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FEEDSTOCKS ARE USED TO MAKE PRODUCTS HAVING MAJOR SOCIETAL VALUE

In response to the European Commission public consultation on the ODS Regulation, EFCTC submitted detailed comments on a range of issues including the important use of Ozone Depleting Substances (ODS) as feedstock. Maintaining the existing measures that allow the use and production of feedstock in the EU is a key requirement for the review. If use or production were to be constrained in the EU, then the downstream products would be imported into the EU.

This Position Paper expands on the response to the consultation and includes a case study on routes to TFE monomer used to manufacture PTFE and other fluorinated polymers. The case study sets out why the process via HCFC-22 (an ozone depleting substance) is the route used globally for large scale production of PTFE.

- The impact of constraining feedstock production and use in the EU.
- Regulatory measures for feedstock use, emissions and reporting.
- Why Ozone depleting substances are used as feedstocks.
- Emissions from the use of feedstocks in the EU.
- Case study on routes to TFE monomer used to manufacture PTFE and other fluorinated polymers.

The impact of constraining feedstock production and use in the EU

Chemical production is highly integrated, with processes designed to optimise raw material utilisation and minimise waste products. Constraining the use of ODS as feedstock could, as a minimum, increase waste destruction which only has the same effect as feedstock use, converting ODS to a non-ODS substances. More likely is the loss of some chemical manufacturing from the EU.

Regulatory measures for feedstock use, emissions and reporting

Regulation 1005/2009 (known as the Ozone Regulation) controls the use of and trade in ozone depleting substances. Consistent with the Montreal Protocol[1], the quantities used as feedstock[2] in

[1] The definition of production under the Montreal Protocol excludes the quantity of controlled substances entirely used as feedstock in the manufacture of other chemicals. Similarly, the definition of consumption excludes controlled substances entirely used as feedstock.

[2] Regulation 1005/2009 sets out a number of administrative measures such as quota limitations, licensing, registration and reporting requirements. However, there is no maximum overall ceiling for the use, thus in reality the amount of feedstock use is not limited.

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the manufacture of other chemicals are excluded from the definition of production and consumption. Emissions from the use of ODS feedstock in the EU must be reported and these are extremely low according to the EEA report on Ozone Depleting Substances 2020. From the 2020 TEAP Progress Report[3] emission rates from use of feedstock in the EU are at the very bottom of the emission range globally.

F-gas Regulation 517/2014, Article 7 "*emissions of fluorinated greenhouse gases in relation to production"* requires that trifluoromethane, produced as a by-product during the manufacturing process, including during the manufacturing of feedstocks for their production, has been destroyed or recovered for subsequent use, in line with best available techniques.

Why Ozone depleting substances are used as feedstocks

Ozone depleting substances (ODS) are widely used as feedstocks[4] to produce a wide range of refrigerants, pharmaceuticals, agrochemicals, monomers, polymers and other substances of major societal value. The chemical reactivity of some ODS allow high yield, resource efficient processes that transform them into non-ODS substances.

The major use of ODS feedstocks globally is to produce fluorine containing substances although carbon tetrachloride is also used to produce chlorine containing final products such as perchloroethylene, synthetic pyrethroids and intermediates for dyes and pharmaceuticals such as antiviral drugs. The 2020 TEAP Progress Report[5] lists common feedstock applications of ozone-depleting substances. The most widely used ODS feedstock is HCFC-22 which in 2018 accounted for 45% of all global ODS feedstock use in metric tonnes. In contrast, as ODP tonnes HCFC-22 accounted for 6.4% of the global total, although it should be noted that ODP tonnes does not equate to emissions. From the total amount of ODS used as feedstock, a relatively minor to insignificant quantity will be emitted depending on the abatement technologies and containment measures utilised.

Some HFCs are also used as feedstock. In the EU, HFC feedstock use[6] currently is almost exclusively the use of relatively small quantities of HFC-23. Very small amounts are occasionally reported for other HFCs.

Emissions from the use of feedstocks in the EU

[3] May 2020 TEAP Progress Report – Volume 1 page 49

[4] Feedstocks are defined by the Ozone Regulation and the Montreal Protocol. More generally feedstocks are intermediates as defined by the REACH Regulation.

[5] May 2020 TEAP Progress Report – Volume 1 Table 5.1 page 40

[6] EEA Report No 15/2020 Fluorinated greenhouse gases 2020

The EEA Ozone-depleting substances 2020 report states that the quantity of controlled substances used as feedstock in the EU was 159,157 metric tonnes in 2019, down by 9% relative to 2018[7] (). In 2019, the emission rate from feedstock uses was 0.03 %, calculated as the ratio between total emissions and quantities of controlled substances used. This is comparable to 2018 and much lower than the emission rate for earlier years. According to the 2019 EEA report, the overall decrease in the relative emission rates suggests that improvements have been made in the control of emissions in industry in recent years and that these measures are still in effect today.

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Globally, according to the 2020 TEAP Progress Report[8] emission rates from use of feedstock depend on a range of factors and notes that for the EU, the relatively low rate of emissions achieved illustrates the effectiveness of local controls, and industrial diligence, in the management and control of ODS emissions in feedstock use.

The EU reports its emissions of HFC-23, produced as a by-product during the manufacture of HCFC-22, as part of its Annual greenhouse gas inventory submission to the UNFCCC[9]. From this, in 2017 the EU share of global HFC-23 emissions, reported in a recent paper[10], was about 0.2%. The EU reported over 98% reduction in emissions in 2017 compared to 1990.

Case study on routes to TFE monomer used to manufacture PTFE and other fluorinated polymers

Why PTFE is used: PTFE provides the chemical and thermal stability and durability required for high performance of applications necessary to modern life such as medical devices, alternative energy technologies and aerospace applications. Tetrafluoroethylene is the required monomer.

The process used globally from HCFC-22: The required monomer tetrafluoroethylene (TFE) is produced commercially from HCFC-22 (chlorodifluoromethane), an ozone depleting substance, by pyrolysis at high temperature producing TFE in high yield with hexafluoropropene as a minor by-product, HCl and some HFC-23 which is destroyed. Hexafluoropropene is also used as a monomer.

[7] 2018 was the second highest level of feedstock use since 2010 at 173,367 tonnes

[8] May 2020 TEAP Progress Report – Volume 1 page 49

[9] EEA/PUBL/2019/051 Annual European Union greenhouse gas inventory 1990–2017 and inventory report 2019 Submission under the United Nations Framework Convention on Climate Change and the Kyoto Protocol page 469

[10] Increase in global emissions of HFC-23 despite near-total expected reductions, Nature Communications https://doi.org/10.1038/s41467-019-13899-4

Alternative proposed route from HFC-23: TFE could also be produced by the pyrolysis of HFC-23, as noted in the support study[11] for the evaluation of Regulation (EC) No 1005/2009 on substances that deplete the ozone layer. The use of HFC-23 to make TFE is discussed in detail in a recent paper which with the HFC-23 being produced by electrochemical fluorination.[12] However higher temperatures are typically required for HFC-23 pyrolysis with large recycle of HFC-23 and reduced selectivity to TFE.

Comparing the HCFC-22 and HFC-23 processes

Introducing fluorine into substances: There are many specialist processes and reactants to introduce fluorinated groups into molecules but for production of relatively simple molecules there are two main approaches:

- Reaction with hydrogen fluoride (HF) to replace chlorine with fluorine and with formation of hydrogen chloride (HCl) as a by-product, or for some substances, reaction of HF with an olefin.
- Reaction with elemental fluorine, generated electrochemically from potassium fluoride and HF, or by direct electrochemical fluorination.

HCFC-22 is efficiently produced from chloroform by reaction with HF in the presence of a catalyst. Over-fluorination results in HFC-23 as a by-product at up to about 3%, with an overall yield of HCFC-22 at about 95%. Chart 1 shows the production route to HCFC-22 and HFC-23 by-product.

[11] 22-02-2019 by: Ramboll, IVM, Table 40 Feedstock uses page 197

[12] ChemEngineering 2019, 3, 77 Energy and Resource Efficient Production of Fluoroalkenes in High Temperature Microreactors

Chart 1: Production route to HCFC-22 and HFC-23 by-product

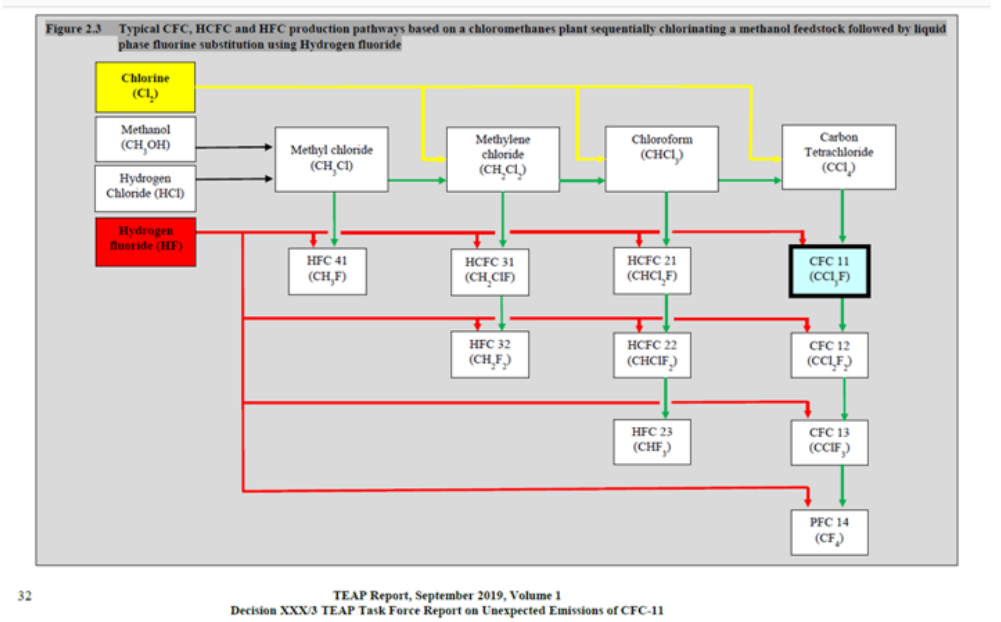

Chart 1 explanatory notes: The chart shows the possible products from reaction of C_1 chlorocarbons with hydrogen fluoride. In practice, for example, carbon tetrachloride is now used as a feedstock for a wide range of other chemicals and not the ones shown.

For HFC-23 there are essentially two process routes for its production:

Using the same process that is used to produce HCFC-22 but modifying the conditions to increase HFC-23 yield, as HFC-23 is a by-product of the current process (*see Chart 1*). This would require increased use of HF and extensive recycle of HCFC-22. There are no advantages of using HFC-23 from this route to produce TFE.

Reaction of methane with fluorine, either directly or using electrochemical fluorination. These processes are normally used to produce PFCs (perfluorocarbons) such as perfluoromethane (CF_4) or perfluoropropane (C_3F_8) and typically operated at a much smaller scale than would be required for TFE demand. Inevitably electrochemical or direct fluorination of methane will produce perfluoromethane (about 30% yield) with partially fluorinated methanes (about 70%) including HFC-23 (CF_3H) as shown in Chart 2. Even if the scale required for TFE production could be achieved, CF_4 by- product would be significant and would have to be destroyed as there is not a demand for such quantities. In addition to the relatively small scale typically used, the poor selectivity for HFC-23 and the high yield of perfluoromethane (CF_4) are major drawbacks. Furthermore, the atmospheric lifetime of perfluoromethane (CF_4) is about 50,000 years making the avoidance of emissions even more critical. Perfluoromethane is much more stable than HFCs such as HFC-23 and is more difficult to destroy[13].

Chart 2: Electrochemical fluorination of methane to perfluoromethane and trifluoromethane

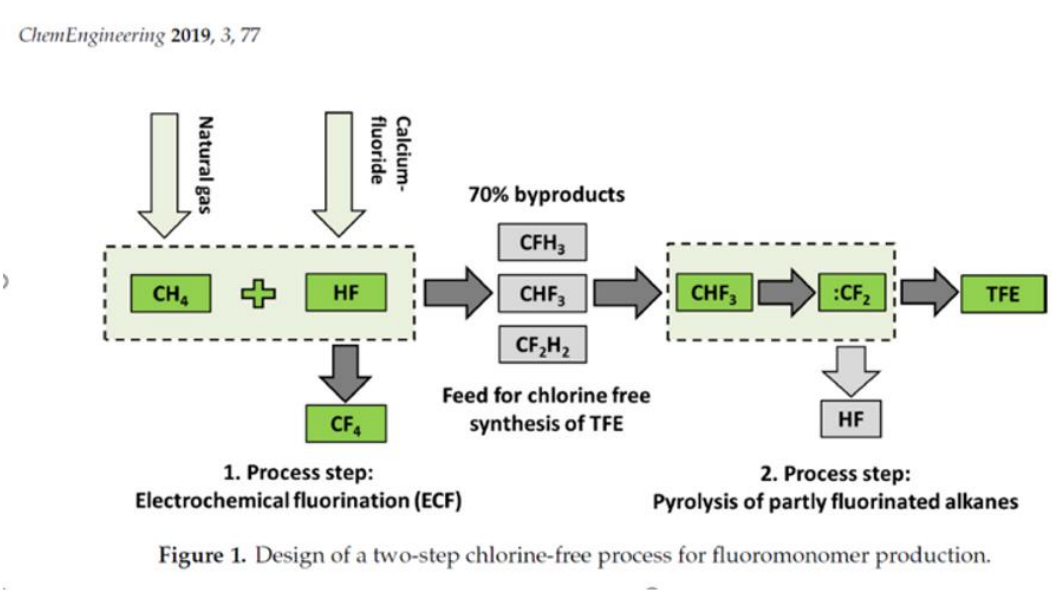

Figure 1. Design of a two-step chlorine-free process for fluoromonomer production.

Reproduced from open access paper Energy and Resource Efficient Production of Fluoroalkenes in High Temperature Microreactors

[13] On the Incinerability of Highly Fluorinated Organic Compounds, W Tsang, D R Burgess, J R & V Babushok, Combustion Science and Technology 1998, 139:1, 385-402, DOI:10.1080/00102209808952095

Furthermore, as well as the major drawbacks of poor selectivity and high yields of perfluoromethane (CF_4), HFC- 23, due to a very low boiling point, has a much higher vapour pressure than HCFC-22 at ambient temperatures hence equipment design pressures, the need to consider refrigerated storage solutions and potentially a higher emission rate for a given leak scenario would all have an impact on the long-term viability and suitability of HFC 23 as a large-scale feedstock for the production of TFE.

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About EFCTC

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.

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