TFA found in the oceans is naturally formed. The effect of the atmospheric breakdown of R-1234yf to form trifluoroacetic acid has been thoroughly investigated. The 2018 Environmental Effects Assessment Report stated that **"There is still no indication that exposure to current and projected concentrations of salts of TFA in surface waters present a risk to the health of humans and the environment.** Since the risk assessment conducted in 2016, no novel studies indicating adverse long-lasting effects of TFA and its salts have been published. In fact, the reverse is true. Previous reports of contact toxicity from exposure to concentrated TFA (as a strong acid used in industry) have not indicated systemic toxicity. **TFA in rain-water is millions of times more dilute than that in industrial solutions and would not cause adverse effects."**

Water Solubility of TFA

It is well established that TFA is a ubiquitous natural component in rivers, lakes, and other surface water bodies. Amounts deposited in flowing surface water will ultimately accumulate in the oceans and salt lakes where water is lost only by evaporation. More than 95% of the salts of TFA found in the oceans are naturally produced. **Because of their high solubility in water and their very small octanol-water partition coefficient, the salts of TFA do not bioconcentrate in aquatic organisms, and do not biomagnify in the food chain. Thus, they present negligible risk to organisms higher on the food chain, including humans.** For an upper range scenario of global HFC use by 2050 it was estimated that

the total additional contribution of TFA to the oceans would be less than 7.5% of the TFA present at the start of the millennium. With the 2016 Kigali Amendment to the Montreal Protocol, the TFA due to global HFC use, and hence TFA formation as a breakdown product, is projected to be lower but partially offset by increased use of HFOs.

A recent comprehensive study investigated the quantities of trifluoroacetate (TFA) found in major rivers across Germany. Following this study, it had been claimed that HFO-1234yf has possible negative consequences for the production of drinking water. However, currently HFO-1234yf is at most an insignificant contributor to the quantities of TFA found. Furthermore, based on a recent study on *Future emissions and atmospheric fate of HFC-1234yf from mobile air conditioners in Europe*, the projected growth in use of R-1234yf and resulting emissions of TFA is expected to have only a small contribution to the quantities of TFA found in German rivers. This is consistent with the conclusions from the 2018 Environmental Effects Assessment.

The European FluoroCarbons Technical Committee is a Cefic Sector Group that monitors legislation related to HFCs (hydrofluorocarbons), and HFOs (hydrofluoro-olefins) in the EU and at global level.

Fluorocarbons are used as feedstock, as refrigerants, as solvents and as blowing agents for insulation plastic foams.

Contact: EFCTC Chairman: Dr. N. Campbell, nick.campbell@arkema.com

EFCTC Secretariat: Angelica Candido, anc@cefic.be