

#### HFO-1234yf: An Examination of Projected Long-Term Costs of Production

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#### I. Why is the Production Cost of Hydrofluoroolefin (HFO)-1234yf Important?

This paper seeks to inform the discussion on what the price of HFO-1234yf (2,3,3,3-tetrafluoropropene) might be over the longer term when application and process patents have expired, economy of scale is achieved at production facilities using the most efficient processes, more producers are involved, and a fully competitive global market takes hold. The analysis focuses on the estimated costs of production based on one process currently in use, and a different process at a recently completed facility. We expect that long-term market prices will reflect broader factors of supply and demand. It is also possible over time that new or improved production processes will allow production of HFO-1234yf at lower costs and prices than estimated here.

With recent agreement by the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) to phase down the production and consumption of hydrofluorocarbons (HFCs), one key issue going forward is the cost of low global warming potential (GWP) substitutes. In particular, concerns have been raised about the high prices of one of these alternatives – hydrofluoroolefin (HFO)-1234yf, which is being used principally as the replacement for HFC-134a in motor vehicle air conditioning (MAC) and as an ingredient in refrigerant blends. However, limited public information is available on the current market price of HFO-1234yf and even less is known about the potential magnitude over time of possible future price decreases.

Current estimates are that HFO-1234yf is selling for approximately \$75-80/kg (\$75,000-80,000/tonne<sup>1</sup>) in bulk quantities purchased by vehicle manufacturers and approximately \$250 to \$350/kg in smaller quantities sold for vehicle MAC service. The bulk quantity market price for HFO-1234yf is approximately 10 times or more the current price of bulk HFC-134a.<sup>2</sup>

The current market price of HFO-1234yf reflects a number of factors: high costs of the complex, multistep production processes for both the new chlorocarbon feedstocks and the HFO products; the

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<sup>&</sup>lt;sup>1</sup> All tonnes are metric tonnes of 1000 kg or approximately 2204.6 pounds

<sup>&</sup>lt;sup>2</sup> Current market price of HFC-134a is estimated at \$6-8/kg. Limited information suggests that HFO-1234yf is being sold by producers to vehicle manufacturers at \$75-80/kg. See section III below.

limited number of current producers supplying rapidly growing markets in Europe and North America driven by regulation and incentives; and the existence of production process patents (for both chlorocarbon feedstocks and HFO products) and HFO application (use) patents held by a limited number of producers restricting market competition until these patents begin expiring after 2023.<sup>3</sup> The long-term price of a product like HFO-1234yf in a competitive market is the sum of its costs of production, marketing, and normal profit, but it is also determined by broader factors determining supply and demand and the availability and costs of alternatives. Experience with substitutes for ozone-depleting substances (ODSs) suggests that the market price of HFO-1234yf will come down over time as production experience is gained, more capacity is added, and especially as more producers enter the market following the expiration of patents.<sup>4</sup>

#### **II. Key Findings**

With estimated long-term costs of HFO-1234yf production presented in this paper at \$13-39/kg, compared to current wholesale market price of \$75-80/kg for HFO-1234yf, there appears to be room for substantial price declines over time as patents expire, more producers enter the market, and competition drives prices down to levels closer to production costs. Influencing factors include:

- National regulations and economic incentives in the European Union (EU), Japan, and United States (US).
- HFO-1234yf being used as the primary replacement for HFC-134a in MACs.
- Current prices for HFO-1234yf that are about \$75-80/kg, roughly ten times the wholesale price of HFC-134a.
- Current prices that reflect the existence of a limited number of producers, smaller-scale production facilities, a complex, multistep process to make the product, and the existence of production and use patents that restrict market entry.

The costs of producing HFO-1234yf at current on-stream or recently completed production facilities using two different processes was estimated to be in the range of \$7,800 to \$15,610/tonne based only on capital recovery costs and variable costs (raw materials and feedstocks, and energy) and a 3.2 per cent annual cost for maintenance of fixed capital assets. Other cost factors (e.g., operating labour and supplies, maintenance labour and materials, plant overhead, taxes and insurance, sales and marketing, interest paid on capital, general and administrative costs, and other costs) could add anywhere from 75-150 per cent to the variable and capital costs of production. Because many of these other costs depend largely on where the

<sup>&</sup>lt;sup>3</sup> A number of HFO patents are also under legal challenge. If ultimately successful, restrictions covered by those patents would be removed and increased competition could occur at an earlier date than when the patents would otherwise expire. See Stephen Seidel and Christine R. Ethridge, *Status of Legal Challenges: Patents Related to the Use of HFO-1234yf in Auto Air Conditioning*, C2ES, July 2016. <sup>4</sup> Additional competition could also occur if current patent holders license the technology to other

additional competition could also occur if current patent holders license the technology to other producers. The extent to which this will impact prices depends largely on the terms of the licensing agreement. To the extent such agreements limit the licensee to supply HFOs to the patent holder, prices remain under control of the patent holder.

plant is built and the local situation such as taxes and labour, this analysis only provides a broad range of these estimated costs.

• Total costs for the two HFO-1234yf production processes were estimated to range from \$13,650-39,025/tonne.

This analysis examined the underlying production costs based on two different production processes, one currently in use, and one in a recently completed facility, both based on confirmed manufacturing techniques. It provides insights into the extent to which the price of HFO-1234yf may fall when patents expire and competition from additional producers is possible.

## III. Use and Market Price of HFO-1234yf in MACs

In response to domestic regulations and economic initiatives in the EU, Japan, North America, and a growing number of other developed countries, automobile manufacturers have progressed well in shifting to HFO-1234yf as a low-GWP coolant in their motor vehicles. HFO-1234yf has a GWP<1 compared to the GWP of 1300 of the HFC-134a that it is replacing or compared to the GWP of 10,200 of chlorofluorocarbon (CFC)-12 that HFC-134a replaced in the 1990s in developed countries and in the 2000s in developing countries.<sup>5</sup> Following an assessment of a range of alternative refrigerants, global auto manufacturers almost unanimously selected HFO-1234yf. As of September 2016, about thirty-five auto manufacturers were producing 125 different vehicle models with HFO-1234yf systems and had manufactured an estimated 10 million cars with this new refrigerant.<sup>6</sup>

The number of companies, models, and automobiles using HFO-1234yf will continue to grow as the following national deadlines for switching to low-GWP alternatives are reached:

- The EU's 2006 MAC Directive requires the use of a refrigerant with a GWP less than 150 in MAC systems in new automobiles starting from 2017;
- The US Corporate Average Fuel Efficiency (CAFE) standard and greenhouse gas emission standards for passenger vehicles provide fuel efficiency credits for vehicles using refrigerants with a GWP less than HFC-134a, and a 2015 US EPA Significant New Alternatives Policy (SNAP) program rule requires phasing out the use of HFC-134a as a refrigerant in MAC systems in new passenger vehicles beginning with model year 2021;
- Canada's proposed HFC regulations would phase out the use of HFC-134a as a refrigerant in MAC systems in new passenger vehicles starting with model year 2021; and
- Japan's updated fluorocarbon regulation targets a GWP of 150 or less by 2023 model year.

HFO-1234yf has become the next-generation standard in mobile air conditioning. The clear majority of automobile manufacturers in developed countries have already or are planning to shift to HFO-1234yf, although there remains some limited interest in other alternatives, particularly for heavy trucks and off road vehicles. In addition, two German automobile manufacturers (Audi and Daimler) have announced plans to deploy several of their larger vehicle models using R-744 (carbon dioxide, GWP=1) as their

<sup>&</sup>lt;sup>5</sup> In this analysis, all GWP values are from IPCC AR5 (Intergovernmental Panel on Climate Change) Assessment Report Five (AR 5) 2014.

<sup>&</sup>lt;sup>6</sup> Honeywell website https://www.1234facts.com.

coolant in 2017. Daimler has been the first to market R-744 models in the EU only, with no immediate plans for sales in North America, where SAE standards required by the US EPA SNAP have not been pursued. In India, a consortium consisting of TATA Motors Limited (TML)/MAHLE/IGSD has received funding for a demonstration project of a secondary loop MAC (SL-MAC) system using either HFC-152a (GWP=138) or HFO-1234yf (GWP<1). A secondary loop system allows for safe use of more flammable refrigerants (HFC-152a) since the system uses a smaller refrigerant charge that is separated from the passenger compartment.<sup>7</sup> In addition, the SL-MAC system reduces refrigerant leakage with a smaller charge, fewer fittings, shorter permeable hoses, and increases fuel efficiency with deceleration cooling and prolonged comfort when the engine is shut down on vehicles equipped with stop/start. Advocates of SL-MACs are organizing a demonstration of suitability in large vehicles to achieve high cooling capacity with a refrigerant charge small enough to satisfy safety criteria.

Limited public information is available on the current market price that auto manufacturers are paying for HFO-1234yf. Estimates range from \$75-80/kg<sup>8</sup> with about 0.5-0.7 kg used to charge an average size automobile, up to about 2 kg for double evaporator systems, with the second cooling point at the rear of a large vehicle, and up to 5 kg for off-road mining and agricultural equipment.<sup>9</sup> In 2013, the average amount of refrigerant for MAC service in independent service facilities was about 0.85 kg. The charge size may be reduced if new MAC automotive systems are redesigned to use HFO-1234yf.

HFC-134a was invented and patented in the late 1970s by about half a dozen fluorocarbon producers, but no company claimed an application patent for any use. When first available in the market in 1990 from Imperial Chemical Industries (ICI) and DuPont (now respectively Mexichem and Chemours), the price of HFC-134a was also very high. However, rapidly over time, as more producers entered the market (including Asahi Glass Chemical, Daikin, Allied Signal (now Honeywell), Elf Atochem (now Arkema), Hoechst, Showa Denko and others), and later as production process patents expired and producers from Article 5 Parties also entered the market price of HFC-134a (\$6-8 kg or less) is now roughly double (in real terms) the amount that had been paid for CFC-12 at the time control measures under the Montreal Protocol first took effect.<sup>10</sup>

HFO-1234yf has been on the market a short time, larger-scale production facilities are only now coming on line, and process and use patents have restricted market entry. The key question is how much prices will decline over time, particularly once patent protection has expired and more producers are free to compete in the market or additional companies are licensed to produce under terms that allow them to sell directly to consumers and set their own prices. In the discussions leading up to agreement on the

<sup>&</sup>lt;sup>7</sup> Stephen O. Andersen, "Technical Options to Replace HFC-134a in Motor Vehicle Air Conditioning with Opportunity to Reduce Refrigerant Charge and Emission and for Increased Energy Efficiency" (side event presentation at the 38th Meeting of the Open-ended Working Group of the Parties to the Montreal Protocol, Vienna, Australia, July 2016)

<sup>&</sup>lt;sup>8</sup> Ibid.

<sup>&</sup>lt;sup>9</sup>With mark-ups by distributors, costs to final consumers for servicing are estimated to be higher. For example, one car manufacturer sets the price at US dealerships at US\$360/kg in 4.5kg (10 lb.) cylinders (Part Number 68224028AA). Ibid.

<sup>&</sup>lt;sup>10</sup> Stephen Seidel, Jason Ye, and Stephen O. Andersen. *Technological Change in the Production Sector Under the Montreal Protocol*. Center for Climate and Energy Solutions (C2ES) and Institute for Governance & Sustainable Development (IGSD). October 2015.

Kigali Amendment that added HFCs to the Montreal Protocol, a number of countries raised concerns about the lack of information on the future costs of HFOs. In the absence of information on future prices, recent studies attempting to estimate the costs of an HFC phasedown have relied on a range of assumptions for future HFO-1234yf prices.<sup>11</sup> Assumptions about the future price of HFO-1234yf have significant implications for any estimate of the long-term costs of an HFC phasedown in those sectors depending on this refrigerant, with MACs alone accounting for over 25 per cent of future refrigerant demand. For example, the price of HFO-1234yf is a critical assumption in projecting the costs associated with possible investment projects under the Montreal Protocol's Multilateral Fund (MLF) (either in the production sector or for the refrigeration and air conditioning sectors) and by individual countries in estimating their potential costs of an HFC phasedown.

# IV. Manufacturing Processes and Associated Variable/Feedstock and Capital Costs of Producing HFO-1234yf

## Key Assumptions<sup>12</sup>

In our cost calculations, we have used ethylene at the US-traded current market price of \$650/tonne, chlorine at a chlor-alkali producer's internal book value as a return to the Electrochemical Unit (ECU) at \$300/tonne, and carbon tetrachloride (CTC) at a nominal \$400/tonne. Where market prices exist for traded chemicals, we have used these in the relevant countries pertaining to chloroform, anhydrous hydrofluoric acid (AHF), methylene chloride, polytetrafluoroethylene (PTFE), and hydrochlorofluorocarbon (HCFC-22).

- Users of the HCFC-22/ tetrafluoroethylene (TFE)/ heptafluoropropane (HFP) process described below will already be integrated into these chemicals and will only be required to build onwards processing units. We expect these to be China- (and perhaps India-) based, where the capacity for HCFC-22, TFE, and HFP is the most copious. Nevertheless, large growth may mean new production investment may be required, but this is not our current outlook.

- The producer(s) of the new F1230xa intermediate for the chlorochemical route described below are supplying this as a service chemical to the fluorochemical company (HFO-1234yf producer) and will require capital return with profits over a 10-year period regardless of fluorocarbon derivative values.

- All our estimated costs of production for HFO-1234yf are based on the variable raw material cost, cost of utilities, capital recovery on the investment in plant, plus a 3.2 per cent annual maintenance cost.

<sup>&</sup>lt;sup>11</sup> For example, a recent analysis uses a price of HFO-1234yf pegged at \$75/kg in calculating the costs of a transition from HFC-134a to HFO-1234yf in the motor vehicle sector. Chandra Bhushan, *Resolving the IPR Issue During HFC Phase-Down*, Centre for Science and Environment, New Delhi (2016). In its analysis of the costs and benefits of HFC phasedown proposals, the Protocol's Technical and Economic Assessment Panel (TEAP) failed to fully address this issue of HFO costs and instead simply assumed that substitute costs would be similar to those incurred in the HCFC phasedown. Technical and Economic Assessment Panel, *Decision Ex.III/1 Working Group Report: On the climate benefits and costs of reducing hydrofluorocarbons under the Dubai pathway.* Sept. 2016.

<sup>&</sup>lt;sup>12</sup> Further explanation of key assumptions about the costs of raw materials and feedstocks is contained in Appendix A.

They do NOT include operating labour and supplies, maintenance labour and materials, plant overhead, taxes and insurance, sales and marketing, interest paid on capital, general and administrative costs, and other costs. Many of these costs depend on where the plant is built and the local situation such as taxes and labour. Based on chemical industry production cost assumptions commonly applicable, it is possible that these factors could increase estimated production costs by around 75-150 per cent above raw materials and capital recovery costs. In addition, none of these cost estimates include profits that could be expected from such production facilities.

- The routes described below concern currently revealed technology. Newer and more cost-effective production process routes are likely to emerge over time, but it is not within the scope of this paper to speculate on what those production process routes might be.

#### **Overview of Processes for Producing Fluorocarbons**

With rare exceptions, fluorocarbons of all genres (CFCs, HCFCs, HFCs, HFOs, halons) utilise the readiness of the fluorine molecule to substitute the chlorine molecule on selected hydro- and halo-carbons. Both molecules can be readily removed from a halo-carbon and/or may be substituted to achieve the desired chemical structure (isomer). The fluorine molecule itself is almost always added in the form of AHF. This is prepared by reacting chemical grade (purer) fluorspar ore with sulphuric acid. Many fluorochemical producers are backwards integrated to supply their own AHF, while others purchase it on the competitive market. The largest producer, China, currently sells AHF at about \$1050-1200/tonne (Source: *China Fluoride*). The basic chlorinated initiating molecules are selected for expected long-term availability and in general for a commodity price in a competitive market (Source: *NSA by direct discussion with producers: USGS Minerals*).

The commodity feedstocks required to produce the older fluorochemicals including CFCs, carbon tetrachloride - CTC, HCFCs, and HFCs are:

- **chloromethanes** (methanol, hydrochloric acid, and chlorine), which include methylene chloride (used to make HFC-32), chloroform (used to make HCFC-22), and CTC (used to make CFC-11 and CFC-12)

- **chloroethanes** (ethylene/ethane, chlorine, hydrochloric acid) to produce trichloroethylene (used to make HFC-134a), perchloroethylene (used to make HFC-134a and HFC-125), and ethylene dichloride or vinyl chloride (used to make T111). T111 is used to make HCFC-141b, HCFC-142b, and HFC-143a. Chloroethanes may involve more complex substitution processes.

Table 1. Indicative Feedstocks Used to Manufacture Fluorochemical Substances

FEEDSTOCK	FLUOROCHEMICALS
Chloromethanes (methanol, hydrochloric acid, and	
chlorine)	
Methylene chloride	HFC-32
Chloroform	HCFC-22, HFC-125
СТС	CFC-11, CFC-12, HFC-245fa
Chloroethanes (ethylene/ethane, chlorine,	
hydrochloric acid)	
Trichloroethylene	HFC-134a
Perchloroethylene	HFC-134a, HFC-125, CFC-113, CFC-113a
Ethylene Dichloride or Vinyl Chloride	1,1,1-Trichloroethane (also known as methyl
	chloroform or T111)
1,1,1-Trichloroethane	HCFC-141b, HCFC-142b, HFC-143a

The complexities of producing the right isomer of fluorocarbon for the intended end-use increases with the chain length of the chlorocarbon: hence chloropropanes and chlorobutanes (CTC plus vinyl chloride to make HFC-245fa, vinylidene chloride plus CTC to make HFC-236fa, 2-monochloropropane plus CTC to make HFC-365mfc). These are known as "Kharasch Reactions" named after the inventor of the process. The Kharasch Reactions process, vital to the development of the new HFOs, is based on the reaction between an olefin (with a C=C double bond) and a chlorinated species such as CTC, chloroform, methyl chloride or even another CFC or HCFC. The chain length of the olefin is extended by C+1 (a C2 ethylene-based product becomes a C3 propane), and the associated chlorine is added to the molecule. This is a feedstock use of CTC not controlled by the Montreal Protocol, providing CTC emissions are *de minimis*.<sup>13</sup> The complexities increase the cost of production considerably; this is especially noted when the desired end product must be a specific unsaturated fluoropropene and depends upon a complicated chlorocarbon structure.

# **Existing Processes for Producing HFO-1234yf**

The following sections describe two distinct process routes for producing HFO-1234yf; one is currently being used commercially and the construction of the other has recently been completed. Multiple production pathways exist because different producers may have different feedstocks available in-house or from nearby suppliers, may be able to partially convert existing facilities (e.g., distillation columns,

<sup>13</sup> Note that the atmospheric measurements of CTC are higher than can be attributed to natural sources and allowed feedstock uses presuming de minimis emissions. The Montreal Protocol Technology and Economics Assessment Panel (TEAP) and the Scientific Assessment Panel (SAP) speculate that emissions are under-reported by chemical companies or that inadvertent production takes place in various chlorine processes. There may also be some large but longer-term legacy emissions. Stephen A. Montzka, Mack McFarland, Stephen O. Andersen, Benjamin R. Miller, David W. Fahey, Bradley D. Hall, Lei Hu, Carolina Siso, and James W. Elkins. *Recent Trends in Global Emissions of Hydrochlorofluorocarbons and Hydrofluorocarbons: Reflecting on the 2007 Adjustments to the Montreal Protocol*, 2016. incineration) for the production of HFO-1234yf, and may own production process patents specific to a pathway. Some apparent feedstocks may not comply with local Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) or Toxic Substances Control Act (TSCA) requirements and therefore may not be shippable. These feedstocks would have to be pipeline-fed to the fluorocarbon producer. This clearly ties the chlorocarbon to the fluorocarbon.

#### A. Production Routes and Costs via Chloroform/HCFC-22

The production route selected to make introductory market volumes of HFO-1234yf was based on the starting point of HCFC-22, which is made from chloroform and AHF. HCFC-22 reacts under pyrolysis to produce the valuable chemical intermediate and monomer tetrafluoroethylene (TFE). One reason to choose this HCFC-22 starting point, particularly in China, was the availability of TFE from Chinese plants with large capacities. TFE plants were developed to meet the hugely growing demand for the perfluorinated polymer PTFE for engineering purposes. TFE is also used as an intermediate to manufacture HFC-125.<sup>14</sup> Similar, but smaller, TFE plants exist in Japan, USA and India. The disadvantage of this route to produce HFO-1234yf is that the resulting production is relatively small scale and depends on many batch reactions as opposed to a more efficient continuous flow reactions. The advantage is that a large part of the infrastructure already exists and does not require new investment.

PTFE has a listed trading price in China that as of September 2016 was around \$6500/tonne. This is not necessarily the intrinsic value of TFE, but gives an idea of its current market value as a precursor. Alternatively, a cost-based evaluation is that just over two units of HCFC-22 are required to make one unit of TFE. HCFC-22 trades in China at \$1500 /tonne, so a raw material value prior to pyrolysis in TFE would be some \$3200 /tonne, with the costs of pyrolysis adding approximately \$300-400/tonne to the variable cost. The next stage in the process involves the production of the intermediate hexafluoropropylene (CF<sub>3</sub>-CF=CF<sub>2</sub>: HFP), also called F1216 in fluorocarbon nomenclature. A typical route to produce F1216 involves pyrolysing TFE with another molecule of HCFC-22 and then de-chlorinating the resultant chlorohexafluoropropane. It can also be produced by reacting TFE and difluorocarbene, which is produced by the pyrolysis of HCFC-22. Typically, with yield losses, one unit of HCFC-22 at \$1500/tonne would be required, and the resultant HFP cost after the pyrolysis stage and dechlorination would be \$5500-6000/tonne. However, this is often sold or used as a monomer in fluoropolymer processing and for other industrial specialities, and the price may reach \$8000-10000/tonne. We will use 57500/tonne for HFP as a base cost. The HFP is then hydrogenated (using a catalytic hydrogen (H<sub>2</sub>) process) to produce F236ea (1,2,2,3,3,3-hexafluoropropane) and then dehydrofluorinated to produce F1225ye (1,2,3,3,3-pentafluoropropene), with a further hydrogenation to yield F245eb (1,2,3,3,3pentafluoropropane). The final stage is a dehydrofluorination to produce the end product 2,3,3,3tetrafluoropropene (HFO-1234yf).

The unit ratio of HFP to HFO-1234yf is close to 1.4-1.5 units per unit of HFO-1234yf. With yield losses and variable production costs (chemical grade hydrogen, catalyst depletion, power for pumps and

<sup>&</sup>lt;sup>14</sup> HFC-125 is used along with HFC-32 in a 50/50 blend widely used as in air conditioning applications as R-410A.

compressors, etc. in these final four stages) amounting to some 20 per cent, we would expect the variable cost of HFO-1234yf from this process to be in the range \$13,000-13,500/tonne. (Note that this calculation is based on the assumed cost to produce TFE, and not its selling price or intrinsic market value.) It does not include capital costs that are discussed below in the context of specific HFO-1234yf production facilities.

The first producing plant in China has been making HFO-1234yf using a similar process route as described above but uses two reactor trains. This producer initiated the business with a two ktpa train, added one ktpa in 2015 and a further three ktpa in 2016. We would expect the variable operating costs to be some 5-10 per cent higher than the larger newly constructed plant described below and the investments to also be some 10 per cent higher, giving variable costs for raw material of \$13,410/tonne plus plant capital costs of \$2200/ tonne for a total of \$15,610 /tonne.

A second HFO-1234yf plant in China that was recently completed but is not yet in production, was constructed with a capacity of seven ktpa with an announced investment of \$94 million for the infrastructure. For this facility, HCFC-22 will be converted to TFE at an adjacent site. This investment amounts to a fixed cost of \$1385/tonne on a 10-year basis. This makes no allowance for alternative use of capital, return on investment, and maintenance considerations. The latter cost is usually considered at 3.2 per cent per annum (pa) on the fixed cost and would add about \$430/tonne to the operational costs, amounting to an estimated \$1800/tonne for capital recovery and maintenance. The estimated materials and capital recovery (plus maintenance) costs to produce HFO-1234yf at this plant therefore is estimated to be \$13,250+1800 = \$15,050/tonne.

A third plant, located in Japan with a small capacity (1,000 tonne/year maximum), uses another variant of the same process route. In this plant, the TFE is reacted by pyrolysis with HCFC-21 (dichlorofluoromethane), which is an extraction product from HCFC-22 production usually left for recycling by refluorination in the initiation reactor. The resultant product is a commercial chemical HCFC-225 (a mixture of 50:50 3,3-dichloro-1,1,1,2,2-pentafluoropropane, or HCFC-225ca, and 1,3dichloro-1,1,2,2,3-pentafluoropropane or HCFC-225cb). The HCFC-225cb isomer must be discarded, and the HCFC-225ca is hydrogenated to F245cb (2,2,3,3,3-pentafluoropropane) and then dehydrofluorinated to create HFO-1234yf. Although the plant was already built for the HCFC-225 stage and is presumably close to amortisation and retirement with little scrap value, its use in the production of HFO-1234yf required an investment of some \$2-3 million. HCFC-225 had a market price close to \$20,000/tonne, but, as this use is declining under the HCFC phaseout, it represents excess capacity. Nevertheless, we would not expect the costs of producing HFO-1234yf at such a small plant to be less than \$20,000 /tonne.

In all cases of chloroform/HCFC-22 production routes to HFO-1234yf, the key is to have access to or integration into TFE and HFP. TFE is not transportable and must be available on-site or from adjacent sites.

#### B. Continuous process route using chlorocarbons

A 10-11 ktpa plant (or, see later, potentially 15 ktpa) recently began producing HFO-1234yf in the United States (US). Essentially it consists of two parts: the supply and receipt of the designated chlorocarbon

from the chlorine producer and derivative specialist by pipeline to the fluorocarbon manufacturer, and the consequent fluorination stages by the end product (HFO-1234yf) manufacturer.

The designated chlorocarbon is F1230xa (1,1,2,3-tetrachloropropene). The process starts with the Kharasch Reaction of ethylene and CTC to produce 1,3,3,3-tetrachloropropane (F250fb) and is a continuous process with two large-scale Kharasch reactors. Effluents from the process are commercially useful and include unreacted CTC, which is used in perchlorination to make PCE, and/or more purified CTC, and anhydrous hydrochloric acid (HCl), which is routed to the production of other chemical products, including ethylene dichloride and methyl chloride produced on the same plant site. There are also some heavy tars that are routed to disposal. Yields are expected to be in the range of 90 per cent.

Using ethylene at a current value of \$650/tonne and CTC at a nominal value of \$400/tonne, taking into account the unit ratios and losses, plus catalyst loss and heat/steam/working electricity, suggest a manufactured variable cost for F250fb of \$650/tonne at this stage. The F250fb is then photo-chlorinated in the presence of CTC to yield F240db (1,2,3,3,3-tetrachloropropane), with a co-production of anhydrous HCl, useful in the production of ethylene dichloride. Using internal chlorine gas at a nominal \$300/tonne (expected return from the chlor-alkali production units), and a unit ratio of about 1.3 of F250fb to F240db, we would expect the internal variable cost with process costs and some tar disposal to be around \$900/tonne. The F240bd is then dehydrochlorinated to produce F1230xa and, again with yield losses and process costs, we would infer a variable manufactured cost of close to \$1050/tonne. It should be noted that these figures reflect a production plant that has captive chlorine, CTC, and ethylene, and a producer that is familiar with all the reaction stages of chlorination, dechlorination, and Kharasch Reactions.

The value of the transferred F1230xa chlorocarbon must also include the fixed investment cost. Public information suggests that the investment in this 18-ktpa unit is \$145 million and further, that it may not be constructed until the end of 2017. There is some evidence that the fluorocarbon producer, in the meantime, has arranged with a Chinese group to supply up to 12 ktpa of F1230xa. At a unit ratio of 1.6 F1230xa to HFO-1234yf (yield losses may make this a higher ratio closer to 1.75:1), that would indicate a potential output limitation of a maximum of 7.5 kt of HFO-1234yf in the initial stages through 2017. The shipment of F1230xa requires stabilisation, as it may decompose over time. The fluorocarbon producer has made a number of patent applications for stabilisation techniques. In the production art, it is known that over-use of stabiliser in chlorocarbons can interfere with fluorination reactors.

The US plant of 18 ktpa F1230xa, with an announced capital cost of \$145 million, amounts to a capital recovery cost over ten years of \$800/tonne before considering return on investment, maintenance and other costs. Hence, on a ten-year capital recovery basis, we would assume that the F1230xa intermediate, prior to normal profit considerations, would amount to the sum of fixed and variable costs of \$1050+800/tonne or \$1850/tonne. A good working transfer value to the fluorochemical producer would be close to \$2750-3000/tonne assuming a plant pay-back period of 10 years and allowing capital recovery of \$145 million, plus just over 3.2 per cent annual maintenance. (Note: maintenance is based on the direct fixed capital and not on the annual depreciated value.)

The fluorocarbon plant associated with the supply of 18 ktpa F1230xa, based on the (precise) unit ratio of 1.6:1 F1230xa:HFO-1234yf, would produce 11 ktpa. Market information places it at closer to 15 ktpa, and this may be credible if external Chinese feedstock is brought into play. We use 15 ktpa capacity in fixed cost calculations.

In the process believed to be adopted, F1230xa is hydrofluorinated with three units AHF to make 1,1,1,2-chlorotrifluoropropene (F1233xf). The value of the three units of by-product HCl generated during this reaction has been assigned as zero, since its usefulness in further oxy-chlorination processing is uncertain. Using a cost level established above as \$3000/tonne for the F1230xa and \$1450/tonne for AHF (note: price reflects US, Chinese price is lower), this would bring the variable cost of F1233xf to some \$3750/tonne, with variable processing costs assessed at \$200/tonne, bringing F1233xf to a total of \$3950/tonne. In the next step, the F1233xf is hydrofluorinated to produce F244bb (1,1,1,2,tetrafluoro-2chloropropane), which in turn is then dehydrochlorinated in the presence of a chromium-based catalyst and an alkali metal to produce HFO-1234yf. The yield can be optimised by increasing the reaction time, and the co-products generated comprise a mixture of F1233xf and F244bb, which can be selectively recycled into the system. This process stage is expected to be more costly in the recycle than in the raw material inputs and outputs to the F1233xf and would imply a processing cost of some \$500/tonne, comprised of electrical and steam power to the system and the recycling, with some implicit losses to tars. The rate of accumulation of F1233xf -- whether it is a steady-state reflux or must be occasionally purged -- is a part of this cost. Hence it is assumed that the variable HFO-1234yf raw material cost by this chlorocarbon route may approach some \$4450/tonne.

The capital cost to construct this plant has been announced to be in excess of \$300 million: we will take it at \$320 million as a conservative cost to construct the capacity, which we have estimated to be 15 ktpa once all feedstock streams are available. With these cost assumptions, the fixed cost per tonne over an eight-year lifetime is just under \$3350/tonne, including 3.2 per cent annual maintenance, which gives a basic fixed and variable total cost of raw material \$4450+ and plant costs of \$3350, for a total of \$7800/tonne (based on an eight-year cost recovery period).

Looking ahead, another large-scale HFO-1234yf production facility is being developed in the US and is due to come on-stream in late 2018. The capacity is assessed at 18 ktpa, and the capital investment is stated by the producer to be \$230 million. The specific production process has not been announced, but it can be presumed that the costs of production, regardless of route, will be roughly in the same range as the chlorocarbon process described above.

#### Summary of Estimated HFO-1234yf Production Costs

The two distinct production process routes described above give a range of possible costs associated with current facilities for manufacturing HFO-1234yf. Please note that for processes using HCFC-22, we generally assume a lower AHF cost based on prices in China. The appendix explains this in more detail. The scale of these production facilities and the resulting cost estimates vary substantially depending on the chemical feedstock, process route selected, and the availability and cost of feedstocks, particularly if

some feedstocks are from plant overcapacity, including substances phased out of emissive uses under the Montreal Protocol and not otherwise usable.

Key assumptions in these cost estimates include:

- Capital costs for the relevant facilities publically announced by producers
- Prices and availability of key feedstocks
- Conversion rates and yields assumed in the analysis.

Capital cost estimates are assumed to be recovered over an 8-10 year period. It is important to note that the estimated production costs are not the same as the market price for HFO-1234yf, which will be determined over time (once patents have expired) by the supply and demand for the refrigerant. This analysis has focused in detail on the capital costs and the costs of raw materials and key feedstocks used in two distinct routes to produce HFO-1234yf. These production cost estimates do not take into consideration other cost factors, including operating labour and supplies, maintenance labour and materials, plant overhead, taxes and insurance, sales and marketing, interest paid on capital, general and administrative costs, and other costs. These additional cost factors vary by location and producer and are outside the scope of this analysis. Based on production cost assumptions commonly applicable, it is possible that the factors described here could increase estimated production costs by around 75-150 per cent of the total estimated raw materials and capital costs. These cost estimates also do not make any assumptions regarding the profits that would be expected from the production facilities.

Finally, the initial cost estimates are based on current processes and do not assume any advances over time, such as utilizing less expensive feedstocks, developing markets for by-products, increasing yields, etc. Table 1 summarizes the production cost estimates for the two process routes and facilities examined in this analysis:

Process Route	Variable Costs	Capital Recovery	Other cost	Estimated Total
	(raw materials and	Costs incl. 3.2 per	factors	Production Costs
	feedstocks)	cent maintenance	<u>(75-150</u>	
			per cent of	
			fixed and	
			<u>capital</u>	
			<u>costs)</u>	
Chloroform/HCFC-	\$13,410	\$2,200	\$11,708-	\$27,317—39,025
22 route		(10 year recovery)	23,415	
Chlorocarbon	\$4,450	\$3,350	\$5,850-	\$13,650-19,500
route (F1230xa)		(8 year recovery)	11,715	

Table 2: Summary of Key Elements of HFO-1234yf Production Costs (per tonne
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# V. Conclusions

By examining two different process routes for producing HFO-1234yf, this analysis shows a wide range of possible production costs. The process that starts with HCFC-22 has a significantly higher overall cost,

but is far less capital intensive and may be accessible to a wide range of current fluorocarbon producers. A second process in which F1230xa is a key feedstock appears to be more capital intensive, but results in a production cost just over half that of the HCFC-22 route. A third process will become operative in late 2018 and at capacity will deliver another 18 ktpa of HFO-1234yf to the market. The process to be used has not been publically stated but is likely to be competitive with the declared lower cost route.

The range of estimated production costs for capital recovery and raw materials spans from \$7800 to \$15610/t. These production costs do not take into account a number of other significant costs that could add as much as 75 -150 per cent to the costs described in this analysis. If these costs are included, estimated production costs for HFO-1234yf could range from US\$13,650 to \$39,025/tonne. This analysis does not make any assumptions about the level of profits earned by the facility. When compared to current market prices of \$80/kg (\$80,000/tonne), there appears to be room for substantial price declines over time as patents expire, more producers of the feedstocks for making the HFOs as well as manufacturers of the HFOs themselves are able to enter the market, and competition is able to drive prices down to levels closer to full production costs.

# List of Acronyms:

AHF	anhydrous hydrofluoric acid
CAFE	Corporate Average Fuel Efficiency
C2ES	Center for Climate and Energy Solutions
CFC	chlorofluorocarbon
СТС	carbon tetrachloride
ECU	electrochemical unit
EU	European Union
EPA	Environmental Protection Agency
GWP	global warming potential
HCFC	hydrochlorofluorocarbon
HCL	hydrochloric acid
HFC	hydrofluorocarbon
HeFP	heptafluoropropane
HFO	hydrofluoroolefin
HFP	hexafluoropropene (also called F1216)
ICI	Imperial Chemical Industries
IGSD	Institute for Governance & Sustainable Development
kg	kilogram
kt	kilo tonne
ktpa	kilotonnes per annum
MAC	mobile air conditioner
MLF	Montreal Protocol Multilateral Fund
NSA	Nolan Sherry & Associates
ODS	ozone-depleting substance
PCE	perchlorethylene (also known as PERC)
ра	per annum
PTFE	polytetrafluoroethylene
R&D	research and development
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SAE	Society for Automotive Engineers International
SL-MAC	secondary loop mobile air conditioner
SNAP	Significant New Alternatives Policy Program (US EPA)
T111	1,1,1-Trichloroethane (also known as methyl chloroform)
TSCA	Toxic Substances Control Act
TML	TATA Motors Limited
TFE	tetrafluoroethylene
tpa	tonnes(s) per annum
US	United States

## Appendix A

## Key Assumptions Regarding Costs of Raw Materials

Several reviewers commented on the raw material prices that we have used in our paper. The following is a more detailed explanation of the basis for the raw materials prices used in the analysis.

1. Anhydrous hydrofluoric acid (AHF). We used a price of US\$1000-1100/tonne reflecting the Chinese price where HFO-1234yf has been produced for 3-4 years, but it is not a universal price. In the US, a price of US\$1400-1500/tonne is typical.

2. Ethylene. We used a price of US\$650/tonne reflecting third quarter 2016. Reviewers have suggested ranges from US\$260/tonne to over US\$1100/tonne. Ethylene is not currently used in any current or planned Chinese route, but pricing there has ranged, during 2015-2016, from US\$825/tonne to a current US\$1140/tonne. Since in China, methanol, and not ethylene, is generally used in producing chloroform and then HCFC-22 as the main feedstock, its value there is not significant. In contrast, in the US, the new HFO-1234yf plant (s) are or will be ethylene based. In the period 2015-2016, US prices (and there are many, from contract to spot to the value of spot ethylene in exported products such as ethylene dichloride or styrene) have moved in the range US\$900+/- tonne to a current US\$550/tonne. The sensitivities around the price of ethylene may impact by as much as US\$100-200/tonne the costs of the F1230xa intermediate but even price changes of this magnitude for F1230xa will have little bearing on the final HFO-1234yf price to the market.

3. Carbon tetrachloride (CTC). The price of CTC largely depends on where the producer is based geographically. Some areas (e.g., Europe) currently have a potentially large but manageable oversupply. China is similar, but companies there need government permission to make the CTC<sup>15</sup> -- it cannot be placed on the market except as a chemical intermediate. Japan does not sell CTC, but with government permission some existing chloromethane capacity could be modified to make CTC for use as a feedstock. The US appears to have the production flexibility to make the predicted demand for feedstock applications, at least at present. Because of the Rotterdam Convention, CTC may be difficult to ship across borders. CTC is not used in the "Chinese" route to producing HFO-1234yf. In selecting a nominal cost of US\$400/tonne for CTC, we considered the following:

- No new CTC plants will need to be built: there is adequate capacity.
- If HFC-134a by its perchloroethylene route process is replaced by HFO-1234yf, more CTC will become available (the perchloroethylene in HFC-134a can readily be produced as CTC instead)

<sup>&</sup>lt;sup>15</sup> The production of carbon tetrachloride has been phased out under the Montreal Protocol. Production for use as a chemical intermediate is permissible.

and, in broad terms per cost of unit tonne capacity of PCE/CTC, CTC capacity becomes cheaper at a higher CTC ratio.

• If HFC134a made by its perchloroethylene route were NOT to be retired, this would limit the ability to produce more CTC from PCE/CTC plants. However, reducing chloroform demand due to the phase-down of HCFC-22 should enable chloromethanes plants to restructure and increase CTC production.

Hence, we have linked CTC to chlorine cost: it may not be exact, but it is indicative. We are not indicating that US\$400/tonne should be a global price, which will depend upon local availability and demand, and supplier/consumer negotiation.

4. Chloromethane (especially chloroform). This is used as a feedstock in the Chinese route to HFO-1234yf. There is also some very small production by this route in Japan and US. Chinese chloroform prices are in general (with rare spikes) some US\$200-250/tonne cheaper than in Europe. In view of the small percentage of chloroform in the overall HFO-1234yf molecule, this is not expected to give anything but a slight cost advantage to producers in China, which would be lost in the overall price of HFO-1234yf at market level.

As a general convention for the purposes of this analysis we have used the concept that if a chemical has an external and saleable value, then that opportunity cost is the value (with some minor downward adjustment) that should be used in HFO-1234yf cost analysis.