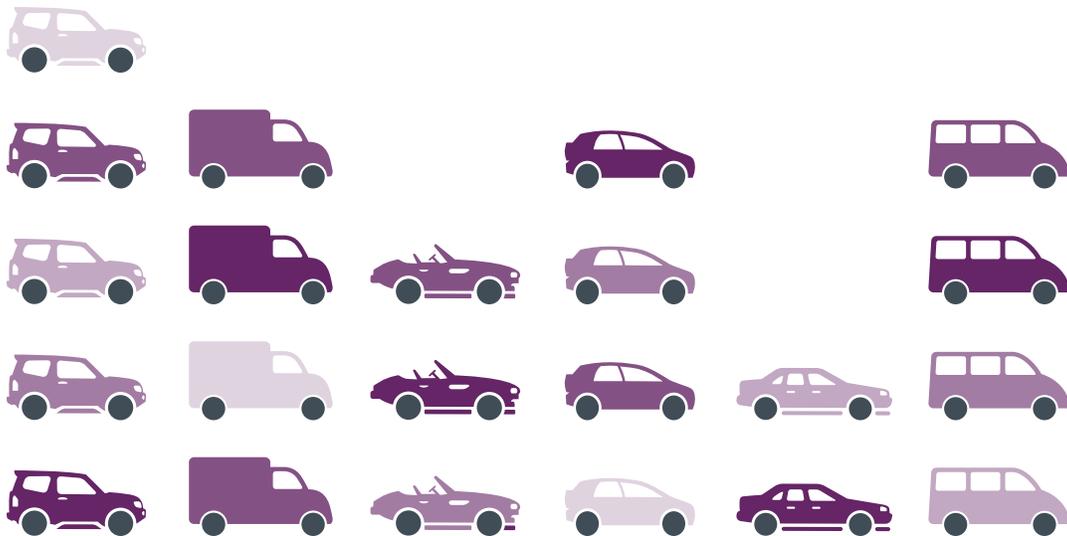




UPSTREAM CLIMATE IMPACTS FROM PRODUCTION OF R-134A AND R-1234YF REFRIGERANTS USED IN MOBILE AIR CONDITIONING SYSTEMS

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GLOSSARY OF CHEMICAL ACRONYMS

Chemical	Name
AC-6	A zeotropic blend consisting of 6% CO ₂ , 9% R-134a, and 85% R-1234ze (1,3,3,3-Tetrafluoropropene)
Cl₂	Chlorine
CTFE	Chlorotrifluoroethylene
CTFP	3-Chloro-1,1,2-trifluoropropene
HCl	Hydrogen chloride
HF	Hydrogen fluoride
HFC	Hydrofluorocarbon
PCA	Perchloroethane (hexachloroethane)
PERC	Perchloroethylene (tetrachloroethylene)
TCE	Trichloroethylene
TCTFE	1,1,2-Trichloro-1,2,2-trifluoroethane (R-113)
R-12	Dichlorodifluoromethane
R-1234yf	2,3,3,3-Tetrafluoropropene
R-133a	1,1,1-Trifluoro-2-chloroethane
R-134a	1,1,2,2-Tetrafluoroethane
R-152a	1,1-Difluoroethane
R-245fa	1,1,1,3,3-Pentafluoropropane
R-744	Carbon dioxide

EXECUTIVE SUMMARY

Essentially all common refrigerants used in air conditioning and refrigeration systems in vehicles today are potent greenhouse gases. One kilogram of the common vehicle air conditioning refrigerant R-134a is equivalent to 1430 kg of carbon dioxide (CO₂). According to the U.S. Environmental Protection Agency, leakage of refrigerants from air conditioning systems accounts for about 5% of greenhouse gas (GHG) emissions from the U.S. passenger vehicle fleet. A number of alternative refrigerants can greatly reduce refrigerants' climate impacts, so governments are actively considering ways to accelerate the transition to these alternatives.

In 2006, the European Union through Directive 2006/40/EC established a limit of 150 on the global warming potential (GWP) of refrigerants installed in vehicle air conditioning systems. This limit applies to new vehicle types as of 2011 and all vehicle types sold as of 2017. In 2010, the United States became the second jurisdiction to promote the switch to low-GWP refrigerants by allowing manufacturers to partially comply with its vehicle GHG emission standards through the deployment of low-GWP refrigerant systems. The U.S. standards took effect with model year 2012 vehicles, and regulators expect that by 2020 nearly all manufacturers will have switched to alternative refrigerants.

There are at least three alternative refrigerants that will enable manufacturer compliance on the basis of their GWP and the status of environmental and safety certifications in the United States and Europe: R-1234yf, R-744 (carbon dioxide), and R-152a. Some manufacturers in the United States and Europe have begun selling vehicles with R-1234yf to comply with the U.S. and European regulations. However, German automakers raised safety concerns in 2012 and stated a renewed commitment to adoption of R-744 systems.

In light of these developments, this paper calls attention to a missing element in European and U.S. regulations: consideration of the upstream climate impacts of refrigerant production. These impacts may be substantial for refrigerants that undergo energy-intensive and complex production processes, require high-GWP inputs, or produce high-GWP waste products that are not disposed of properly. Each of these aspects will likely reduce the climate benefit of the alternatives under consideration.

This paper assesses the upstream climate impacts of the two refrigerants used in passenger vehicles today, R-134a and R-1234yf. The analysis is based on first principles of basic chemistry, chemical reaction properties, energy balance fundamentals, and conventional life cycle methods. Energy consumption was estimated using CHEMCAD modeling of production processes. Emission factors of energy and material inputs were obtained from the ecoinvent database.

Our study shows that the upstream GHG emissions of R-1234yf are about 3 times those of R-134a. The findings indicate that in terms of kilograms of CO₂-equivalent per kilogram of refrigerant produced, R-134a and R-1234yf production generate GHG emissions of 3.6 kg CO₂e/kg and 10.9 kg CO₂e/kg, respectively. For every kilogram of R-1234yf that could replace R-134a, this study estimates a net reduction in CO₂-equivalent emissions of 98.7% on a life cycle basis. In comparison, current European and U.S. regulations assume a 99.7% reduction based on existing GWP values without inclusion of the life cycle impacts analyzed here. For perspective, this analysis suggests that if GWP values were to take upstream emissions into account, R-1234yf would have an equivalent GWP of

15, whereas under existing regulations R-1234yf has a GWP value of 4. If a 20-year time horizon GWP were applied, the climate impact relative to CO₂ would be doubled (i.e., GWP of 24 rather than 12).

Although upstream emissions of refrigerant production are substantial, R-1234yf is expected to generate nearly the same magnitude of climate benefit when upstream impacts are included because its GWP is substantially lower. Nonetheless, this research points out that future analysis of the life cycle emissions of new refrigerants, new materials, and manufacturing processes may be warranted to ensure that full climate impacts beyond the vehicle tailpipe are known.

1. INTRODUCTION

Refrigerant emissions have become a high-priority target for international climate policy. In the past 4 years, signatories to the Montreal Protocol have proposed an amendment to more rapidly phase out the production and consumption of refrigerants with high global warming potential (GWP). In June 2013, an agreement was reached between the United States and China to work together in support of this amendment, which increases the likelihood of its adoption this year (The White House, Office of the Press Secretary, 2013). In separate actions, the Japanese government has now adopted legislation to improve recycling of high-GWP refrigerants, while the European Parliament has taken steps to set limits on high-GWP refrigerants across sectors (Environmental Investigation Agency, 2013a, 2013b).

Refrigerants in vehicles account for 20% of global refrigerant emissions (UNEP, 2011). The dominant vehicle refrigerant R-134a,¹ with a 100-year GWP (GWP_{100}) value of 1430, is a key target because of its high climate impact and the potential for rapid transition to low-impact alternatives. In 2006, the European Union adopted regulations to reduce emissions of high-GWP refrigerants used in motor vehicle air conditioning systems. In the United States, refrigerant leakage alone can account for as much as 5% of fleet-wide GHG emissions (U.S. EPA and NHTSA, 2012), and vehicle emission regulations now promote a switch to alternative, low-GWP refrigerants.

Future refrigerant emissions in the passenger vehicle sector are dominated by three trends. First, a rapid phase-down of R-12 refrigerant with a GWP of 10,900 has been under way since the early 1990s in response to a ban on production and consumption under the Montreal Protocol. This has led to an overall decline in GHG emissions associated with refrigerant leakage as R-134a, with a GWP nearly 87% lower, has replaced it. Second, rapid growth in the size of the global passenger vehicle fleet is occurring. The International Energy Agency (IEA, 2012) projects the passenger fleet to grow to about 1.7 billion vehicles by 2030, from about 900 million in 2010 (Façanha et al., 2012). Third, by 2020, more than 95% of the global vehicle fleet will be equipped with mobile air conditioning (MAC) systems, versus 82% in 2000 (Papasavva, Hill, & Andersen, 2010). The combination of fleet growth and more vehicles having air conditioning systems will ensure that refrigerant emissions will continue to contribute a large share of the overall climate impact of the transportation fleet. As a consequence, refrigerant emissions control will remain a key strategy for climate change mitigation in the coming years.

Several countries have sought to promote refrigerants that have both zero ozone depletion potential and low GWP. In Europe, Directive 2006/40/EC on MAC systems requires the use of alternative refrigerants with GWP less than 150 beginning in 2011 for new vehicle types and 2017 for all new vehicles sold (European Union, 2006). In the United States, automakers are required to reduce the GHG emissions of vehicles sold beginning with model year 2012 and can earn credits toward this goal by switching to low-GWP refrigerants. For context, manufacturers that deploy low-GWP refrigerants in the United States can achieve as much as 14 to 17 g CO₂-equivalent (CO₂e) per mile in emission reduction credit per vehicle toward compliance with U.S. standards of approximately 250 g CO₂e per mile in model year 2016 and 163 g CO₂e per mile in model year 2025 (U.S. EPA, 2010; U.S. EPA and NHTSA, 2012).

¹ See the glossary.

A variety of low-GWP refrigerants would permit automaker compliance with these regulations and could reduce the climate impacts of existing refrigerant emissions by as much as 99% (Minjares, 2011). These include R-152a systems, R-1234yf systems, and R-744 systems. Today R-134a is the predominant refrigerant used in MAC systems. Automakers have pursued cooperative research facilitated by SAE International to explore refrigerant alternatives. The industry has attempted to unite behind a single global refrigerant, R-1234yf, to facilitate a rapid and cost-effective transition. In response, Honeywell and DuPont, the companies that hold patents on and manufacture the refrigerant, have signed purchasing contracts with manufacturers and have made major investments to increase the scale of production and distribution to satisfy global demand. In 2012, a group of European automakers signaled their desire to move away from a single global alternative and adopt R-744 (carbon dioxide) as a refrigerant. Safety testing and risk assessment continues for other alternatives as well, such as AC-6.

The primary motivation to switch to alternative refrigerants is to reduce the direct climate impact of refrigerant leakage. U.S. and European regulations are designed to restrict the use of refrigerants on the basis of their GWP, a measure of climate impact. However, the standard method for calculating GWP does not capture the full life cycle impacts of a substance. Missing from the GWP calculations are emissions impacts generated during production and transport of the refrigerant, production, transport and assembly of system components, system operation over the life of the vehicle, and end-of-life recycling (Papasavva et al., 2010). As a consequence, these regulations likely overestimate the full climate benefit of low-GWP alternatives.

A few studies provide insight into the life cycle impacts of alternative refrigerants used in passenger vehicles. Koban (2009) estimated that indirect emissions from use of an R-134a MAC system account for 78 to 94% of total life cycle GHG emissions, depending on the location of vehicle use. The same study estimated 99.8% indirect emissions share for an R-1234yf MAC system and an overall 17 to 20% reduction in life cycle emissions versus an R-134a MAC system. All things being equal, indirect emissions should be higher for R-1234yf given the large reduction generated in direct impacts. Papasavva et al. (2010) considered the full life cycle impacts of an R-1234yf MAC system and estimated that a global switch to R-1234yf in all new vehicles by 2017 would reduce GHG emissions by 30 million metric tons CO₂e in 2017.

These studies provide no information regarding assumptions and estimates for upstream emissions, particularly indirect emissions from refrigerant manufacturing. Refrigerant manufacturing is potentially GHG-intensive. In addition, the potential for fugitive emissions of high-GWP chemicals used in the production process, or of wastes generated in the process, may exist.

This study aims to estimate cradle-to-industry gate (upstream) GHG emissions of R-134a and R-1234yf to assess the potential contribution of upstream emissions to the life cycle climate impacts of each. For illustration purposes, a revised GWP estimate is given for each on the basis of the additional impacts contributed by upstream emissions. These are used to reevaluate the relative benefit of R-1234yf and to verify whether this refrigerant still meets the definition of alternative refrigerant (GWP < 150) under U.S. and European regulations.

2. METHODOLOGY AND DATA

The life cycle climate impacts of refrigerants can be assessed with a variety of methods, including total equivalent warming impact (TEWI), life cycle analysis (LCA), and life cycle climate performance (LCCP). TEWI estimates GHG emissions produced both from the energy consumed during operation of MAC systems and from refrigerant leakage over the life cycle of MAC systems (including end-of-life disposal) (AIRAH, 2012). LCCP is broader than TEWI and includes upstream GHG emissions from manufacturing of a refrigerant, MAC components, and MAC assembly. LCCP is a cradle-to-grave life cycle analysis of a whole air-conditioning system (Papasavva et al., 2010). A widely used LCCP model for MAC systems is the GREEN-MAC-LCCP, developed collaboratively by the U.S. EPA and industry groups.

Here, we used LCA to estimate cradle-to-industry gate GHG emissions of R-134a and R-1234yf. R-134a was chosen as the reference refrigerant because it is currently used in the vast majority of passenger vehicles. R-1234yf was chosen for comparison because vehicle manufacturers and government officials have publicly stated the likelihood that it would be adopted as a single global refrigerant to meet existing regulations.

To calculate upstream emissions, we used the ecoinvent² database (data v2.2, 2010) to calculate embodied GHG emissions of inputs used in the manufacturing of refrigerants. For estimation of GHG emissions from process energy consumption, CHEMCAD modeling (Chemstations Inc., 2013) was used to simulate energy consumption in R-134a and R-1234yf production. Because some of the inputs and outputs involved in the production process have high GWP values, fugitive emissions were estimated using the standard U.S. EPA method to determine whether fugitive emissions contribute appreciable GHG emissions in the production process. Because the ecoinvent database contains emission factors of energy and chemical inputs derived from industry located in Europe, upstream GHG emissions of R-134a and R-1234yf estimated in this study correspond to production processes located there. (See the Appendix for background information on ecoinvent GHG emission factors of chemical and energy inputs.) GHG emissions from transportation of input chemicals (from storage facilities or industry plants to a refrigerant production plant) are typically negligible and were not included (McCulloch & Lindley, 2003).

During refrigerant production, valuable by-products such as hydrochloric acid and R-245fa are produced. These co-products are removed as distillates during distillation. GHG credits for HCl and R-245fa were estimated using the displacement method. Equation 1 represents an allocation scheme used for R-134a and R-1234yf:

$$\text{Net GHG} = \text{GHG}_{\text{gross}} - M_{\text{co-product}} \times E_{\text{co-product}} \quad (1)$$

where $\text{GHG}_{\text{gross}}$, $M_{\text{co-product}}$, and $E_{\text{co-product}}$ are the gross GHG emissions of a refrigerant, mass of a co-product, and GHG emission factor of a co-product, respectively. The GHG emission factor for HCl was obtained from ecoinvent; the GHG emission factor for R-245fa was provided by DuPont.

² For details about the ecoinvent database, see www.ecoinvent.ch.

2.1. CHEMCAD MODELING

CHEMCAD is commonly used in academia and industry to model chemical processes. Users can analyze new processes by comparing different alternatives to determine their feasibility, or simulate an existing process to identify optimal conditions and bottlenecks that might improve current processes. Details about the processes involved in R-1234yf and R-134a are provided below. Energy consumption and design specifications for the chemical reactors and distillation columns are provided in Tables D and E in the Appendix. Tables A, B, and C contain information about raw material inputs to each of the processes. Fugitive emissions are estimated below and summarized in Tables G, H, and I.

A review of patents revealed that R-1234yf could be produced in a variety of ways (Bektesevic et al., 2011; Kopkalli, Chiu, & Tung, 2011; Van Der Puy, 2011). Because R-1234yf production uses proprietary technology, it is not known which production pathway major manufacturers such as Honeywell and DuPont have actually used to produce R-1234yf at industrial scale.

This report follows the production process laid out in U.S. patent 8,071,826 (Van Der Puy, 2011) that starts with CTFE and methyl chloride as initial inputs. Because the raw material input of CTFE to the R-1234yf process is not represented in the ecoinvent database, this study analyzed processes earlier in the supply chain. Therefore, two separate processes were modeled for production of CTFE followed by production of R-1234yf.

2.1.1. CTFE production

The production of CTFE is carried out in a two-step reaction sequence (Ebnesajjad, 2011). The process starts with the reaction of tetrachloroethylene (PERC) and Cl_2 to produce an intermediate product stream consisting of hexachloroethane (PCA) (Equation 2). PCA reacts with HF to form TCTFE (also called R-113) and HCl (Equation 3). Finally, TCTFE is dechlorinated via pyrolysis to form CTFE and Cl_2 (Equation 4).

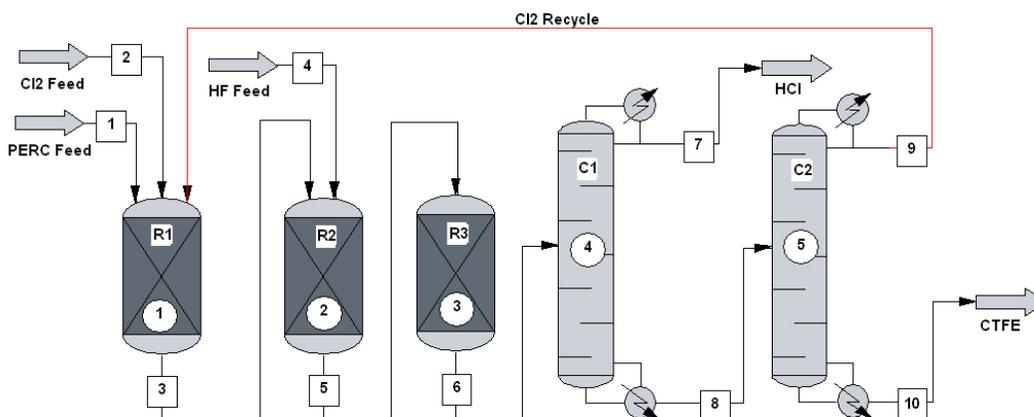


Figure 1 Process diagram for CTFE production.

Figure 1 shows a schematic diagram of the process flow for CTFE production. This process produces about 16,400 metric tons per year of CTFE, the amount required to produce the desired amount of R-1234yf described below. PERC, fresh Cl₂, and recycled Cl₂ are fed into reactor R1 in a 1:1 ratio at 25°C and 1 atm. Because process pressure is not known, atmospheric pressure was assumed. In reactor R1, the reaction in Equation 2 occurs isothermally at 140°C. The resulting product stream of PCA is fed into reactor R2, where it is reacted with fresh anhydrous HF to form TCTFE and HCl isothermally at 140°C, as described in Equation 3. This reactor temperature was assumed because actual reactor temperature is unknown. The effluent from reactor R2, which consists of TCTFE and HCl, is fed into reactor R3, where the product CTFE is formed along with Cl₂ isothermally at 600°C, as described in Equation 4. Conversion in all reactors was assumed to be 100% because of the lack of information about reaction conversion. The product stream mixture from reactor R3, which consists of CTFE, Cl₂, and HCl, is fed into a separations system, where a two-column distillation train is used to separate the mixture into two purified component streams. Column C1 recovers the HCl in the distillate, with the remainder of components present in the bottoms. The bottoms of column C1 are fed into column C2, where the desired product of CTFE is taken off in the bottoms, and Cl₂ is taken off in the distillate and recycled back as feed to reactor R1. The by-product HCl can be sold to the commodity market. Process streams for the CTFE production process are summarized in Table A.

2.1.2. R-1234yf production

This process starts with the reaction of CTFE and methyl chloride (CH₃Cl) to produce an intermediate product stream consisting of a variety of CTFP isomers (here assumed to be all 3-chloro-1,1,2-trifluoropropene because specific isomeric compositions are not known) and HCl (Equation 5). This intermediate stream is then reacted with HF to produce R-1234yf and HCl (Equation 6), and a simultaneous side reaction between R-1234yf and HF occurs that yields the by-product R-245fa (Equation 7).

The selectivities of R-1234yf and R-245fa are 0.87 and 0.13, respectively. Taking into account the selectivity of the side reaction, the overall chemical reaction stoichiometry for the production of R-1234yf (including the side reaction and the selectivity) is shown in Equation 8. Component data for CTFP are not contained in CHEMCAD, so the UNIFAC group contribution method (Fredenslund, Gmehling, & Rasmussen, 1979) tool built into CHEMCAD was used to estimate the thermodynamic properties of CTFP. Similarly, component data for R-1234yf are not contained in CHEMCAD, so a component with similar physical properties, 3,3,3-trifluoropropene (which does have thermodynamic data in CHEMCAD), was used as an approximation.



The R-1234yf production process is shown in Figure 2. This process produces approximately 14,000 metric tons of R-1234yf per year.

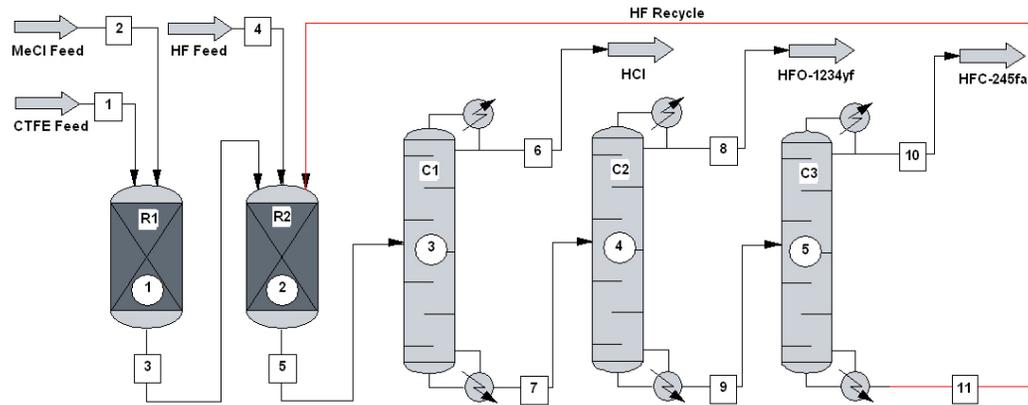


Figure 2 Process diagram for R-1234yf production.

CH_3Cl and CTFE are fed into reactor R1 in a 1:1 mole ratio at 25°C and 1 atm. Process pressure is not known, and the patent indicates that a range of pressures are appropriate, with no specific recommendation. Therefore, 1 atmospheric pressure is assumed. Reactor R1 carries out the reaction in Equation 5 at a conversion of greater than 99%; for the simulation, this was assumed to be 100% for ease of calculation. Reactor R1 is isothermal at 725°C . The product stream from reactor R1 (consisting of CTFP and HCl) enters reactor R2, where it is combined with a stream of fresh anhydrous HF and recycled HF in a 2:1 HF:CTFP mole ratio at 25°C and 1 atm. Again, conversion was assumed to be 100% with the stoichiometry described in Equation 8. Reactor R2 is isothermal at 335°C . The resulting product stream consists of unreacted excess HF, the product R-1234yf, and the by-products HCl and R-245fa. The product stream mixture from reactor R2 is fed into the separations system, where a three-column distillation train is used to separate the mixture into purified product streams. Column C1 separates HCl in the column distillate, with the remainder of components in the bottoms. The bottoms of column C1 are fed into column C2, where the desired product of R-1234yf is taken off in the distillate, with the remainder of components in the bottoms. These bottoms are fed into column C3, where the by-product of R-245fa is recovered in the distillate, and HF is taken off the bottoms, where it is recycled back to reactor R2. The by-product HCl can be sold to the commodity market, and the by-product R-245fa can be sold to the specialty chemical market. Process streams for the R-1234yf production process are summarized in Table B.

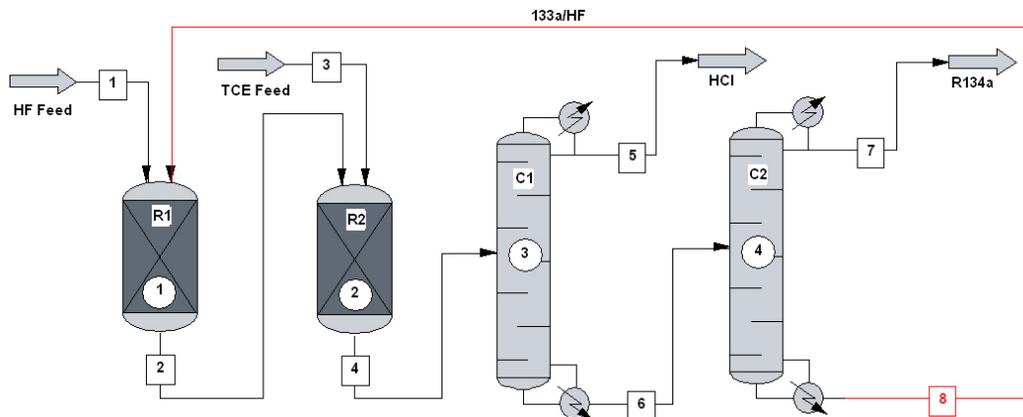


Figure 3 Process diagram for R-134a production.

2.1.3. R-134a production

This report follows the production process for R-134a described in U.S. patents 5,382,722 and 5,654,494 (Scott & Steven, 1995; Tung et al., 1997) and consists of a two-step reaction sequence. The process starts with the reaction of TCE and HF to produce an intermediate product stream consisting of R-133a and HCl (Equation 9). This intermediate stream is then reacted with HF to produce R-134a and HCl:



The R-134a production process is shown in Figure 3. This process produces approximately 11,500 metric tons per year of R-134a. In this process, the reaction sequence is reversed, meaning reactor R1 carries out the reaction in Equation 10, whereas reactor R2 carries out the reaction in Equation 9. This arrangement increases the yield of R-134a to nearly 100%. Anhydrous HF at 25°C and 1 atm and the recycle stream from the end of the process (which consists of the intermediate R-133a and unreacted HF) are fed into reactor R1, where the reaction in Equation 10 is carried out isothermally at 329°C and 1 atm. The entire process was assumed to be performed at 1 atm, because a pressure preference is not stated in the patent literature. The effluent from reactor R1 consists of R-134a, HCl, and unreacted HF. This stream is sent to reactor R2, where it is combined with fresh TCE, and the reaction in Equation 9 is carried out isothermally at 341°C. The resulting effluent consists of the product R-134a, R-133a, HCl, and unreacted excess HF. Conversion in all reactors is assumed to be 100% based on the patent literature. The product stream from reactor R2 is fed into the separations system, where a two-column distillation train is used to separate the mixture into purified component streams. Column C1 recovers HCl in the distillate, with the remainder of the components in the bottoms. The bottoms of column C1 are fed into column C2, where the desired product of R-134a is recovered in the distillate, and the intermediate product R-133a and unreacted HF are recycled back into reactor R1. The by-product HCl can be sold to the commodity market and hence can create GHG credits from displacement of HCl in the market. Process streams for the R-134a production process are summarized in Table C.

2.2. Fugitive emissions

Fugitive emissions can be estimated using a method developed by the U.S. EPA (1995). In practice, this involves taking actual on-site readings of emission concentrations near leak points, and using correlation equations to calculate the flow rate of fugitive emissions. Because this report is based on theoretical process models, it is not possible to make actual measurements. However, the EPA provides average estimates for the amount of fugitive emissions for specific components such as valves and connectors. In this case, detailed equipment knowledge is unavailable; to estimate fugitive emissions from simulation of production processes, we assume at least one valve on each stream, with two connectors per valve (one on either side of the valve). We also assume at least one connection point where a stream joins a unit operation. On the basis of these criteria, a crude estimate of fugitive emissions can be calculated according to the average equipment emissions given in Table F. This table assumes that the equipment has a constant rate of fugitive emissions, regardless of actual flow rates through the equipment.

Tables G, H, and I show the amount of fugitive emissions for the CTFE, R-1234yf, and R-134a processes, respectively. These were calculated using the stream table information (Tables A, B, and C), fugitive emissions factors of Table F, and the aforementioned equipment assumptions.

2.3. ENERGY CONSUMPTION CALCULATION

Energy use calculations for various reactors and distillation columns are provided in Tables D and E. Because both exothermic and endothermic reactions are involved in refrigerant production, energy is required for both heating and cooling. For example, reactors R1 and R2 in CTFE production involve exothermic reactions as indicated by negative heat values (MJ/hour). Energy is used for cooling these reactors, whereas reactor R3 involves energy consumption, as indicated by a positive heating value. Extra energy must be supplied to maintain the given reaction temperature. Energy is used in distillation columns to distill, condense, and separate products. Because estimation of GHG emissions from process energy requires knowledge of both the quantity of energy consumed and the type of energy source (electricity, natural gas, coal, etc.), certain assumptions were made regarding the efficiency of heat production from energy sources and types of energy supply. For distillation column reboilers, a natural gas-fired boiler with efficiency of 85% was assumed. In the case of distillation column condensers, cooling duty may come from a cryogenic refrigerator; hence, electricity use was assumed for distillation condensers. Energy for reactor cooling pipes was also assumed to come from electricity. In the absence of knowledge about the coefficient of performance (COP) for refrigeration, it was assumed that 1 joule of electricity removes 1 joule of heat from condensers. The same was assumed for cooling pipes. For reactor heating, a natural gas-fired heater was assumed to achieve an efficiency of 95%.

2.4. ADDITIONAL SCENARIO ANALYSIS

Estimates of upstream GHG emissions are conservative (i.e., actual emissions would be greater) because the calculations assume a 100% conversion of reactants to intermediate products and final products. This idealized conversion was used in the central analysis because actual industrial production data were inaccessible and the patents we analyzed offered little information on conversion rates. In addition, a conservative approach was used for estimating fugitive emissions. For sensitivity of emissions estimates to these assumptions, an additional case was analyzed assuming a 95% conversion rate for CTFE production, R-1234yf production, and R-134a production—double the amounts of fugitive emission in the main case—and lower efficiencies of natural gas boilers (80%) and heaters (95%).

3. RESULTS

To identify major contributors to upstream GHG emissions, we analyzed three sources of GHG emissions: embodied GHG emissions of input chemicals used in refrigerant production, direct and indirect GHG emissions from process energy consumption at a plant, and fugitive GHG emissions from equipment. Embodied GHG emissions refer to GHG emissions associated with production of inputs. Table 1 shows GHG emission contributions by chemicals, process energy, and fugitive emissions in R-134a production. Unless otherwise indicated, GHG emissions reflect GWP₁₀₀ values.

As can be seen from Table 1, embodied GHG emissions of HF are the main contributor to upstream GHG emissions (42.3%) of R-134a, followed by electricity (32.0%), natural gas (13.6%), and TCE (11.9%). HF is carbon-intensive and is used in large quantities. GHG contributions from fugitive emissions are negligible because of small leakage rates, although TCE and R-134a have an appreciable GWP. Fugitive emissions of chemicals with GWP values greater than 1 range from 5 to 15 g/hour.

Table 2 shows GHG emissions from R-1234yf production. Embodied GHG emissions of PERC are the main contributor and account for 46.7% of upstream emissions. HF contributes 16.3% of upstream GHG emissions, the second greatest share. Natural gas and electricity combined contribute 23% of upstream emissions. R-134a has slightly lower GHG emissions (2.3 kg CO₂e/kg) from process energy consumption than R-1234yf (3.2 kg CO₂e/kg).

Table 1 Upstream carbon dioxide-equivalent emissions in R-134a production.

Input	GHG emission contribution (kg CO ₂ e per kg of R-134a produced)	GHG contribution (%)
Chemicals		
Trichloroethylene	0.6	11.9
Hydrogen fluoride	2.1	42.3
Process energy		
Natural gas	0.7	13.6
Electricity	1.6	32.0
Fugitive emissions	0.01	0.3
Total	5.0	100

Note: These values do not include GHG credits from co-products, which would cause decreases in absolute GHG emission values. However, it would not affect the percent contribution of each component to total GHG emissions.

As illustrated in Figure 4, overall embodied GHG emissions of chemicals are the major contributor to upstream GHG emissions of the refrigerants analyzed. Embodied GHG emissions alone account for 54.2% and 76.8% of total upstream emissions for R-134a and R-1234yf, respectively. In contrast, fugitive emissions account for about 0.2% of upstream GHG emissions for R-1234yf. Similarly, fugitive emissions account for about 0.3% of upstream GHG emissions for R-134a. This is despite the fact that some of the inputs and outputs involved in production of R-1234yf have a high GWP, such as TCTFE (GWP = 5000) and R-245fa (GWP = 1030). The upstream emission estimates are not sensitive to assumptions for fugitive emissions. An increase by one order of magnitude

in the assumption for fugitive emissions would result in a total contribution of about 2% of total GHG upstream emissions—a small change in the current estimate.

Table 2 Upstream carbon dioxide-equivalent emissions in R-1234yf production.

Input	GHG Emission Contribution (kg CO ₂ e per kg of R-1234yf produced)	GHG Contribution (%)
Chemicals		
Tetrachloroethylene	6.4	46.7
Chlorine	0.3	2.5
Methyl chloride	1.5	11.3
Hydrogen fluoride	2.2	16.3
Energy		
Natural gas	1.0	7.6
Electricity	2.1	15.4
Fugitive emissions	0.03	0.2
Total	13.7	100

Note: These values do not include GHG credits from co-products, which would cause decreases in absolute GHG emission values. However, it would not affect the percent contribution of each component to total GHG emissions.

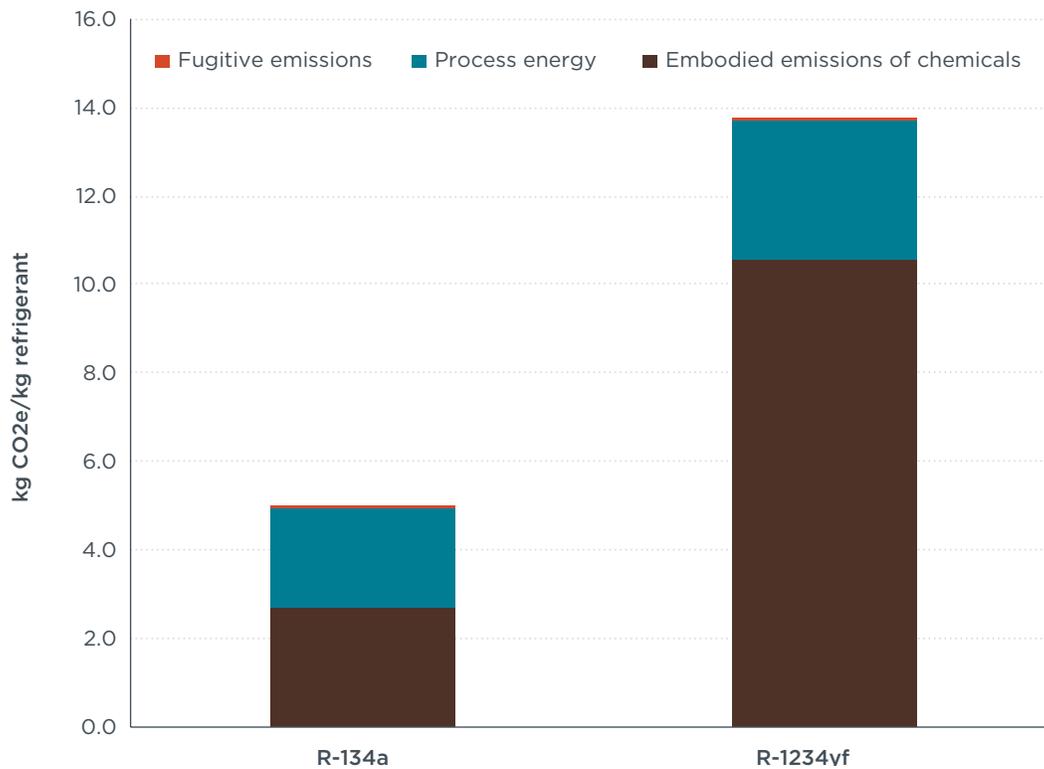


Figure 4 Breakdown of upstream GHG emission contribution by source (without GHG credits for co-products).

Upstream GHG emissions of R-1234yf and R-134a obtained using cradle-to-industry gate LCA show that R-1234yf has higher GHG emissions than R-134a per kilogram of refrigerant produced, as shown in Figure 5. The upper error bars in the figure represent the estimates for a sensitivity case involving 95% reactant conversion rate and lower efficiencies of natural gas boilers and heaters, as described above. The estimated upstream emissions of R-1234yf are 13.7 kg CO₂e/kg product without taking into account GHG credits from co-products; when co-product GHG emissions are accounted for, the estimate decreases to 10.9 kg CO₂e/kg.³

These results show that upstream GHG emissions of R-1234yf are about 3 times those of R-134a, indicating that higher upstream GHG emissions may offset a fraction of the climate mitigation benefits offered by the low GWP value (4) of R-1234yf.

As shown in Figure 5, our estimate for R-134a with co-product GHG credits (3.6 kg CO₂e/kg) is lower than DuPont's estimate of 9.4 kg CO₂e/kg (Krieger, Bateman, & Sylvester, 2004). One possible reason for this difference is that the DuPont analysis is based on an R-134a production route that starts with catalytic fluorination of PERC followed by hydrogenation, whereas in our study, it involves fluorination of TCE. However, our estimate for R-134a without GHG credits (i.e., 5.0 g CO₂e/kg) is somewhat close to the upstream GHG emissions of 6.6 g CO₂e/kg reported by McCulloch and Lindley (2003). This estimate is based on a similar production route for TCE applied in our study and does not allocate GHG emissions between R-134a and HCl. McCulloch and Lindley separately modeled the process energy consumption for TCE production via ethylene only, whereas our study used the cradle-to-industry gate GHG emissions factor for TCE obtained fromecoinvent, which is based on the aggregate TCE production data in Europe for both acetylene and ethylene routes (Boustead, 1997a). Differences in this method could have contributed to differences in results.

³ Along with R-134a, HCl is produced as a by-product, which when sold in the market reduces the need for production of an equivalent amount of HCl. Hence, GHG emissions associated with the displaced HCl are avoided and are counted as credits. Similarly, production of R-1234yf involves two valuable products, HCl and R-245a, which earn GHG credits.

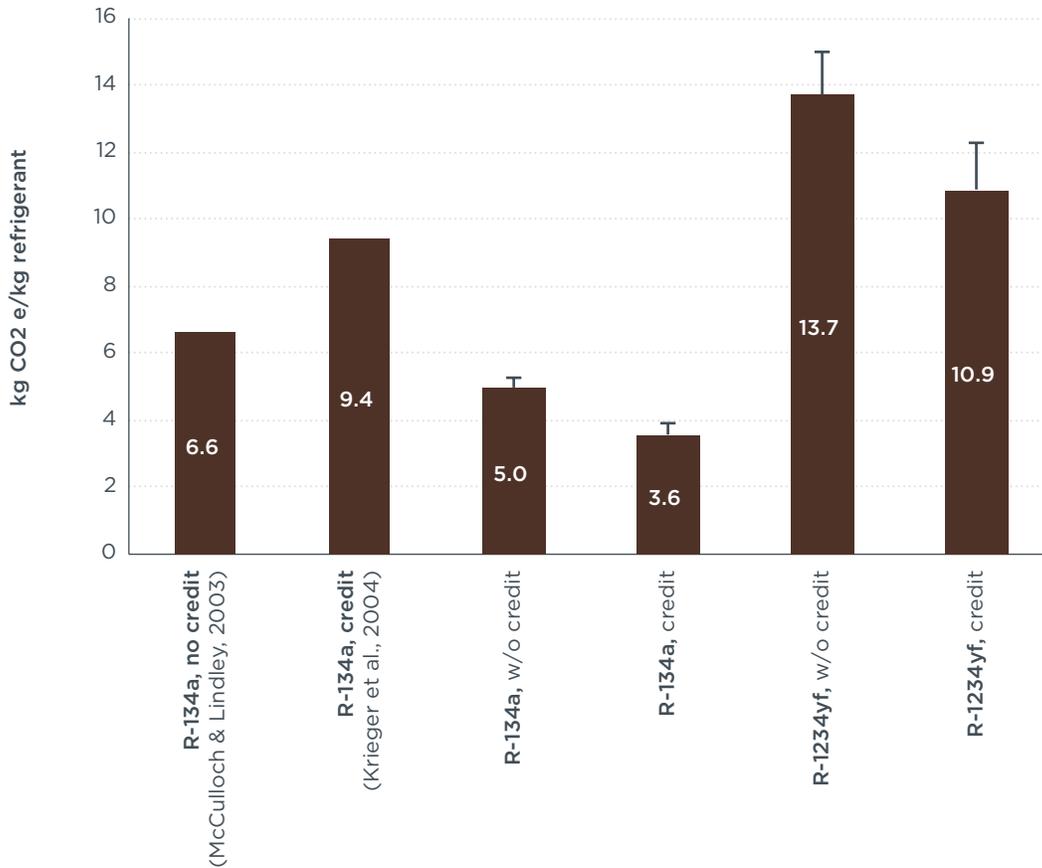


Figure 5 Comparison of upstream GHG emissions of R-134a and R-1234yf. The upstream GHG emissions of R-1234yf are 305% and 275% those of R-134a with and without co-product GHG credits, respectively. The co-products HCl and R-234fa displace HCl and R-234fa in the market, resulting in avoided GHG emissions.

4. DISCUSSION

Our study provides the first independent review of upstream GHG emissions of R-1234yf, evaluating them transparently with state-of-the-art CHEMCAD modeling of processes and life cycle analysis. The intent of this analysis is to rigorously estimate upstream GHG emissions of R-1234yf and to compare these to the incumbent refrigerant, R-134a.

Under existing regulations in the United States and Europe, the climate benefits of a switch to R-1234yf from R-134a would be equal to a 99.7% reduction in GHG emissions on a mass-equivalent basis, based on GWP estimates. When upstream emissions of R-134a and R-1234yf estimated in our study are included, the expected benefit is revised to a slightly smaller 98.7%. Our study indicates that a switch to R-1234yf would realize 1% fewer climate benefits than currently projected under direct emission reductions alone. This estimate also takes into account the average refrigerant leakage rate and the total refrigerant use per vehicle over its life cycle derived from Papasavva et al. (2010). The regular sedan-size car has an initial charge of 550 g. On average, refrigerant leakages result in a loss of about 835 g of refrigerant over the average vehicle

lifetime of 14 years, including end-of-vehicle leaks, and hence require one additional charge per lifetime with total refrigerant use of 1085 g per vehicle.

For perspective, this analysis suggests that if upstream GHG emissions of R-1234yf were considered, its overall climate impact would be akin to a refrigerant with a GWP of 15, rather than its GWP of 4 under existing regulations. On a GWP_{20} basis, the value would rise from 12 to 24.⁴ Similarly, for R-134a, the GWP value would increase from 1430 to 1434 if upstream GHG emissions were included. On a GWP_{20} basis, the value for R-134a would rise from 3830 to 3834. Under this scenario, the modifications to existing regulatory programs as suggested by this result would, however, be modest. The European regulatory program, which limits the use of refrigerants on the basis of their GWP value, would continue to allow the use of R-1234yf if our results were taken into account. Despite a rise in its GWP value by a factor of 3 on a GWP_{100} basis, R-1234yf would remain substantially under the 150 limit.

5. CONCLUSION

We find that upstream GHG emissions of R-1234yf are higher than those of the incumbent vehicle air conditioning refrigerant R-134a by a factor of ~3. However, upstream GHG emissions do not have a substantial effect on the total climate mitigation potential of R-1234yf, because its direct GWP is still so much lower (i.e., 99.7%) than that of R-134a. The findings from this assessment confirm that the use of the alternative refrigerant R-1234yf will deliver large climate benefits despite higher upstream emissions and is a viable solution to achieve the goals of existing U.S. and E.U. vehicle regulations that promote its use.

Our study constitutes the first publicly available estimate of upstream GHG emissions of R-1234yf using the state-of-the-art CHEMCAD modeling, a consistent and rigorous LCA method, best practices regarding co-product allocation, and good-quality data from ecoinvent. By looking into upstream emissions in a transparent manner, our study provides important information for analyzing the climate impact of new refrigerants expected to proliferate under new climate mitigation policies. Because of the limited availability of refrigerant production process information, the results represent an idealized case based on the best available chemical production and process models. A more precise picture of upstream emissions would require some level of information sharing by industry, whether through voluntary participation or regulatory compliance.

This work demonstrates the value of analyzing the upstream emissions of alternative refrigerants. Analyses like this help to ensure that existing policies do not have perverse impacts or tradeoffs outside of their regulatory context. Our study also demonstrates the value of LCA in understanding the implications of existing and future climate policy. Regulators may wish to explore the potential for broader application of these life cycle tools to capture the full climate implications of their decisions.

4 R-134a and R-1234yf are short-lived forcing agents whose impacts are not properly characterized by the GWP_{100} metric; that is, the short-term impact is diminished when measured in a 100-year time frame, so it is not appropriately accounted for in climate policies. Hence, GWP_{20} values are also provided here for comparison.

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APPENDIX

ecoinvent GHG emission factors: Background information

Natural gas is burned in a boiler (<100 kW). The emissions data include fuel input from a low-pressure (CH) network, infrastructure (boiler), and electricity needed for operation. Natural gas input (low pressure) and emission data for Europe are extrapolated from data for Switzerland.

Electricity refers to electricity production in Great Britain (high voltage at grid). Emissions data also take into account the average technology used to transmit and distribute electricity, including underground and overhead lines.

Chlorine is produced using the electrolysis process in a diaphragm cell. In addition, the following process steps are included: brine production, brine purification, brine resaturation, and the final handling of the electrolysis products, without chlorine liquefaction. Estimates are based on the present state of technology used in European diaphragm cells and represent European average values.

Hydrogen fluoride is produced from fluorspar and sulfuric acid; ecoinvent uses production data from different countries and uses its own assumptions for disaggregation of published cumulative data on energy use.

Hydrochloric acid is obtained from the reaction of hydrogen with chlorine. GHG emissions take into account precursor compounds, auxiliary materials, transports, and infrastructure. The data represent a current cross-section of actual plants in Europe.

Methyl chloride production includes emissions from raw materials, processing energy, energy services, and transports. Infrastructure is only partly included, with no infrastructure of main process included. Inventory data are from Boustead (1997b) and cover 78% of the total European methyl chloride production. Emissions represent the average of two production routes: methane chlorination and methanol hydrochlorination.

Trichloroethylene production includes emissions from raw materials, processing energy, energy services, and transports. Infrastructure is only partly included, with no infrastructure of main process included. Data are from various plants within Europe. Data refer to actual technology used by the companies. Emissions represent the average of production routes from acetylene and ethylene (Boustead, 1997a).

Tetrachloroethylene is mostly produced as co-product along with trichloroethylene in the chlorinated oxychlorination of ethylene dichloride. Another process that produces tetrachloroethylene is the chlorinolysis of chlorinated wastes. Production includes emissions from raw materials, processing energy, energy services, and transports. Infrastructure is only partly included, with no infrastructure of main process included. Inventory data are from Boustead (1997a) and cover 76% of the total European tetrachloroethylene production. Emissions refer to the average of two production routes from ethylene dichloride and chlorinated wastes.

Table A Stream table for CTFE production.

Stream no.	1	2	3	4	5	6	7	8	9	10
Stream name	PERC feed	Cl ₂ feed		HF feed			HCl		Cl ₂ recycle	CTFE
Temperature (°C)	25	25	140	25	140	600	-84.41	-34.04	-35.95	-26.93
Pressure (atm)	1	1	1	1	1	1	1	1	1	1
Enthalpy (MJ/hour)	-797.16	-0.01	-2,626.90	-13,250.00	-16,325.00	-11,578.00	-5,439.80	-10,017.00	-365.44	-9,648.40
Vapor mole fraction	0	1	0	1	1	1	0	0	0	0
Total flow rate (kmol/hour)	16.14	0.1	16.2	48.42	64.62	80.76	48.52	32.25	16.11	16.14
Total flow rate (kg/hour)	2,676.55	6.99	3,824.56	968.69	4,793.29	4,793.31	1,773.13	3,020.18	1,141.02	1,879.16
Chemical flow rates (kg/hour)										
CTFE	0	0	1.88	0	1.88	1,881.64	1.88	1,879.76	1.88	1,877.88
TCTFE	0	0	0	0	3,024.12	0	0	0	0	0
Cl ₂	0	6.99	0	0	0	1,144.38	5.87	1,138.51	1,137.37	1.14
PCA	0	0	3,820.81	0	0	0	0	0	0	0
HF	0	0	0	968.69	0.04	0.04	0	0.04	0	0.04
HCl	0	0	1.77	0	1,767.14	1,767.14	1,765.38	1.77	1.77	0
PERC	2,676.55	0	0.1	0	0.1	0.1	0	0.1	0	0.1

Table B Stream table for R-1234yf production.

Stream no.	1	2	3	4	5	6	7	8	9	10	11
Stream name	CTFE feed	CH ₃ Cl feed		HF feed		HCl		R-1234yf		R-245fa	HF recycle
Temperature (°C)	25	25	725	25	335	-84.44	-13.69	-25.12	19.63	14.45	23.55
Pressure (atm)	1	1	1	1	1	1	1	1	1	1	1
Enthalpy (MJ/hour)	-9,227.20	-1,321.70	-448.73	-4,988.50	-15,621.00	-3,613.60	-14,505.00	-8,958.70	-5,539.10	-1,302.50	-4,240.20
Vapor mole fraction	1	1	1	1	1	0.01	0	0	0	0	0
Total flow rate (kmol/hour)	16.11	16.11	32.22	18.23	62.34	32.20	30.14	14.03	16.11	2.12	13.99
Total flow rate (kg/hour)	1,876.08	813.25	2,689.33	364.71	3,334.12	1,175.04	2,159.08	1,596.56	562.52	282.45	280.08
Chemical flow rates (kg/hour)											
CH ₃ Cl	0	813.25	0	0	0	0.00	0	0.00	0	0.00	0
CTFE	1,876.08	0	0	0	0.00	0	0	0	0	0	0
CTFP	0	0	2,102.03	0	0	0.00	0	0.00	0.00	0	0
HCl	0	0	587.31	0	1,174.61	1,173.44	1.17	1.17	0	0	0
HF	0	0	0	364.71	280.36	0	280.36	0.28	280.08	0.28	279.8
R-1234yf	0	0	0	0	1,598.17	1.60	1,596.57	1,594.98	1.6	1.6	0
R-245fa	0.00	0	0	0	280.98	0	280.98	0.13	280.85	280.57	0

Table C Stream table for R-134a production.

Stream no.	1	2	3	4	5	6	7	8
Stream name	HF feed		TCE feed		HCl		R-134a	R-133a/HF
Temperature (°C)	25	329	25	341	-84.44	10.47	-22.46	19.07
Pressure (atm)	1	1	1	1	1	1	1	1
Enthalpy (MJ/hour)	-14,159.00	-56,660.00	-558.85	-57,601.00	-4,357.50	-60,989.00	-11,880.00	-49,073.00
Vapor mole fraction	1	1	0	1	0	0	0	0
Total flow rate (kmol/hour)	51.74	193.89	12.94	193.89	38.78	155.11	12.96	142.15
Total flow rate (kg/hour)	1,035.12	5,152.89	1,699.94	6,852.86	1,414.70	5,438.16	1,320.41	4,117.76
Chemical flow rates (kg/hour)								
TCE	0	0	1,699.94	0	0	0.00	0	0.00
HF	1,035.12	3,361.54	0	2,585.01	0.00	2,585.01	0	2,585.01
HCl	0	471.26	0.00	1,414.75	1,413.34	1.42	1.42	0.00
R-133a	0	0	0.00	1,533.01	0.04	1,532.97	1.54	1,531.44
R-134a	0	1,320.09	0	1,320.09	1.32	1,318.77	1,317.45	1.32

Tables D and E summarize the reactor and distillation column specifications, respectively. In these tables, a negative energy consumption indicates a cooling demand, and a positive energy consumption indicates a heating demand.

Table D Chemical reactor specifications.

Equipment no.	CTFE process			R-1234yf process		R-134a process	
	1	2	3	1	2	1	2
Name	R1	R2	R3	R1	R2	R1	R2
Thermal mode	Isothermal	Isothermal	Isothermal	Isothermal	Isothermal	Isothermal	Isothermal
Temperature (°C)	140	140	600	725	335	329	341
Pressure (atm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Key chemicals	PERC	PCA	TCTFE	CTFE	CTFP	R-133a	TCE
Fraction. conversion	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Heat of reaction (kJ/kmol)	-126,780	-76,809.55	186,589.98	499,582.75	-331,315.97	30,592.98	-96,310.38
Heat duty (MJ/hour)	-1,464.33	-448.53	4,747.41	10,100.17	-5,943.06	6,571.40	-381.88

Table E Distillation column specifications.

Equipment no.	CTFE process		R-1234yf process			R-134a process	
	4	5	3	4	5	3	4
Name	C1	C2	C1	C2	C3	C1	C2
Number of stages	12	100	9	17	49	8	18
Feed stage	6	50	5	9	25	4	9
Light key component	HCl	Cl ₂	HCl	R-1234yf	R-245fa	HCl	R-134a
Heavy key chemicals	CTFE	CTFE	R-1234yf	HF	HF	R-134a	R-133a
Reflux ratio	4.03	11.76	4.03	0.7	18.98	12.4	11.15
Condenser type	Total	Total	Total	Total	Total	Total	Total
Pressure (atm)	1	1	1	1	1	1	1
Condenser duty (MJ/hour)	-4,038.94	-4,051.63	-2,677.30	-507.94	-1,113.79	-8,592.38	-3,514.47
Reboiler duty (MJ/hour)	160.79	4,054.62	176.06	515.69	1,110.14	846.49	3,550.71

Table F Average fugitive emission factors for equipment units.

Equipment	Type	Emission rate (kg/hour per unit)
Valves	Gas/vapor	0.0060
	Light liquid	0.0040
	Heavy liquid	0.0002
Pumps	Light liquid	0.0200
	Heavy liquid	0.0086
Flanges/connectors	Gas	0.0018
	Light liquid	0.0002
	Heavy liquid	0.00003
Compressors	-	0.2285
Relief valve gas (gas/vapor)	-	0.1042
Open-ended lines	-	0.0017
Sampling connections	-	0.0150

Average fugitive emission factors for equipment units.

In Tables G to I, GWP values are only shown for the chemicals for which estimates by the Intergovernmental Panel on Climate Change (IPPC) are available. For chemicals such as HCl, HF, and Cl₂, GWPs are expected to be negligible.

Table G Fugitive emissions for CTFE process.

Chemical	Fugitive emissions (kg/hour)	GWP
CTFE	0.013	-
TCTFE	0.0082	5000
Cl ₂	0.0212	-
PCA	0.0131	-
HF	0.0113	-
HCl	0.0144	-
PERC	0.0113	-

Table H Fugitive emissions for R-1234yf process.

Chemical	Fugitive emissions (kg/hour)	GWP
CH ₃ Cl	0.0113	4
CTFE	0.0113	-
CTFP	0.0102	-
HCl	0.01	-
HF	0.0205	-
R-1234yf	0.0147	4
R-245fa	0.0089	1030

Table I Fugitive emissions for R-134a process.

Chemical	Fugitive Emissions (kg/hour)	GWP
TCE	0.0047	45
HF	0.0302	-
HCl	0.0086	-
R-133a	0.0062	-
R-134a	0.0118	1430