LCA Case Studies

Fire Extinguishers: A Case Study of CFC Replacements

(Part I)

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Abstract

In some well-known TEWI (total equivalent warming impact) analyses of CFC alternatives, global warmer emissions in production have not been considered. The authors show that TEWI can be affected significantly by these production emissions, which suggests they should be considered in some TEWI analyses.

The paper describes a TEWI analysis for one production sequence, that which leads from chloroform to tetrafluoroethylene and thence to HFC-227ea, a fire extinguishing agent. Numerous other commercial products stem from this sequence as well, including refrigerants, polymers and surfactants – these are summarised in the paper. Particular emphasis is placed on describing the production sequence and its global warming parameters to show that these can indeed be estimated from published information. The TEWI profile is presented at the close.

Keywords: Automobile air-conditioning; CFC alternatives; chlorofluorocarbons; eco-impact, CFC alternatives; fire extinguishers; fluorocarbons; global warming; HFC-227ea, fire extinguishing agent; LCA; Montreal Protocols; tetrafluoroethylene; TEWI; total equivalent warming impact (TEWI)

1 Introduction

As the ban on production of chlorofluorocarbons (CFCs) begins to take effect, choosing replacements for CFCs becomes an ever more pressing and timely issue. This series of two articles examines CFC replacement from a life-cycle perspective in two applications: fire-extinguishing and automobile air-conditioning.

In addition to reporting valuable data, the first case study suggests that conventional TEWI (total equivalent warming impact) analyses should in some cases be extended to the production of fluorocarbons. The second case study shows how important the usage phase of the life-cycle can be to the overall eco-impact.

2 TEWI: What It Is and How It Relates to LCA

TEWI is a life-cycle approach for comparing global warming impacts. It was invented by the chlorofluorocarbons (CFC) industry to compare replacements for its products, the production of which has been banned under the Montreal Protocols. However, industry-led TEWI studies [1] omit what can be a significant part of the system: **production.** This paper demonstrates the significance of production in the TEWI of a commercially important industry sector, gaseous fire extinguishers.

3 Method of the Study

The methods used in this study are consistent with state-of-the-art practice of life-cycle assessment (LCA). The rigour of the analysis is appropriate to the main question being addressed, i.e.: Which phases of the life cycle cause the most TEWI? The rigour with which any subordinate question was addressed depended on:

(1) its significance to the main question

(2) the degree to which plausible answers to the question differ

(3) the availability of data.

3.1 Definition of function and product

Fire extinguishing systems are used to protect life, property and the environment from the propagation of fires. Automatic systems work by spraying a fire extinguishing agent – traditionally water or foam – into the area being protected. In rooms where valuable items, such as computers, are housed, where the valuables would be damaged by foam or water, gaseous extinguishing agents often are used. These gaseous agents extinguish the fire by physical and/or chemical action. In applications where an entire room is protected by the agent, these are called "total flooding" systems.

A CFC, halon 1301, was the gaseous extinguishing agent of choice for total-flooding applications until its production began to be phased out for environmental reasons. An alternative type of gaseous systems was introduced with commercial success using HFC-227ea as the agent, which is sold under the trade name of FM200. This alternative has been approved by fire-protection authorities; it works by essentially the same method as halon 1301, i.e. flooding the atmosphere of the room that is to be protected.

FM200 systems are seen by the marketplace and by technical experts [2] as suitable for rooms housing valuables such as computers or other electronics, libraries and art galleries.

3.2 Functional unit

For this study, the functional unit used for the LCA is defined as a room in the UK containing valuable items (say, computer equipment) for which an automatic, gaseous fire extinguishing system is deemed necessary. Examples of this are commonplace and can be found in many office buildings and industrial locations.

The base case of the analysis was conducted for a room of 220 m^3 volume over a system lifetime of 15 years, because 220 m^3 is a typical size for room where such fire protection is installed and 15 years corresponds to lifetimes used in other expert studies of such systems [2]. The results of the study would hold for a larger room, because the relationship of TEWI to room size is essentially linear.

3.3 System boundaries and scope

The boundaries to the systems studied are where: raw materials and fuels are extracted from the environment; emissions to ambient air occur from operations, after treatment; and residual wastes are landfilled. The systems studied were scoped to focus on TEWI-relevant emissions from direct manufacturing, transport, use and disposal operations that comprise the life cycle. These are the relevant ones to the main question under study. A number of possible system elements were not included in the scope, because they are not significant and/or relevant to the main question. More detailed discussion of this reasoning may be found in the literature [3,4]: direct-overhead operations, indirect-overhead operations and provision of capital goods and financial resources.

One other element excluded due to a simple lack of data is emissions from landfill. This is a recognised deficit in LCA as commonly practised. However, given the nature of the wastes being landfilled in the systems studied here – i.e. mostly inorganics – it can be observed qualitatively that the contribution would likely be negligible.

3.4 Allocation rules

For most unit operations in the system, we used the common convention of allocating impacts (in this case TEWI- and ODP-relevant emissions) by proportional mass of the economically useful products. For instance, if a process's output is 40 kg of A, 40 kg of B and 20 kg of waste, A and B each are credited with half of the emissions.

Allocation for two types of processes in the systems studied was more complex; these are outlined in the following subsections.

3.4.1 Production and use of chlorine

The accepted practice of the chlor-alkali industry (represented by the trade group Eurochlor, Brussels) and other practicioners is to apportion according to mass of the two major outputs, chlorine and caustic soda (sodium hydroxide). This can be done in ratio of: mass of chlorine to mass of sodium hydroxide, i.e. 47% to chlorine; or atomic mass of chlorine to sodium, i.e. 60.7% to chlorine. We have used the former technique, i.e. allocating 47% to chlorine.

Chlorine is used as a processing aid in the production of FM200, but it is not present in the final product (heptafluoropropane). In the synthesis steps from chloroform to FM200, all of the chlorine used just passes through the processing chain and is emitted, from whence it may be recovered and then used elsewhere. Thus, chlorine outputs in this sequence have been treated as a processing aid, not as a co-product. This means they are economically useful, but they are products only in the same sense that capital goods are products.

3.4.2 Recycling

There are three main occurrences of recycling in the systems being studied:

(1) the system hardware

(2) intermediates in the FM200 manufacturing chain

(3) end-of-life FM200.

The first two cases are unequivocally of the closed loop type, where used or off-spec materials are reprocessed back into target products, and the third case has been treated as such. So-called downcycling, which legitimately can cloud arguments about allocation, is not encountered (except for chlorine, which, as mentioned above, is treated as a processing aid).

We have defined the systems to include these loops. Used or off-spec materials are treated as economically useful outputs, and emissions are allocated to them in proportion to their masses. Are these materials really economically useful? When they are recovered by commercial organisations for profit, yes. Steel scrap, for example, is traded widely in free markets and has a well-established commercial value.

Mathematically speaking, in the systems' closed loops we have considered virgin material to be recycled to extinction, and then we have allocated the impacts of all its lifetimes equally over each functional unit of use.

Recycling of end-of-life FM200 has been analysed as a closed-loop, established system, but it has not been recycled to extinction. It is assumed to have two lifetimes as a fire-extinguishing agent and then is destroyed. This recognises that considerable effort is being spent currently by chemical manufacturers to develop other alternatives to halon 1301 – it is highly plausible that a replacement to FM200 will be found within 30 years.

3.5 Energy and transport

Modules for UK and US power generation, process heat and steam have been used throughout the above-described system. These include pre-combustion emissions in production and processing of fuels. For electricity, primary sources of data were official publications of the US and UK governments [5,6]. Heat and steam modules were developed from standard references [3,7,8,10 plus private communications]. For transport – road, rail and ship – modules were developed from standard LCA references [3,7,8].

4 The Branch of Fluorine Chemistry Studied

The sequence of conversions chosen for study by the authors is presented in Figure 1 labelled *Commercial Production of HFC-227ea*. The processes studied most closely are labelled with numbered circles (steps 1-6). Key fluorochemicals are presented in Table 1.

TFE and HFP are primary building blocks in the modern organofluorochemicals business. Downstream commercial products [9,10] include: PTFE resins such as Teflon® (Du Pont) and Fluon® (ICI), plastics like Teflon® FEP and PFA (Du Pont) and ETFE, sold as Tefzel® (Du Pont), Hostaflon® ET (Hoechst) and Aflon® COP (Asahi Glass), elastomers and other products.

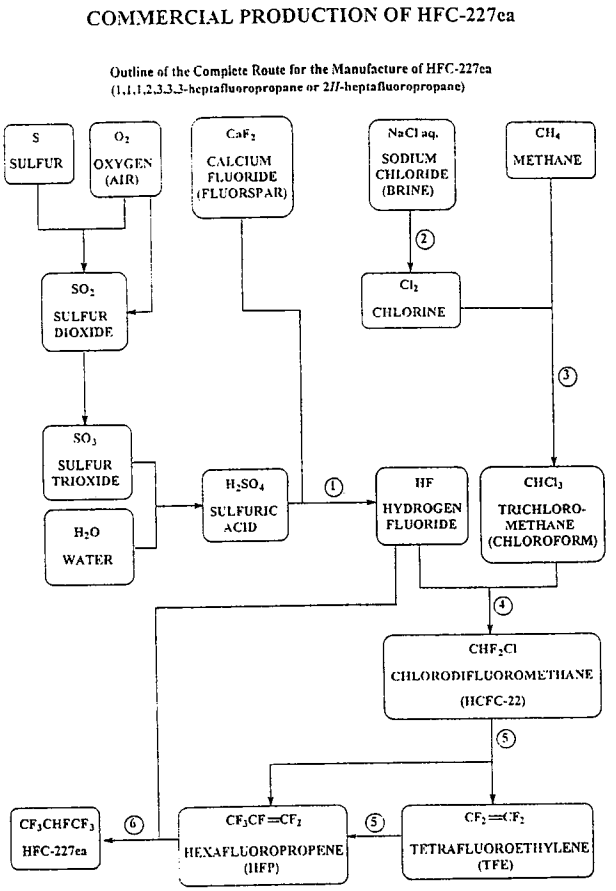

Fig. 1: Commercial Production of HFC-227ea

5 The Production Sequence and Its Global Warming Parameters

Published information, patent literature and chemical/engineering knowledge were used to estimate direct emissions of global warmers and energy consumption in the production sequence described above. An increasing amount of journal literature and regulatory documents are available

Table 1: Fluorocarbons in this study

Fluorocarbon Name	*Chemical Name*	*Trade Name(s)**	*GWP***
HFC-227ea	2*H*-heptafluoropropane	FM-200[a]	3300
HCFC-22	chlorodifluoromethane	Freon-22[b], Arcton-22[c]	1700
HFC-23	trifluoromethane	Suva-23[b], Klea 23[e]	12100
FC-1114	tetrafluoroethlyene	-	ND[d]
FC-1216	hexafluoropropene	-	ND[d]

*Not all are given. An extensive list of trademarks and manufacturers of CFC alternatives is given in: Fluorine Chemistry: A Comprehensive Treatment (ed. M Howe-Grant), John Wiley: New York, 1995, p 275.
**Tonne/tonne CO_2 equivalent, 100 year time horizon
[a]Great Lakes Chemical Corporation (USA)
[b]E I Du Pont de Nemours & Co, Inc (USA)
[c]ICI (UK)
[d]Not determined, as far as the authors are aware

for use in such estimates. In this study, references [11,12,13, 14,15] were particularly useful for estimating direct emissions; reference [16] proved useful for estimating energy requirements.

For each processing step, only emissions and energy for direct processing steps were estimated. Due to a lack of data, indirect, "overhead" activities such as the incineration of residues, recovery of halocarbons and packaging operations were not included in the model. If they had been, the final conclusions would have been strengthened.

It was recognised that plants in operation exhibit a range of performances, *i.e.* some consume less/more energy and emit less/more global warmers than others. Thus, emissions and energy were estimated under low, high and medium scenarios, based respectively on the combined best, worst and average performances. The final conclusion is not affected significantly by choice of scenario. Four processing steps (3-6), namely those involving the manufacture of chloroform through to HFC-227ea, contribute most significantly to direct emissions of global warmers.

5.1 Chloroform production (step 3, *Figure 1*)

The chlorination of methane to produce chloromethanes, including chloroform, is a long-established process. This process is being replaced by the chlorination of methanol. The latter process is carried out in two stages – the reaction of HCl with methanol to form methyl chloride followed by the reaction of this monochloride with chlorine to produce higher chloromethanes [17,18] Emissions are assumed to be in line with Warren Spring Laboratory's survey of UK VOC emissions [13], which indicates that "at each conversion stage of a chemical process, between 0.5 and 2% of the organic feedstock is lost".

The mid-range losses from production and use are assumed to be 1.25% of the amount of chloroform used. These losses have been apportioned equally between steps 3 (production) and 4 (consumption) as shown in **Figure 1**. The lower and upper likely total emissions have been taken as 0.5% and 2.0% of the amount of chloroform.

5.2 HCFC-22 production (step 4, *Figure 1*)

MIDGLEY and FISHER [14] give accurate, recent data based on a survey of members of AFEAS. They estimate that their results represent the performance of over 90% of world manufacturing capacity for HCFC-22 (bp -41°C). They concluded that approximately 2.5% of the gross manufactured volume is lost prior to sale via plant vents and packaging operations. This figure has been accepted by AFEAS in its 1995 assessment of HCFC-22 [19]. The emissions data are considered to be accurate to ± 0.5% of total production. In this assessment, the emissions have been assumed to be in the range 1.25-2.5% of production. This is a conservative estimate, taking MIDGLEY and FISHER's averages as the "high" case in this work.

No data have been found concerning release of HCFC-21, the "under-fluorination" product of chloroform, but "over-fluorination" to give HFC-23, a powerful greenhouse gas, is a well known phenomenon associated with the manufacture of HCFC-22. Emissions of HFC-23 occurring during the manufacture of HCFC-22 have been documented in the US. It has been estimated that 3000 to 5000 tonnes of HFC-23 are released to atmosphere in the US as a by-product of HCFC-22 production [20]. The US government [21] has estimated that the HFC-23 emission rate is 2-4% of HCFC-22 production.

The major US-based producers of HCFC-22 are committed, under the US Climate Change Action Programme, to reduce these emissions by 50% by the year 2000. Given the high volatility of HFC-23 (bp -82°C), the capital cost and energy requirement of emissions reduction will be high and progress beyond a 50% reduction is likely to be difficult. In the UK, ICI plan to make a substantial reduction in HFC-23 emissions, although it is recognised that this will be costly [22].

5.3 Production (step 5, *Figure 1*) of TFE (bp -76°C) and HFP (bp -29°C)

Here, TFE is produced by the pyrolysis of HCFC-22. This is a well established process with good quality public information on the releases, energy use and impacts. DOORENBUS [16], gives details of the energy consumption, process yields and wastes.

MIDGLEY and FISHER [14] indicate that a loss to atmosphere of 1% of HCFC-22 used as a chemical feedstock is to be expected. Upper and lower expected levels are assumed to be 1.5 and 0.5%, in line with the accuracy of MIDGLEY and FISHER's data.

Losses from a UK Plant manufacturing PTFE [23], which performs the pyrolysis operation and purifies the TFE produced, are 2 tonnes of TFE by fugitive emission and 90 tonnes from process vents. These are 0.067% and 3% of production respectively. 3% has been taken as the high estimate of TFE release, with the medium and low values at 2.5% and 2.0%

Patents [e.g. 24,25] were used to infer yields (of TFE and HFP) and reaction conditions. Emissions are estimated to be 10 kg/tonne of HCFC-22 feed and 25 kg/tonne of TFE produced in the medium case, based on references [13, 14, and 23]. This stage also involves the pyrolysis of tetrafluoroethylene (TFE) to make hexafluoropropene (HFP). Typical of a pyrolysis reaction, the selectivity to the desired product is not good. NELSON [26] quotes a yield of 82% of HFP from TFE. By using recycling of by-products, TEN EYCK and LARSON [27] claim that yields approaching 100% could be achieved, though this is unlikely to be practicable due to the difficulty and cost of separating by-products from products. A yield of 82% has been assumed for the high impact case, with 90 and 100% for the medium and low cases respectively.

Releases of materials will include feeds and raw materials, as well as by-products. In the absence of specific data, emissions of the raw material and product are assumed to be in the range of 0.5-1.5% of the feed and 2-3% of product. This assumption is based on the similarity of both process and chemicals to the production of TFE, which is discussed above.

5.4 Production (step 6, *Figure 1*) of HFC-227ea

The manufacture of the Halon 1301 (CF_3Br) alternative HFC-227ea [28] via the HF/HFP reaction is carried out in the US by a company that utilises units previously employed for other products, including Halon 1301 [12]. Clearly, because equipment designed for other products is being re-used, it is almost certain the process cannot be carried out in an optimal way. Also, older plant tends to have been designed with less attention to emissions control than modern plant. Conversely, the previous product, Halon 1301(bp -58°C), has a lower boiling point than HFC-227ea (bp -16.5°C) and this may mean that any vent condensers, if operated to their full capacity, would operate more efficiently.

The reaction used can have yields approaching 100% with respect to the raw material HFP [11]. Data submitted to US regulatory authorities [12] recognised that yields will be below 100%, as heavy organic residues are formed. However, it has been assumed here that the yield loss will be small. Yields with respect to HF reported in this patent were about 40-60%. This may indicate that a significant excess of HF is required, although appropriate design would minimise this. The low impact case assumes 100% yield with respect to HF, while the high case takes 60%.

Estimates of HFC-227ea production indicate that current production is in the range 1000 – 2000 tonnes per year, with a long-term potential annual market of 5000 tonnes [29,30,31]. Typical losses through fugitive and other emissions for similar VOCs would be in the range of 1-2% of throughput in a chemical process [13,14]. This would indicate losses in the range of 10-40 tonnes per annum. This range is in reasonable agreement with the data contained in the US EPA filing [12] for allowable emissions from the Great Lakes plant of 37.6 tonnes per annum of HFC-227ea/HFP. It is likely that the vents are associated with downstream (i.e. after the reactor) units in the process where the HFP has mostly been converted to HFC-227ea. It is thus reasonable to assume that HFC-227ea makes up between 50 and 90% of the emissions for this stage. On the basis of the available information, the emissions are judged to be in the range 0.5%-1% of HFC-227ea production, which is at the low end of the available data.

6 TEWI Analysis

Using medium-scenario direct and indirect emissions estimates, TEWI was calculated for a gaseous fire extinguishing system which uses HFC-227ea. Notionally the system is located in the UK and is representative of commercial practice there. Although the analysis was focused on global warming, it was done in accordance with state-of-the-art practice of life-cycle assessment, from raw materials production through disposal.

Global warming potentials for a 100-year integrated time horizon were used [32], because these best represent the climatic effects that these fire-extinguishing systems would create over the next several decades. Policy makers typically use this time-horizon for climate-related analyses.

Not surprisingly, the bulk of the global warming occurs in the use phase of the life cycle, as shown below in **Table 2**. Nonetheless, almost one-third of the TEWI occurs in the production of the alternative, which is significant, and, in this case is even greater than the TEWI contribution of the disposal phase.

Table 2: Total equivalent warming of a fire extinguishing system using HFC-227ea

Location: UK
Room Size: 220 m^3
Charged quantity of HFC-227ea: 121 kg

		Tonnes CO_2 Equivalent per		
LC Phase	*LC Subphase*	*Phase*	*Subphase*	*% TEWI*
Production		119.5		31
	Hardware		0.3	
	Initial Fill of Agent		92.2	
	Replacement Fills		26.9	
Use [2, 33]		180.5		48
	Discharge Testing		1.3	
	Discharge on Fires		89.6	
	Non-planned Discharges		89.6	
Disposal [2]		79.9		21
	Agent Not Recovered (20%)		79.7	
Sum		379.6		100

7 Conclusions

In refrigeration and solvent applications, TEWI (total equivalent warming impact) has been used to evaluate options for replacing CFCs. The authors' research reveals that TEWI can be affected significantly by emissions during the *production* of an alternative, not just emissions connected with its use and eventual disposal.

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