

Technology and Economic Assessment Panel (TEAP)

Response to Decision XXXIV/7: Strengthening institutional processes with respect to information on HFC-23 by-product emissions

Keiichi Ohnishi, Helen Tope, Jianjun Zhang
Medical and Chemical Technical Options Committee (MCTOC) Co-chairs
on behalf of the TEAP

Decision XXXIV/7: Strengthening institutional processes with respect to information on HFC-23 by-product emissions

To request the TEAP to prepare a report for the 35th Meeting of the Parties to include:

- a) Information on the possible chemical pathways that could be used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product;
- b) Compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances, the reporting of which is required under Article 7 of the Montreal Protocol;
- c) Best practices available to control these emissions.

Overview of report in response to decision XXXIV/7

- MCTOC, with its relevant chemical production expertise, led the preparation of this report on behalf of the TEAP.
- Report responds to decision, which focuses on chemical pathways used in the production of Annex C, Group I, and Annex F substances that may generate HFC-23 as a by-product.
- Report includes contextual information on other HFC-23 generation and emissions:
 - Chemical pathways used in the production of substances that are not Annex C, Group I, or Annex F substances
 - Feedstock uses
 - Consumptive uses, in consultation with TEAP experts
 - To help broader understanding of the relative importance of the chemical pathways that are focus of the decision.

Definition of key terms used in the decision

- **Generation** is defined as the total HFC-23 produced as a by-product, without taking into account abatement of emissions.
- **Emissions** are defined as the total HFC-23 emitted from a facility that generates HFC-23 as a by-product, after any abatement.
- A **by-product** is considered a secondary product of a primary process to create an intended product. A by-product may be secondary, but it is not necessarily unwanted if it is commercially valuable.

Chemical pathways that may generate HFC-23 as a by-product

- **Chemical pathways used to produce Annex C HCFC-22:** Estimated at 95% of total global HFC-23 by-product generation, the main source of HFC-23 by-product generation.
- **Chemical pathways used to produce other Annex C HCFCs (other than HCFC-22) or Annex F HFCs:** Estimated at up to 1% of total global HFC-23 by-product generation.
- **Chemical pathways used to produce substances other than Annex C HCFCs or Annex F HFCs:** Around 3–4% of total global HFC-23 by-product generation.

Chemical pathways that may generate HFC-23 as a by-product: Mechanisms of Generation

- There are several chemical mechanisms that can generate HFC-23 as a by-product in production processes, including:
 - ***Over- or under-reaction of chemicals*** present in the reaction vessel enroute to the intended product, e.g., HFC-23 is an over-fluorination of HCFC-22.
 - ***Presence of impurities in the feedstocks that are being reacted***, e.g., chloroform impurity in dichloromethane feedstock, used to produce HFC-32, is hydro-fluorinated to HFC-23.
 - ***Unintended side reactions***, where the feedstock follows a different reaction path than the one that is desired to make the product, e.g., cleavage of carbon–carbon bond in the production of HFC-125 from perchloroethylene, with subsequent hydro-fluorination of the resulting mono-carbon molecule to form HFC-23.

Chemical pathways that may generate HFC-23 as a by-product:

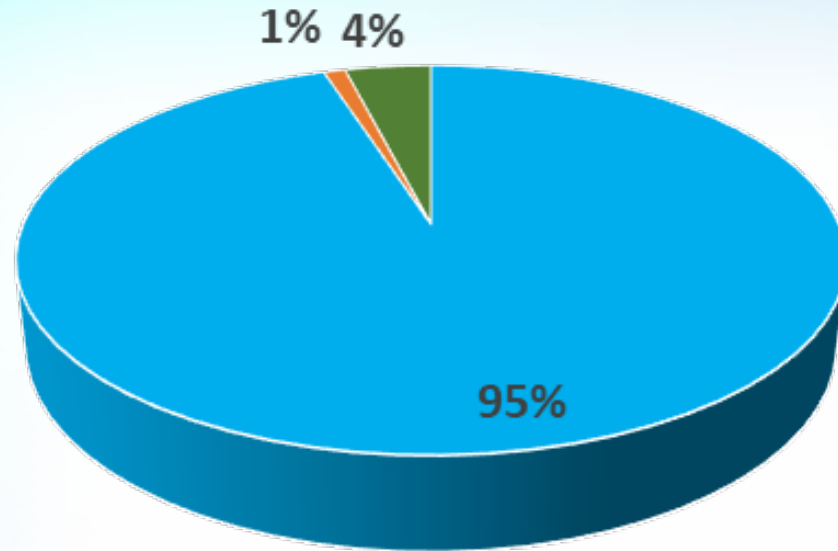
HFC-23 By-Product Generation Rates

- For economic reasons, the design intent of most plants is to minimise generation of unwanted by-products to the extent possible to maximise desired feedstock to product conversion ratios, within the limits of chemistry and available engineering.
- In some cases, it may be economically attractive to increase the production rate of the desired product at the expense of a higher by-product generation rate.
- HFC-23 generated as a by-product will only be emitted if it is not captured, used as feedstock, or destroyed before it leaves the process.
- With an effectively operated HFC-23 mitigation step, e.g., thermal oxidation, HFC-23 emission rates can be significantly lower than the HFC-23 by-product generation rates because destruction efficiencies can exceed 99%.

Chemical pathways that may generate HFC-23 as a by-product: Estimation of Global HFC-23 By-Product Generation

- The estimated global generation of HFC-23 as a by-product is around 25,000 tonnes per year for the range of chemical pathways considered in this report.
- This estimate is based on current expert knowledge of production quantities and HFC-23 by-product generation rates by process.

Chemical pathways used to produce Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product



- HCFC-22 production
- Other Annex C HCFCs and Annex F HFCs production
- Other chemical pathways including eg TFE/HFP production

Contribution to estimated total global HFC-23 by-product generation.

Estimated global generation of HFC-23 as a by-product is around 25,000 tonnes per year for the range of chemical pathways considered in this report.

Chemical pathways that may generate HFC-23 as a by-product: Level of Evidence

- Some chemical pathways used to produce Annex C HCFCs and Annex F HFCs have good evidence of HFC-23 generation and associated rates (e.g., HCFC-22 from chloroform).
- Other chemical pathways have more limited evidence of HFC-23 generation due to insufficient data, with a lack of emissions reporting and a lack of reference to HFC-23 generation in patents.
- Nevertheless, HFC-23 generation is theoretically feasible for many processes producing fluorinated substances and potentially present in trace amounts.
- For some chemical pathways, the rate of HFC-23 generation may be so low (practically zero) that HFC-23 would remain undetected in routine analysis.

Chemical pathways used to produce Annex C HCFCs or Annex F HFCs that may generate HFC-23 as a by-product

- With these data qualifications in mind, chemical pathways that could be used to produce Annex C HCFCs and Annex F HFCs that may generate HFC-23 as a by-product are:
 - HCFC-22 from chloroform, including co-production of HCFC-21
 - HFC-32 from dichloromethane
 - HFC-125 from perchloroethylene, including co-production of HCFC-124 and HCFC-123
 - HFC-134a from trichloroethylene, including co-production of HCFC-133a
 - HCFC-142b from vinylidene chloride or trichloroethane
 - HFC-152a from vinyl chloride
 - HFC-143a from trichloroethane
 - HFC-227ea from hexafluoropropylene (HFP)
 - HFC-245fa from pentachloropropane

Other chemical pathways that may generate HFC-23 by-product (other than Annex C HCFCs or Annex F HFCs)

- Of these *other* chemical pathways, the largest contributor to global HFC-23 by-product generation is likely to be the pyrolysis of HCFC-22 to make tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), which can be used to produce fluoropolymers.
- Other chemical pathways where HFC-23 by-product generation is theoretically feasible include those used to produce CFCs, namely CFC-113 from perchloroethylene and CFC-114 from perchloroethylene.
- Other chemical pathways are currently estimated to account for around 3–4% of total global HFC-23 by-product generation.

Information on amounts of HFC-23 generation and emissions from facilities that manufacture Annex C HCFCs or Annex F HFCs: Sources of Information

- UNFCCC submissions by Annex 1 countries
- Intergovernmental Panel on Climate Change (IPCC)
- Article 7 data reported under the Montreal Protocol
- Data reported to the Executive Committee (ExCom)
- Science Assessment Panel (SAP)

Information on amounts of HFC-23 generation from facilities that manufacture Annex C HCFCs or Annex F HFCs

- Reported data for HFC-23 by-product generation are mostly available for HCFC-22 production.
- Based on IPCC default factors, HFC-23 by-product generation from HCFC-22 production is expected to be in the range of about 15,000 to 30,000 tonnes per year.

Information on amounts of HFC-23 emissions from facilities that manufacture Annex C HCFCs or Annex F HFCs: Reported versus Atmospheric Monitoring

- HFC-23 emissions data reported under Article 7 are incomplete for 2019, 2020 and 2021 due to timing of reporting obligations and when parties ratified Kigali Amendment. The dataset for 2021 is the most complete.
- The combined HFC-23 emissions reported (UNFCCC and under Article 7) as by-product from HCFC-22 production is 2,572 tonnes in 2021.
- SAP 2022 Assessment reports estimated HFC-23 emissions, derived from atmospheric monitoring, of $17.2 \pm 0.8 \text{ Gg yr}^{-1}$ (17,200 tonnes) in 2019, and $16.5 \pm 0.8 \text{ Gg yr}^{-1}$ (16,500 tonnes) in 2020.

Compilation of information on amounts of HFC-23 emissions from sources considered in this report

Reported emissions from HCFC-22 production (A7 and UNFCCC) (2021)	2572
Potential emissions from other HCFC-22 plant waste streams	100 to 1000
Impurity released from HCFC-22 bank (2020)	40
Estimated emissions from TFE/HFP manufacture	100 to 1000
Electrochemical fluorination (2020)	10 to 100
Emissions from use as feedstock (2021)	10
Fire protection emissions (2022)	50
Low temperature refrigerant emissions (2021)	10 to 100
Semiconductor and electronics manufacture emissions (2021)	90
Total reported and estimated emissions from all sources	3000 to 5000
Emissions from atmospheric monitoring (2020)	16500
Gap between atmospheric monitoring and reported/estimated emissions (2021)	10000 to 12000
Emissions from atmospheric monitoring (2021)	15000
from the presentation by Steve Montzka at OEWG Slide 18	

Best practices available to control HFC-23 by-product emissions

- Consistent with those used to control other emissions associated with chemical manufacturing.
 - Optimising plant design, equipment, operation, maintenance
 - Instrumentation and monitoring of process and emissions
 - Training and instruction for plant operators
 - Periodic mass balancing
 - Technologies for destruction (i.e., thermal oxidation) or for separation and chemical transformation to treat unwanted co-products or by-products and abate their emissions
 - Regulatory controls to provide the framework to ensure emissions mitigation measures are implemented by operators, and to require emissions and other reporting.
- Report also summarises a sample of measures implemented or being implemented by parties to control emissions of HFC-23 by-product.

Recommendation

- Uncertainties and data discrepancies have been identified in this report that impact the accurate estimation of global HFC-23 generation and emissions based on currently available data.
- With improved data, more refined estimates and conclusions could be drawn.
- Parties may wish to consider measures to improve the reported data for HFC-23 generation and emissions, including their accuracy and their scope.