# Briefing: One step forward, two steps back

## A deep dive into the climate impact of modern fluorinated refrigerants

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## Executive summary and policy recommendations

Attempts have been made to reduce the negative environmental impacts of refrigerants by replacing old generations of F-gases with new ones. But replacing one synthetic refrigerant with another has not proved to be a sustainable solution. Even if new refrigerants have a low direct GWP, there exist a number of other climate impacts coming from their production and their degradation in the atmosphere. These impacts, however, are mostly ignored by policymakers. Information about the full impact of refrigerants is scarce, and the way it is presented is sometimes misleading.

In view of the revision of the EU F-Gas Regulation and the Industrial Emissions Directive, we urge the European Commission to take into account the following considerations and recommendations:

- Specific measures and thresholds used in policies need to be adapted as our knowledge of GWP values of these gases develops. We believe that a **continuous and dynamic review process** is more adequate to consider the improvements in understanding atmospheric processes. In parallel, other time-scale references (a GWP over 20 years, instead of 100) would highlight the drastic global warming impacts of individual substances in a shorter timeframe and provide policymakers and the public with an accurate snapshot of the short-term climate benefit of fast action on HFCs[1].
- GWP values are always substance-specific threshold values. As a result, they do not give any information about the additional global warming impact (that can also be expressed in GWP values) that could result from degradation products. The **definition of a lifecycle GWP** that considers the manufacturing as well as the degradation impacts of refrigerants would give a better view of their real emissions and should be considered by policy measures or standards.
- The current transition from HFCs to HFOs and other low-GWP refrigerants will not maximise the benefits for the climate. Due to the HFC phase-down, companies are now at their decision-making momentum on whether to develop new cycles for new refrigerants or not. We therefore encourage the **shift towards truly future-proof alternatives**, such as natural refrigerants and, more particularly, hydrocarbons. They not only have a low-GWP, but also a very low manufacturing carbon footprint as shown in this briefing.
- Technically **unavoidable losses** [1] due to corrosion, fatigue and production errors, together with a foreseeable increase of HVACR systems **will still result in continuous emissions** – both directly from their release into the atmosphere and indirectly from their energy-intensive production and degradation products.
- Last but not least, **information on lifecycle emissions of all refrigerants should be better tracked** in order to overcome the scarcity of data which poses transparency issues and eventually hinders decision-making.

History has taught us that the shift to refrigerants that are better for the climate has never been done the right way. The new generation of fluorinated refrigerants is yet another example of a false solution that has proven unsustainable in the long term. It is now clear that policies and standards supporting low-GWP fluorinated refrigerants should only be transitional tools and contribute to the development of a high-scale usage of natural refrigerants. We must not repeat the mistakes of the past.

[1] Joint environmental NGOs position paper "Strengthening the F-Gas Regulation to Address Hydrofluorocarbons and Sulphur Hexafluoride", September 2020

# Introduction

Modern fluorinated gases (hereafter F-gases) were developed to replace earlier generations of gases that had devastating impacts on our environment. However, the climate impact of the new generation of F-gases is still considerable, and may be larger than we know. In addition, the demand for F-gases is potentially increasing. Without intervention, the impact of F-gases could severely set back climate mitigation efforts. The current regulatory context in Europe, with the upcoming revision of the F-Gas Regulation and the Industrial Emissions Directive, provides an opportunity to address this threat and enhance the use of climate-friendly and sustainable alternatives, such as natural refrigerants.

F-gases make up approximately 80% of all refrigerants used worldwide. Refrigerants are common in the heating, ventilation, air-conditioning and refrigeration sectors (HVACR), where they are used in vapor compression cycles. These markets are rapidly growing, which is in part a result of national renewable energy action plans that rely on vapor compression technologies, such as heat pumps, to achieve decarbonisation. However, the use of F-gases in these applications may reverse some of their benefits, due to the negative climatic impact of the gases. Even though F-gases 'only' account for approximately 3% of the greenhouse gas (GHG) emissions in the European Union by weight[2], their contribution to the radiative forcing is about 20%, thus being a major contributor to global warming after all [2].

**Radiative forcing** is the difference between the sunlight absorbed by the Earth and the energy given back to space. Changes in radiative forcing can be caused by changes in the concentration of greenhouse gases in the atmosphere, thus leading to global warming.

It is a widespread practice among policy-makers to measure the effective radiative forcing of F-gases and other substances in terms of Global Warming Potential over 100 years (or GWP-100, referred to hereon as GWP). Common evaluations of the climate impact of F-gases, as well as international and EU policies, are based on GWP values as described by the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4 report) almost 15 years ago. However, this definition of GWP underestimates the actual contribution of F-gases to global warming, as the value considers the radiative forcing of the gases themselves but overlooks other aspects. The life cycle of F-gases also comprises emissions associated with their manufacturing and the degradation of these gases into other harmful substances once they are emitted into the atmosphere, which adds to the climate impact. Furthermore, GWP values are constantly reviewed, and more recent scientific evidence shows substantially higher GWP values of F-gases emissions [2] than those currently referred to for policy making purposes.

[2] EEA Report No 15/2020 Data reported by companies on the production, import, export and destruction of fluorinated greenhouse gases in the European Union, 2007-2019

This briefing aims to demonstrate the importance of phasing down F-gases as a part of the global response to the climate crisis and how essential is a turn towards more climate-friendly and sustainable alternatives like natural refrigerants (e.g. propane, or R-290). We show how modern fluorinated refrigerants (HFOs, HCOs, HCFOs, HFCs and their mixtures) contribute to climate change through both the carbon footprint of their manufacturing, as well as their degradation once they are emitted into the atmosphere.

**Fluorinated gases (or F-gases)** are artificial gases that can be found in different products, from fridges to air conditioners as refrigerants, and from electric equipment to aerosols. While harmless for the ozone layer, F-gases still have a big impact on the climate.

**Refrigerant fluorinated gases include** hydrofluorocarbons (HFCs), hydrofluoro-olefins (HFOs), hydrochloro-olefins (HCOs), hydrochlorofluoro-olefins (HCFOs) and their blends.

## 1. F-gases in the spotlight

This paper focuses on the new generation of low-GWP fluorinated refrigerants, such as low-GWP HFCs and HFOs, which are seemingly gaining appeal within the industry as a promising alternative to HFCs. In their Corporate Social Responsibility communications[3], some appliance manufacturers point to HFOs as a good future refrigerant for a wide range of products and settings. The interest in HFOs is further confirmed by ongoing applied research projects[4] in Europe. These sources reveal a particular interest in the following fluorinated refrigerants: R-125, R-134a, R-32, R-1234ze(E), R-1336mzz(Z), R-1233zd(E), R-1234yf, R-1130(E). An overview of these refrigerants in their pure substance form can be found in Table 1. If given GWP values are Except for R-32, most refrigerants classified as HFCs are being phased out under the restrictions imposed by the EU F-Gas Regulation and will not be used as pure substances in the future. Table 1 also includes a non-fluorinated natural refrigerant, propane (or R-290).

The refrigerants in Table 1 may however also be used in blends such as R-452B, R-448A, R-449A, R-454B, R-454C, R-513A, R-514A.

Table 1: Pure F-gases of interest. Safety and toxicity classification schemes based on the non-EU standard definitions of ASHRAE as used in several technical EU standards. Direct and indirect GWP values for Propane taken from [3].

| Species | Class | Chemical name | Chemical formula | CAS[5] | ASHRAE Safety / Toxicity classification | Direct / Indirect GWP |
|---|---|---|---|---|---|---|
| **R-290** | HC | Propane | $C_3H_8$ | 74-98-6 | A3 | 0,2 / 3,5 |
| **R-32** | HFC | Difluoromethane | $CH_2F_2$ | 75-10-5 | A2L | 675 / ? |
| **R-125** | HFC | Pentafluoroethane | $C_2HF_5$ | 354-33-6 | A1 | 3500 / ? |
| **R-134a** | HFC | 1,1,1,2-Tetrafluorethane | $C_2H_2F_4$ | 811-97-2 | A1 | 1430 / ? |
| **R-1130(E)** | HCO | Trans-1,2-Dichloroethylene | CHCl=CHCl | 156-60-5 | B2 | ≈1 / ? [6] |
| **R-1234yf** | HFO | 2,3,3,3-Tetrafluoro-1-Propylene | $CF_3CF=CH_2$ | 754-12-1 | A2L | <1 / ? |
| **R-1233zd(E)** | HCFO | Trans-1-Chloro-3,3,3-Trifluoropropylene | $C_3H_2ClF_3$ | 2730-43-0 | A1 | ≈4 / 175-300 or larger[6] |
| **R-1234ze(E)** | HFO | Trans-1,3,3,3-Tetrafluoro-1-Propylene | $CF_3CH=CFH$ | 29118-24-9 | A2L | ≈1 / 350-700 or larger[6] |
| **R-1336mzz(Z)** | HFO | Cis-1,1,1,4,4,4-Hexaflouro-2-Butylene | $CF_3CHCHCF_3$ | 692-49-9 | A1 | 2 / ?[6] |

This paper focuses on the manufacturing-related emissions and degradation processes of the pure substances in Table 1, and compare them, when possible, with better alternatives such as R-290.

[3] For instance: Daikin's Policy and Comprehensive Actions on the Environmental Impact of Refrigerants, July 2020

[4] Such as the project Dry-F funded by Energy Innovation Austria, research on high-temperature heat pumps funded by the Swiss SCCER-EIP program as well as the EU-funded projects RES4BUILD or CHESTER.

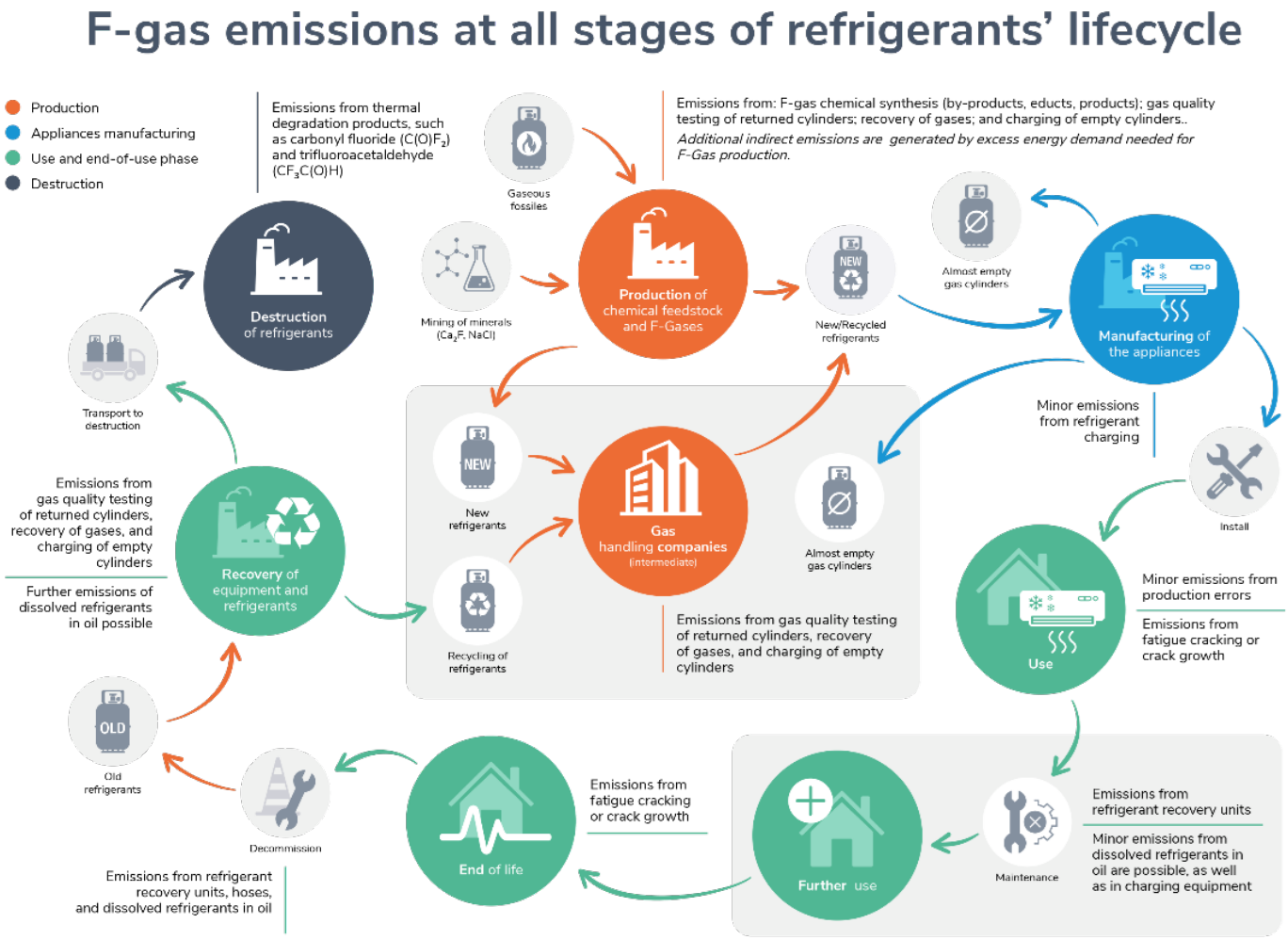
[5] CAS: The CAS is a registry number system to clearly identify substances which was introduced by the American Chemical Society.

[6] See Table 5 within this position paper below to understand the basis from which indirect or lifecycle GWP could be derived. Due to recent publications possible values are available for the indirect GWP values of R-1233zd(E) and R-1234ze(E). Since these refrigerants degrade also to other substances this value cannot be considered as a final value for the indirect GWP.

To understand how refrigerants are emitted from HVACR appliances, it is important to understand their lifecycle. In theory, F-gases are kept in closed systems throughout their lifecycle, but in practice, there are moments when the substances can escape a cylinder or appliance and leak into the atmosphere.

Figure 1 below shows the processes in the lifecycle of refrigerants and the losses that may occur at various points of their lifecycle.

Figure 1: Cycle for the use of F-gases as refrigerant. Grey marked areas are optional sideways that can be bypassed in case of direct B2B relationships between F-gas and equipment manufacturers (upper marked area) or if equipment is not designed for repair (lower marked area). Economical and technical reasons are usually the main drivers for the shown loss processes. Gas cylinder icons represent transport processes. Loss processes of gas cylinders in between these steps (e.g. during transport and/or storage) are not shown, but could also happen.




## 2. How 'future-proof' are GWP values?

GWP is often a key figure in policies regulating substances with potentially high climate impact. A problem with environmental policy based on GWP values is that it does not always keep up with

the scientific progress. Scientific knowledge is constantly evolving, which generates new and presumably more accurate estimates of GWP. To demonstrate this, Table 3 compiles GWP values as defined over the last three decades by the World Meteorological Organisation (WMO) [4] and the IPCC respectively [5]. We also include a recent scientific publication by Hodnebrog et al. (one of the contributors to the latest WMO report) [2] that represents the current state of art. Here it becomes clear how reference GWP values change as research progresses.

In policy making however, once a reference GWP value is selected, it does not change until the policy is revised, which may only happen decades later. The IPCC values are often used by government institutions as a reference for policy measures and to some extent, these values may also be affected by political compromise. In the EU, the IPCC AR4 report from 2007 has been used when drafting the F-Gas Regulation in 2014. In comparison with the more recent sources listed in Table 3 though, the 2007 IPCC values are low. The choice of reference values has an important impact on the use of certain F-gases. For instance, R-32, which is a refrigerant commonly used in air-conditioning, would have been prohibited by the 2025 bans if more recent reference values had been used in the current EU F-Gas Regulation[7].

Table 2: Development of the GWP values as published in WMO [4] as well as IPCC Reports [5] within the last 25 years. Blue marked fields represent values as used for the EU F-Gas Regulation which measures are based on IPCC AR4. Only non-official report data were taken from Hodneborg et al. [2] in the last column.

| Refrigerant \ GWP | WMO | IPCC | WMO | IPCC | WMO | WMO | IPCC | WMO | WMO | IPCC | WMO | H. et al. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1994 | 1995 | 1998 | 2001 | 2002 | 2006 | 2007 | 2010 | 2014 | 2014 | 2018 | 2020 |
| **R-32** | 580 | 650 | 880 | 550 | 543 | 675 | 675 | 716 | 704 | 677 | 705 | 809 |
| **R-125** | 3200 | 2800 | 3800 | 3400 | 3450 | 3500 | 3500 | 3420 | 3450 | 3170 | 3450 | 3940 |
| **R-134a** | 1300 | 1300 | 1200 | 1300 | 1320 | 1430 | 1430 | 1370 | 1360 | 1300 | 1360 | 1600 |
| **R-23** | 12100 | 11700 | 14800 | 12000 | 12240 | 14760 | 14800 | 14200 | 12400 | | 12690 | 15500 |

The notion of these fluctuations has important implications for how GWP values are used for underpinning policies. First, we should expect that future GWP research results may deviate from our current best knowledge. Secondly, based on the evaluation of the most recent developments presented below in this paper, more accurate evaluation methods will probably result in higher GWP values than those used today. This should be accounted for when designing policy, in the interest of respecting the EU's Precautionary Principle, which allows decision makers to adopt precautionary measures in case of scientific uncertainty.

Another issue with GWP values of F-gases used in policy is the significant difference between GWP over a 100-year period (GWP-100) and a 20-year period (GWP-20) respectively. If we use GWP values from the IPCC Fifth Assessment Report (2014), in the case of the widely used HFC-134a, GWP-20 (3.710) is up to three times higher than the GWP-100 (1.300). Similarly, for R-32, GWP-20 (2.430) is almost four times higher than GWP-100 (677). This leads to a severe

[7] The EU F-Gas Regulation will prohibit as from 1st January 2025 "Single split air-conditioning systems containing less than 3 kg of fluorinated greenhouse gases, that contain, or whose functioning relies upon, fluorinated greenhouse gases with GWP of 750 or more" (Annex III, Placing on the Market Prohibitions Referred To In Article 11(1))

underestimation of the climatic impact of refrigerants in the short term, which matters to EU policy objectives for 2030 and 2050.

We argue that more frequent reviews of the thresholds used in policies are needed, such as GWP values in the F-Gas Regulation, to avoid that environmental policy is based on outdated data. In addition, inclusion of GWP values for shorter time horizons, next to the widespread GWP on a 100-year horizon, will better capture the real climate impact of a substance and highlight the benefits of acting fast to phase-down harmful substances such as HFCs[8].

In the next sections, we will show that even if GWP values remain fundamental to climate policy and underpin the HFCs phase-down, there are other aspects of F-gases that considerably contribute to global warming and that are not captured by GWP.

# 3. Lifecycle impact of F-gases

In section 2 above, we discussed how GWP values are used to quantify climate impact of gases in climate policy, and how a frequent review of the reference values is required to keep up with scientific advancements. In this section, we will put the focus on another shortcoming of the current approach by looking at the climate impact of F-gases from a more complete lifecycle perspective. Specifically, we look into the additional impact of the manufacturing process and of the degradation that refrigerants undergo once emitted into the atmosphere.

It must be noted that the data used for the analysis of carbon footprints of manufacturing heavily relies on assumptions. Chemical manufacturers have so far successfully concealed relevant information about the life cycle emissions of refrigerants. Data on global warming from degradation of products is based on the current knowledge of atmospheric chemistry. Whenever emissions from manufacturing, degradation processes or yield rates are not known completely, it has been marked accordingly (e.g. with a question mark or as 'not known').

## 3.1. Manufacturing emissions of refrigerants

When referring only to the GWP of the end product, emissions associated with the manufacturing of refrigerants remain invisible. For an accurate quantification of their climate impact, emissions from the manufacturing process should also be accounted for. However, the precise process for producing current and new generation of F-gases is largely unknown outside the industry. Despite the international commitments such as the Montreal Protocol and the available information on the detrimental effect F-gases have on the environment and the climate, studies that disclose data on emissions from the manufacturing phase of refrigerants are surprisingly scarce. The few that are available are presented below to illustrate an estimated range of emissions associated with F-gas manufacturing.

[8] Joint environmental NGOs position paper "Strengthening the F-Gas Regulation to Address Hydrofluorocarbons and Sulphur Hexafluoride", September 2020

Throughout the manufacturing phase of F-gases, various activities give rise to emissions: chemical feedstock, heating and cooling along the process, catalysts in chemical reactors, distillation columns and pumping systems.

Table 3: Carbon footprints of F-gases manufacturing phase

| Refrigerant | Carbon footprint [kg $CO_{2eq}$ / kg refrigerant] Minimum to Maximum | References |
|---|---|---|
| R-22 | 205-393 | [7] |
| R-32 | 86-295 | [7] |
| R-125 | 72-248 | [7] |
| R-134a | 10-87 | [7] |
| R-290 | 0,9-2,5 | [7], Own |
| R-600a | 0,9-2,5 | [7], Own |
| R-717 | 2-2,5 | [7] |
| R-744 | 0,7-2,5 | [7] |
| R-1130(E) | Not known | Not available |
| R-1234yf | Not known | Not available |
| R-1233zd(E) | Not known | Not available |
| R-1234zd(E) | Not known | Not available |
| R-1336mzz(Z) | Not known | Not available |

Again, very few comprehensive and recent studies on the climate impact of manufacturing of F-gases are publicly available. One early analysis was made by Frischknecht [6] based on figures from 1998. A more recent and extensive review building on Frischknecht was made by Johnson [7] in 2010 which covers a number of HFCs. The carbon footprints of the manufacturing phase for the refrigerants covered in [7] are quoted in Table 3. However, resources on the manufacturing-associated emissions of the more modern refrigerants have proved very difficult to find. The specifics of the production process are not known to the public. Consequently, the carbon footprints of these refrigerants have been marked as 'not known' in Table 3 .

Based on Table 3, non-fluorinated refrigerants such as propane (R-290) and isobutane (R-600a), as well as CO2 (R-744), have a very low carbon footprint, and we can therefore insist on their climate-friendly properties in the manufacturing process vis-à-vis fluorinated substances such as R-32 that on the contrary, have quite high manufacturing emissions.

In the lack of independent assessments, there are examples of studies commissioned by the industry. In 2012, for instance, the International Council on Clean Transportation (ICCT) published a study on the carbon footprint of R-1234yf [8], which was directly supported by the chemical company Chemours.

The ICCT concludes that R-1234yf has a carbon footprint of 10,9 kg CO2-eq per kg refrigerant, but there are reasons to question this outcome. First, this result was achieved in part by accounting streams of hydrofluoric and hydrochloric acid (HF, HCl) as useful by-product streams and therefore allocating part of the carbon footprint there, rather than with the refrigerant product. These streams of HF and HCl are however contaminated with trace substances from the F-gas production. Because of the necessary but expensive purification process, it does not make economic sense to use them as by-products and they are therefore typically disposed of instead [9]. In the remote scenario where HF and HCl were to be reused, allocating the emissions from the purification process completely to the by-product streams, as was done in the ICCT study, is a questionable practice. Second, the production in China is based on the feedstock of R-22 [10], while in the United States it is most probably based on chloroform with halogen exchange reactions in between, before reaching the final product [11]. If we take this into account, it means that the carbon footprint of R-1234yf production should also comprise the additional emissions for the chemical feedstock like R-22 used in China or chloroform in the US. Referring to documented carbon footprints of R-22 in Table 3, it would then be 205-393 kg CO2 equivalent per kg refrigerant plus an unknown factor for the production in China.

## 3.2. Degradation consequences of the new generation of F-gases

As we saw in **Figure 1**, refrigerants that are lost throughout their lifecycle are emitted into the atmosphere, where they undergo a degradation process that can last thousands of years. The GWP values we discussed earlier in this paper give information on the radiative forcing of the refrigerants themselves, but they do not reflect the effects of the degradation of these gases. As we will illustrate in this section, the degradation products of some fluorinated refrigerants have GWP values even higher than the F-gas they originate from.

For almost four decades, atmospheric scientists have been studying the degradation of F-gases and its consequences. The research relies mainly on simulating atmospheric conditions in so-called 'atmospheric chambers'. Thanks to a more accurate state-of-the-art equipment in such chambers in recent years, it has been shown that first-generation F-gases can undergo degradation towards substances that have an even larger climate impact, expressed in GWP, than their source gases [12]. This risk of spontaneous production of harmful degradants applies also to the new generation of low-GWP fluorinated refrigerants, such as HFOs and blends. Below in Table 5, we compiled information on relevant fluorinated refrigerants based on an already available table from EFCTC, the association of fluorinated refrigerants manufacturers.

*Table 4:* Important fluorinated refrigerants and their degradation products (adapted based on an EFCTC table[9]). Degradation products marked with down-arrows (↓) are usually removed due to rainout (such substances have no further atmospheric effects, but could still have other environmental impacts). To contrast the large difference on how degradation information is published, degradation products from the original

[9] See here: https://www.fluorocarbons.org/wp-content/uploads/2020/10/HFC-HFO-and-HCFO-Substances-degradation-products-and-TFA-yields-Final-21_10_2020-1.xlsx (last proof on availability at 5th January 2021)

table of the EFCTC as well as information that we determined are included and marked accordingly. Attention: the troposphere to stratosphere share for degradation products is often estimated.

| Refrigerant | Formula | Intermediate degradation products[10] | Secondary (mid- to long-term stability) and final degradation products[11] | | References | Comment |
|---|---|---|---|---|---|---|
| | | | **Troposphere** | **Production/ injection into stratosphere** | | |
| **R-32** | $CH_2F_2$ | $C(O)F_2$ | $C(O)F_2$, $CO_2$, HF↓ | $C(O)F_2$ (later also $CO_2$, HF), $CO_2$, HF | [4], [13], [14], [16] | Long-term climate warming due to $C(O)F_2$ when degradation takes place in UTLS[12]. |
| **R-125** | $CHF_2CF_3$ | $C(O)F_2$, $CF_3$ | $C(O)F_2$, $CO_2$, HF↓ | $C(O)F_2$ (later also $CO_2$, HF), $CO_2$, HF | [4], [13], [14], [16] | Long-term climate warming due to $C(O)F_2$ when degradation takes place in UTLS. |
| **R-134a** | $CH_2FCF_3$ | $CF_3C(O)F$ (20 %), HC(O)F, $CF_3$ | HCOOH↓, $CO_2$, HF↓, $CF_3COOH$↓, $CF_4$ (0,0025 %) | $CF_4$, $CO_2$, HF | [12], [16], [17] | Yield rate and stratospheric injection of $CF_4$ in UTLS and above unknown. |
| **R-1130 (E)** | Trans-CHCl=CHCl | HC(O)Cl, $CHCl_2C(O)H$, $CO_2$, HCl, CO | Not known | Not known | [18], [19] | Incomplete investigation. No information on degradation product lifetimes share above/below UTLS. |
| **R-1234 yf** | $CF_3CF=CH_2$ | $CF_3C(O)F$ (92-100 %, HCHO | $CF_3COOH$↓, $CO_2$, HF↓, $CF_4$ (?) | $CF_4$ (?), $CO_2$ | [12], [20], [21], [22] | Due to needed short UV-wavelengths a channel to $CF_4$ is not very probable. |
| **R-1233 zd(E)** | Trans-CHCl=CHCF3 | $CF_3C(O)H$ (25 %), HC(O)Cl, HCl, $CF_3CH=CHOH$ | EFCTC: $CO_2$, HF↓, HCl↓, small amount of $CF_3COOH$↓ | | [15], [21], [24], [25], [26] | Degradation routes of $CF_3C(O)H$ [26] need a review, see work of Hansen et al. [15]. Unclear what happens to $CF_3CH=CHOH$. |
| | | | Own: CO2, HF↓, HCl↓, $CHF_3$ (2,8-3,8 %) | Own: $CHF_3$ (much later also $CO_2$, HF), HF, $CO_2$ | | |
| **R-1234 ze(E)** | Trans-$CF_3CH=CFH$ | $CF_3C(O)H$ (50 %), HC(O)F | $CO_2$, HCOOH↓, HF↓, $CHF_3$ (5,5-7,5%) | Own: $CHF_3$ (much later also $CO_2$, HF), HF, $CO_2$ | [15], [21], [23], [24] | Degradation routes of $CF_3C(O)H$ [26] need a review, see work of Hansen et al. [15]. |
| **R-1336 mzz(Z)** | Cis-$CF_3CH=CHCF_3$ | $CF_3C(O)H$ (<1 %), $CF_3CHClC(O)CF_3$ | EFCTC: $CO_2$, HF↓, small amount of $CF_3COOH$↓ | | [5], [15], [24], [27], [28] | Further fate of $CF_3C(O)Cl$ and $CF_3O_3CF_3$ unclear. |
| | | | Own: $CF_3C(O)Cl$, $C(O)F_2$, $CF_3O_3CF_3$, $CHF_3$ (<< 1%) | Own: $CHF_3$ (much later also $CO_2$, HF), HF, $CO_2$ | | |

[10] Important and known yield rates are listed in brackets in atmospheric zones behind degradation products where the major channels are suspected. Secondary yield rates are adapted to smaller amounts if primary yield rates are known.

[11] This list is non-comprehensive in terms of final degradation products, but it tries to include the most recent state-of-the-art in degradation channels. If possible it was distinguished between degradation in tropo-and stratosphere. The EFCTC degradation table as mentioned above does not include such a distinction.

[12] Upper Troposphere / Lower Stratosphere

Table 5 gives an overview of the main intermediate and secondary substances that result from the degradation of commonly used fluorinated refrigerants. It also shows the paradoxical situation where modern HFCs and HFOs, which are proposed by manufacturers as valid alternatives to high-GWP HFC phase-down, degrade into the same substances that they were supposed to replace, such as the very harmful R-23 (GWP 14,800 according to IPCC AR4). In fact, modern HFCs and HFOs degrade primarily to carbonyl fluoride (C(O)F2) and trifluoroacetaldehyde (CF3C(O)H) and the latter further degrades into R-23.

The carbonyl fluoride C(O)F2 concentration has grown as a result of F-gas (long-term stable HCFCs, HFCs, as well as mid-term to short-term stable HFCs) degradation in the atmosphere. An increasing quantity of this highly toxic gas is already proven to be present in the stratosphere (cf. Duchatelet [12] and Harrison et al. [13]), yet it is considered to have no lifetime. Consequently, neither realistic GWP value nor realistic radiative forcing is associated with it. Bilateral discussions with atmospheric scientists in preparation of this briefing have shown that carbonyl fluoride C(O)F2 could have a GWP of about 200-500 CO2-eq based on the knowledge of its abundance in the Upper Troposphere / Lower Stratosphere (UTLS) and above, as well as considering its IR-spectrum[13].

In a very recent work, Hansen et al. [15] studied the photolytic behaviour of trifluoroacetaldehyde CF3C(O)H at 308nm wavelength, which is a common UV wavelength even at sea level. After their experimental investigation, they concluded that CF3C(O)H degradation leads to a small, but significant production of the harmful R-23[14] (11-15% yield). Assessment of other wavelengths is missing, but the accompanying theoretical analysis for shorter wavelengths suggests that production of harmful degradants may be even higher.

In order to give the reader an idea of what kind of impact could be associated with the climate impact of the degradation products, we referred to the existing GWP values in Table 5.

Table 5: GWP of primary and secondary or even final degradation products taken from all WMO reports [3] as well as Hodneborg et al. [2].

| GWP | 1994 | 1998 | 2002 | 2006 | 2010 | 2014 | 2018 | Hodneborg |
|---|---|---|---|---|---|---|---|---|
| **$C(O)F_2$ (primary from R-125, R-32 etc.), lifetime: 5 years** | Unknown but relevant GWP in UTLS and above. Nevertheless, it could remain important even after a complete CFC removal due to very high abundance caused by HFC emissions | | | | | | | |
| **$CF_3C(O)H$ (primary from R-1234ze(E) etc.)** | Short living substance – no direct climate warming impact, but large impact as intermediate for long-living greenhouse gases as secondary degradation products ($CHF_3$) | | | | | | | |
| **R-23/$CHF_3$ (secondary), lifetime: 228 years** | 12100 | 14800 | 12240 | 14800 | 14200 | 14200 | 12690 | 15500 |
| **$CF_3$ (primary from R-125, R-134a etc.)** | Short lifetime. No climate warming impact known. | | | | | | | |
| **$CF_3COOH$ (primary, secondary)** | Short lifetime due to rainout. No climate warming impact known. | | | | | | | |
| **HC(O)F (primary)** | Unknown but relevant GWP in UTLS and above. | | | | | | | |

[13] See for example here: https://webbook.nist.gov/cgi/cbook.cgi?ID=C353504&Units=SI&Mask=80#IR-Spec.

[14] According to the research of [15], CF3C(O)H would have a channel and a yield rate of 11-15% towards fluoroform or HFC-23 for atmospheric conditions.

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|---|---|---|---|---|---|---|---|
| $CF_3C(O)F$ (primary from R-134a etc.) | Short living substance – no direct climate warming impact, but large impact as intermediate for long living greenhouse gases as secondary degradation products ($CF_4$) | | | | | | |
| $CF_4$ (secondary), lifetime: 50000 years | 6300 | 5700 | 7390 | 7390 | 6630 | 6630 | 7830 |

The long lifetimes that degradation products have are not captured by GWP values with a 100-year horizon, but radiative forcing could be significant for very long-lived substances such as $CF_4$.

In this section we have widened the scope of the climate impact of F-gases beyond the GWP, and looked into the manufacturing as well as spontaneous degradation processes in the atmosphere. It is clear that GWP values alone do not provide the full picture of the climate impact of fluorinated refrigerants. Climate impact from the manufacturing process is omitted. Furthermore, while new generation F-gases are considered as 'low-carbon' and a promising alternative to high-GWP refrigerants, their degradation products also have a harmful impact on the climate. Sometimes their degradants are even the very same substances that new F-gases were supposed to replace.

## Conclusions

The climate impact of fluorinated gases usually refers to their capacity to absorb sunlight and cause greenhouse effect once they are emitted into the atmosphere (the so-called Global Warming Potential or GWP). However, there exist a number of other climate impacts coming from emissions associated with the production and degradation of commonly used fluorinated refrigerants, and they are mostly ignored by policymakers. Unfortunately, even the new generation of low-GWP fluorinated refrigerants (such as HFOs, HCOs, HCFOs, HFCs and their blends) bring about very worrying emissions.

In this briefing, we showed how low-GWP fluorinated refrigerants contribute to global warming through the emissions associated with their manufacturing, as well as their degradation. We compiled a literature review and public data (where available), and illustrated the lack of disclosure of information by manufacturers. Finally, we urge regulators to take these impacts into account in decision making for hydrofluorocarbons (HFCs) to be replaced with truly sustainable and future-proof alternatives, such as natural refrigerants.

*Disclaimer: A previous version of this briefing published in May 2021 contained minor numeric errors. In this version they have been corrected and sources have been added in the bibliography.*

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