Environmental Impact of HFO Refrigerants

Global Warming Potential of HFOs and HFO Blends

As part of the phase-out of high-GWP hydrofluorocarbons (HFCs), **hydrofluoro-olefins (HFOs)** have been developed as potential alternative refrigerants. HFOs are short-lived in the atmosphere and therefore have low global warming potentials (GWPs), since they are, by definition, unsaturated compounds containing at least one **carbon–carbon double bond** [1].

This double bond reacts rapidly with hydroxyl radicals (•OH) in the atmosphere—much faster than the single bonds present in HFCs such as R134a. As a result, HFOs typically have **atmospheric lifetimes of only a few days**, compared with years or even decades for HFCs. Consequently, their GWPs are correspondingly low.

Table 1 lists the GWP values of selected HFOs and HFO/HFC blends currently in use or expected to be introduced as refrigerants.

Table 1. *Examples of HFOs and HFO/HFC blends [1,2]*

Refrigerant	Alternative name(s)	GWP
HFO-1234yf	Solstice® YF, R-1234yf, Opteon™ YF	< 1
HFO-1234ze	Solstice® ZE, HFO-1234ze(E)	6
HFO-1233zd	Solstice® ZD, HFO-1233zd(E), HCFO-1233zd	7
HFO-1224yd	Amolea® 1224yd(Z)	< 1
HFO-1336mzz	Opteon™ 1100, HFO-1336mzz(Z)	2
HFO-1243zf	—	0.8

HFO/HFC blends

Blend	Composition	Trade name	GWP
R-448A	R-32/125/1234yf/134a/1234ze(E) (26.0/26.0/20.0/21.0/7.0)	Solstice® N40	1387
R-449A	R-32/125/1234yf/134a (24.3/24.7/25.3/25.7)	Opteon™ XP40	1397
R-450A	R-134a/1234ze(E) (42.0/58.0)	Solstice® N13	604
R-452A	R-32/125/1234yf (11.0/59.0/30.0)	Opteon™ XP44	2141

Manufacturers: Solstice® (Honeywell); Opteon™ (Chemours); Amolea® (Asahi Glass).

Although HFOs have very low GWPs, many are **mildly flammable**, classified as **"2L"** under ASHRAE Standard 34. The flammability of a refrigerant affects its usability because safety codes limit the use of flammable refrigerants in certain applications. One solution is to blend HFOs with **non-flammable HFCs**, producing mixtures that remain non-flammable yet have reduced GWPs.

Such blends typically consist of a **high-GWP, non-flammable HFC** and a **low-GWP, flammable HFO**, resulting in an overall GWP reduction (see Table 1) [1,3]. According to **ASHRAE Standard 34** [3] and its supplements, more than **100 blends** have been assigned specific refrigerant designations, about **40 of which contain at least one HFO**.

Non-flammable blends generally include relatively high proportions of **R134a** and/or **R125**, which limits how low their GWP values can be. A 2020 study [4] reported that **17 of 24 blends** listed in ASHRAE 34 are non-flammable, yet all have GWP values above 540, and **12 exceed 1000**. However, these are still markedly lower than conventional HFC blends such as **R410A (GWP 1924)** and **R404A (GWP 3943)** [4].

Degradation Products of HFOs and Their Environmental Implications

HFOs contain the same atoms as HFCs—**carbon, hydrogen, and fluorine**—but are **unsaturated organic compounds** (they contain at least one double bond). Commercially available HFOs are generally based on **linear alkenes**, such as propene (e.g., R1234yf or R1234ze), and occasionally butene (e.g., R1336mzz) or ethene (e.g., R1132a).

Because the double bond makes the molecule less stable, HFOs degrade rapidly in the atmosphere. Both HFCs and HFOs form **halogenated carbonyl compounds**—including **CF_2O** and **CF_3CFO** (trifluoroacetyl fluoride, TFF)—as intermediate products. The specific intermediates and final degradation products depend on the original compound [5,6].

Figure 1 shows simplified degradation pathways for two refrigerants: **R134a (an HFC)** and **R1234yf (an HFO)**. Between **7–20 %** of R134a molecules form TFF as an intermediate, while **each molecule of R1234yf produces one molecule of TFF**.

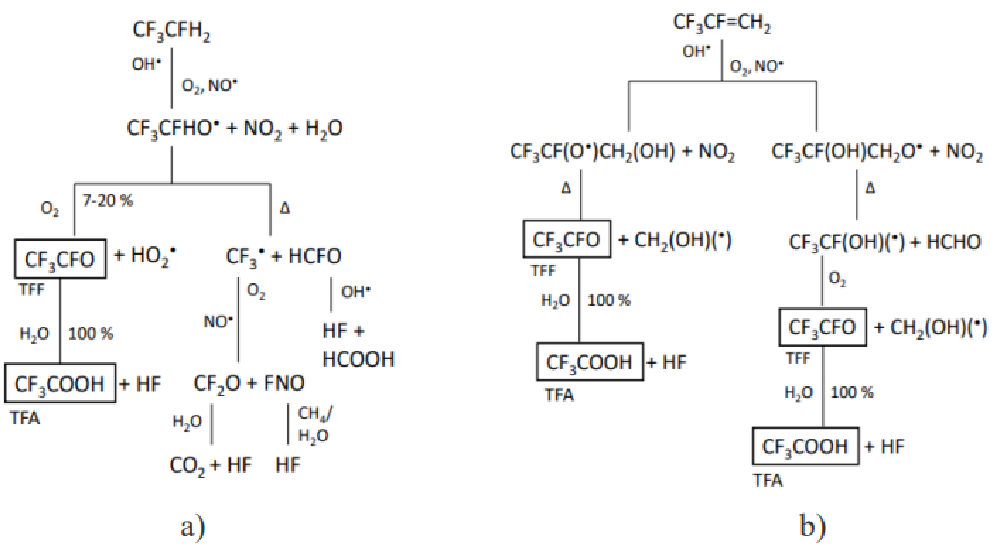

Figure 1. *Simplified OH-initiated atmospheric degradation of (a) R134a and (b) R1234yf [6].*

Subsequent reactions yield the stable end products **CO_2 (carbon dioxide)**, **HCOOH (formic acid)**, **HCl (hydrogen chloride)**, **HF (hydrogen fluoride)**, and **CF_3COOH (trifluoroacetic acid, TFA)**. Among these, **TFA** is the only compound that persists in the environment. Formic acid, by contrast, decomposes rapidly in air and water to CO_2/H_2 or CO/H_2O.

The environmental effects of TFA are **controversial** and have been discussed previously [7]; here, we summarize recent findings. TFA does not occur naturally in freshwater, soil, or the atmosphere, though trace amounts exist in seawater—likely originating from **submarine volcanic activity**. When HFOs degrade in the atmosphere, the resulting TFA is quickly absorbed into **water droplets** and deposited via **rain, snow, or fog** onto terrestrial and surface waters. Being a strong acid, it readily forms **trifluoroacetate salts (CF_3COO^-)** with minerals in soil and water.

As shown in **Table 1**, some refrigerants (notably R1234yf) generate substantially more TFA than others. **Table 2** summarizes the molar TFA yield and major degradation products for several HFCs and HFOs.

Table 2. *Degradation products and TFA yields of selected refrigerants [6]*

Substance	Molar TFA yield	Main degradation products
HFC-245fa	up to 10 %	CF_2O, $CF_3C(O)CHF_2$
HFC-134a	7–20 %	HC(O)F, CF_3CFO
HFO-1234yf	100 %	CF_3CFO, HCOCl
HFO-1234ze(E)	up to 10 %	CF_3CHO, HC(O)F
HFO-1336mzz (E,Z)	up to 20 %	CF_3CHO, CF_3CClO
HFO-1243zf	up to 10 %	CF_3CHO, HCOCl, XCH_2COCF_3
HFO-1225zc	up to 100 %	CF_3CHO, CF_2O, CF_3COCF_2X, CF_3CClO
HFO-1225ye (E,Z)	up to 100 %	CF_3CFO, HCFO

Projected HFO Emissions to 2050

Implementation of **EU Regulation 517/2014** allows forecasts of refrigerant consumption and emissions through 2050. Such projections must account for the **types and quantities** of refrigerants expected to be used, as well as **emissions during production, operation, and disposal**.

A recent report by the **German Environment Agency** [6] provides a comprehensive analysis of expected demand, emissions, and degradation products of halogenated refrigerants in the EU up to 2050. **Table 3** summarizes the projected demand and emissions for three major HFOs (EU-28, tonnes).

Table 3. *Projected demand (E) and emissions (U) of selected HFOs in the EU-28 (tonnes) [6]*

år	2018		2020		2030		2050	
Substans	E	U	E	U	E	U	E	U
R1234yf	4,016	2,926	20,003	6,903	46,030	37,439	51,223	47,658
R1234ze	35	4	9,289	4,289	12,339	5,491	12,717	6,769
R1336mzz	129	8	878	99	3,513	637	3,513	1,159
total	**4,180**	**2,938**	**30,170**	**11,291**	**61,882**	**43,567**	**67,453**	**55,586**

The forecast predicts a **strong increase in HFO use** as substitutes for high-GWP HFCs, with **R1234yf** expected to dominate the **mobile air-conditioning** sector by 2050.

The expected atmospheric formation of **TFA** has been estimated based on projected European (EU-28) emissions of HFOs and HFC-134a between 2000 and 2050. The results are shown in **Table 4**.

Table 4. *Estimated annual formation of TFA from HFO and HFC-134a emissions in the EU-28 (tonnes) [6]*

Substance	2000	2010	2020	2030	2040	2050	Total
R134a	3895	7595	6352	1756	1084	836	202781
R1234yf	0	0	6902	37432	45469	47650	1125699
R1234ze	0	0	429	549	617	677	18741
R1336mzz	0	0	14	89	127	161	3233

The report shows that the **highest contributions to TFA formation** originate from the degradation of **R134a and R1234yf** during 2000–2050, together accounting for **96 %** of total TFA produced from refrigerants in the EU. The majority stems from **R1234yf (81.3 %)**, compared with **R134a (14.7 %)**.

Figure 2 illustrates the opposing trends in emissions and resulting TFA quantities for R134a and R1234yf. In 2000 and 2010, R134a accounted for **93 % and 87 %** of annual TFA formation, respectively, while HFOs contributed negligibly. From 2020 onward, R1234yf becomes dominant, producing **47 %** of TFA by 2020 and **96 %** by 2050—indicating a growing TFA burden in future years.

Figure 2. *Emission trends of major TFA-forming refrigerants and resulting TFA formation in the EU-28 through 2050 [6].*

Toxicity and Environmental Persistence of TFA

For substances not occurring naturally in the environment—such as TFA—it is essential to ensure they are **harmless to humans and ecosystems**, particularly if they are **persistent**. Currently, there is **no evidence** that TFA is acutely toxic to humans or environmentally harmful at existing or expected concentrations.

However, **laboratory studies** have shown that the **freshwater alga *Selenastrum capricornutum*** is sensitive to elevated TFA levels [8,9]. Because TFA is non-degradable, there is concern that environmental concentrations could rise over time and eventually reach harmful levels.

A recent report [8] cites research showing **liver effects in rats** fed diets with elevated TFA levels for ≥ 90 days [9]. Rats were given feed containing 0, 160, 1 600, or 16 000 ppm TFA—approximately 0, 10, 100, or 1000 mg TFA per kg body weight per day. No visible symptoms occurred, but all animals exposed to 16 000 ppm had **enlarged livers**, and some males at 1 600 ppm showed liver changes. The report concludes that **emissions contributing to TFA formation should be minimized**.

Measurable TFA concentrations have already been detected in **German drinking water**, where the limit value is **60 µg/L**, based on an intake of ≤ 1.8 mg TFA per kg body weight. The **German Environment Agency (UBA)** recommends maintaining levels below **10 µg/L** [8]. Importantly, **no known treatment methods** can currently remove TFA from water.

Unlike the **global** impact of HFCs, the effects of TFA are likely to be **localized** near population centers, since HFOs have short atmospheric lifetimes and TFA forms close to emission sources. Increasing emissions—particularly of **HFO-1234yf**—may eventually lead to **unexpectedly high TFA concentrations**, potentially exceeding safe thresholds.

Therefore, when evaluating refrigerants, attention must be given not only to their **GWP**, **toxicity**, and **flammability**, but also to their **persistent degradation products**. Otherwise, the shift to HFOs—while a step forward in reducing GWP—could represent **two steps back** if long-term environmental and health effects are overlooked.

References

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