Carbon Dioxide Emission Implications if Hydrofluorocarbons are Regulated: A Refrigeration Case Study

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The U.S. is strongly considering regulating hydrofluorocarbons (HFCs) due to their global climate change forcing effects. A drop-in replacement hydrofluoroether has been evaluated using a gate-to-grave life cycle assessment of greenhouse gas emissions for the trade-offs between direct and indirect carbon dioxide equivalent emissions compared to a current HFC and a historically used refrigerant. The results indicate current regulations being considered may increase global climate change.

Introduction

The U.S. Environmental Protection Agency announced on April 24, 2009 that six compounds or classes of compounds (carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride) that contribute to global climate change are human health hazards (*1*). Emissions of these compounds continue to rise yearly (*2*). While carbon dioxide is of largest concern, hydrofluorocarbons (HFCs) are included due to their long-term impacts through extended atmospheric lifetimes. Hydrofluoroethers (HFEs) are not considered in the legislation but are primary candidates to replace the soon-to-be regulated HFCs.

Hydrofluorocarbons were introduced for use in a wide spectrum of processes when the Montreal Protocol (*3*) was implemented to phase out chlorofluorocarbons due to their destruction of the protective ozone layer surrounding earth. This paper focuses on refrigeration because it has one of the largest demands for HFCs (*4*). The general history (*5*) of refrigerants began with the use of ammonia as the heat transfer media in the refrigeration loop. Due to ammonia's toxicity, low molecular weight hydrocarbons were introduced. These species have negative aspects due to their high flammability. In the 1930s CFCs were synthesized and introduced, but the destruction of the ozone layer was discovered in the 1980s, leading to the regulation of CFCs. Hydrochlorofluorocarbons were briefly introduced before they were removed from consideration, also due to ozone depletion concerns. Hydrofluorocarbons are currently the main refrigerants as CFC stockpiles diminish without the possibility of new production.

An interesting question is: what are the major alternative chemicals if the U.S. regulates HFCs? Hydrofluoroethers are considered for almost the entire range of products and processes where HFCs are in use due to their physical and chemical similarities. Figure 1 shows a plot of the number of cumulative U.S. patents granted that involve the use of HFEs, illustrating that they are an emerging class of compounds. They are about to be widely implemented, but the possible total environmental consequences are unknown due to a lack of chemical and physical property data, which prevents analysis.

This paper quantifies the environmental impacts of refrigeration for R-12 (the CFC CCl_2F_2), which was used prior to the Montreal Protocol, R-134a (the HFC CH_2FCF_3), and an emerging HFE (CF_3OCH_3), which has properties appropriate for drop-in replacement from a temperature and vapor pressure perspective. A review of the literature shows only one other HFE (CF_3OCHF_2) with suitable properties for low temperature cooling applications, but calculations showed that the chemical is not feasible for technical reasons.

Prior work evaluated refrigerants for their environmental impacts. Bovea et al. (*6*) investigated HFCs and replacement materials with a cradle to end-of-use life cycle assessment. Their work showed trade-offs among different impact categories as different refrigerants are used. However, they did not compare direct to indirect GWP impacts. Jimenez-Gonzalez and Overcash (*7*) did similar analyses for other refrigerants from a historical perspective, but did not consider HFEs.

Methods

Refrigeration is discussed briefly to set the context of where direct and indirect greenhouse gas emissions are incurred. A refrigeration system involves a circulating working fluid called a coolant that removes heat from the refrigerator at low temperatures, vaporizing the fluid and absorbing energy. The vapor stream enters a compressor where the gas is pressurized, increasing the temperature. A secondary fluid, commonly water or air, is used to remove the heat from the refrigerant to form a saturated liquid stream at high pressure. The pressure is lowered to utilize the Joule−Thomson effect through partial vaporization, which drops the temperature to the point where the fluid can again be passed through the refrigerator. The compressor requires energy, which leads to off-site carbon dioxide emissions due to energy creation. Additional energy is required to either pump cooling water or to use a fan to move air, leading to additional indirect CO_2 emissions. There is also leakage of the refrigerant that results in direct CO_2-equivalent emissions.

Several starting assumptions set the scope of this work. We assumed the refrigerator delivered a 10 ton cooling duty as this is typical of small-scale industrial/commercial facilities (*8*), much like the duty required for the freezer section of a grocery store. The temperature of the refrigerator was assumed to be −17.7 °C as required by law for freezer applications (*9*). To minimize energy costs by avoiding vacuum conditions, we assumed the lowest pressure in the calculations to be atmospheric pressure.

Chemical engineering heuristics from Seider et al. (*10*) provided constraints on the system design. These constraints include an inlet cooling water temperature of 25 °C, a minimum temperature approach of 11.1 °C for above-ambient heat exchangers, a minimum temperature approach of 5.6 °C for cryogenic heat exchangers, and a maximum water release temperature of 48.9 °C. In this work, we did not include a water cooling tower with water recycle back to the cooling system but used a single-pass heat exchanger. We performed a pinch point analysis to avoid violating temperature approaches. We also assumed there was single-stage compression of the refrigerant even though pressure

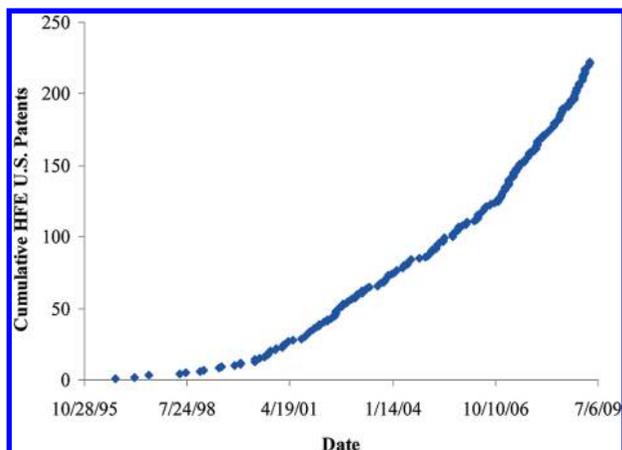* Corresponding author e-mail: blowers@email.arizona.edu.

FIGURE 1. Cumulative patents issued with "hydrofluoroether" as a keyword where the text supports that HFEs will be used industrially, since 1996 when the first one was issued.

TABLE 1. Summary of Physical Property Data of Refrigerants Compared in This Work[a]

property	R-12	R-134a	HFE-143 m
vapor C_p			
a	33.862(27)	18.667(28)	32.024(23)
b	0.1521	0.2652	0.2160
c	−0.00005	−0.001	−0.0001
liquid C_p			
a	100.28(29)	142.64(30)	233.06[b]
b	−0.1187	−0.3095	−1.0426
c	0.0006	0.0011	0.0026
vapor pressure			
a2	3.8111(27)	3.9992(31)	6.5113(32−34)
b2	782.072	782.0893	1083.288
c2	−37.773	−51.8311	−8.86048
liquid density (kg m^{-3})	1461[29]	1203(35)	1051(36)
ΔH_{vap}	23295	22202	21066
GWP (100 yr)	8500(37)	1600(37)	458(24)
ODP	1[37]	0	0

[a] Where $C_p = a + bT + cT^2$ (units are J mol^{-1} K^{-1} when T is in K), $\log_{10}P^* = a2 - b2/(T + c2)$ (P^* unit is bar when T is in K), ΔH_{vap} is in J mol^{-1} (all ΔH_{vap} from Clausius−Clapeyron equation from P^* data), GWP is in units of kg CO_2-equivalents (kg CO_2)$^{-1}$ at the 100 year time horizon, and ODP is the ozone depletion potential. [b] From corresponding states method (11) using gas-phase C_p data.

ratios were greater than suggested by heuristics. A compressor efficiency of 75% was assumed. The implications of these decisions on the analyses are explored later. We used standard chemical engineering equations and principles for calculating entropies, heat duties, work requirements, and Joule−Thomson cooling effects (11). Details are shown in the Supporting Information.

Carbon dioxide emissions were estimated for both direct and indirect contributions. For direct GWP contributions, we assumed a refrigerant leakage rate of 9%/year (8). We selected coal as the fuel source to evaluate indirect contributions due to the rapid growth of coal as a primary fuel for electricity generation. Coal produces 39% of electricity in the U.S. and is the dominant source of electricity worldwide (12). It should be noted that there are a range of values available in the literature for the emissions factor for CO_2 for electricity from coal. Schreiber, et al. (13), performed an LCA for coal-fired power plants in Germany and found CO_2 emissions to be 0.796 kg/kWh when they considered impacts due to materials procurement, coal supply, combustion, and some postcombustion treatment. It is unclear how they handled details about transport as this was not discussed in their paper. Odeh and Cockerill examined coal combustion for UK coal-fired power plants, including coal mining, transport, and power generation in their analyses and found emissions to be 0.957 kg/kWh (13) or 0.984 kg/kWh (14). Similar values were reported by Spath (15) for U.S. coal-fired plants and Hondo (16) for Japanese plants, with values of 1.042 and 0.975 kg/kWh, respectively. Meier, et al. (17), used an economic input−output LCA approach to estimate the total CO_2 emissions for coal plants as 1.044 kg/kWh. Koornneef, et al. (18), evaluated pulverized coal with and without carbon capture and sequestration with a cradle-to-grave LCA for coal facilities in The Netherlands and found that CO_2 emissions were 1.05 kg/kWh. Dinca, et al. (19), obtained similar numbers for generic European Union facilities with a value of 0.984 kg/kWh. Finally, Pacca and Horvath (20) estimated the emissions to be about 0.87 kg/kWh for a typical coal fired power plant in the U.S. With this range of values, we chose the values of Koornneef of 1.05 kg CO_2/kWh (14, 18) as it was based on the most complete life cycle analysis of coal-fired power plants. The amount of energy required to pump water from aquifers to the use-destination is 3000 kWh/10^6 L (21). Electricity transmission losses from power plant to use-destination are approximately 7.2% (22).

There was a lack of peer-reviewed and publicly available physical property data for the HFE so predictive tools were validated to obtain the missing information. Only three HFE heat capacities have been reported in the literature, and

CF_3OCH_3 was not among them. Computational chemistry and statistical thermodynamics were used to predict heat capacities for the existing HFE data points and were in close agreement with the measurements. The same approaches were used to predict the heat capacity of CF_3OCH_3 (23). Corresponding states equations estimated the liquid heat capacity from the gas-phase heat capacity functions. The same methods were applied to the R-12 and R-134a data and were accurate compared to experimental data. Heats of vaporization were computed from experimentally determined vapor pressure curves using the Clausius−Clapeyron equation. Radiative forcing was predicted using computational chemistry approaches (24−26) while experimentally based kinetic tropospheric degradation removal rates through reaction with hydroxyl radical attack were used to obtain the refrigerant global warming potential CO_2-equivalent.

Results and Discussion

Table 1 shows the physical property data used to evaluate the refrigerants in this work along with the sources of the information.

A series of other scenarios were considered using different assumptions. We investigated the use of an air-cooled condenser, multiple compressor stages with interstage cooling, water recycle through a cooling tower with evaporative losses, and varying operating conditions but the trends in the results did not change.

The refrigerant GWPs suggest that switching to the HFE would be desirable to prevent global climate change through greenhouse gas emissions. However, our results in Table 2 show the drop-in replacement HFE for R-134a is unfavorable from an overall use-to-disposal lifecycle perspective. Unfortunately, there is an increase of indirect emissions through both the increased compressor requirements and increased cooling water needs. The compressor significantly contributes to greenhouse gas emissions with between 69 and 72% of the electricity needs, which make up between 76 and 98% of the total CO_2-equivalents.

The primary reason that the HFE leads to larger compression needs is that the heat of vaporization of the HFE is the lowest among the refrigerants, resulting in the largest

TABLE 2. Comparison of the Results and Data That Highlight the Environmental Trade-Offs between CO_2-Equivalents Due to Direct and Indirect Impacts for Freezer Applications with 10 Tons of Cooling[a]

parameter	R-12	R-134a	HFE-143 m
refrigerant charge (kg)	128	149	169
T_{hot} (K)	356	345	345
P_{high} (atm)	14.06	15.96	14.25
V (percent vaporized in valve)	41	54	59
W_s, compressor (J s^{-1})	19,545	29,259	33,956
mass of water (g s^{-1})	625	802	897
electricity (kWh yr^{-1})			
compressor	171,214	256,309	297,455
water movement	59,130	75,895	84,879
transmission losses	17,872	25,774	29,664
total	248,216	357,978	411,997
GWP CO_2-equivalents			
direct	97,920	21,456	6966
indirect	260,627	375,877	432,597
total	358,547	397,933	439,563

[a] Where refrigerant charge is the mass of refrigerant needed to deliver 10 tons of cooling, T_{hot} and P_{high} are the conditions after compression, V is the fraction of refrigerant vaporized to provide Joule−Thomson cooling across the valve, and W_s is the work required.
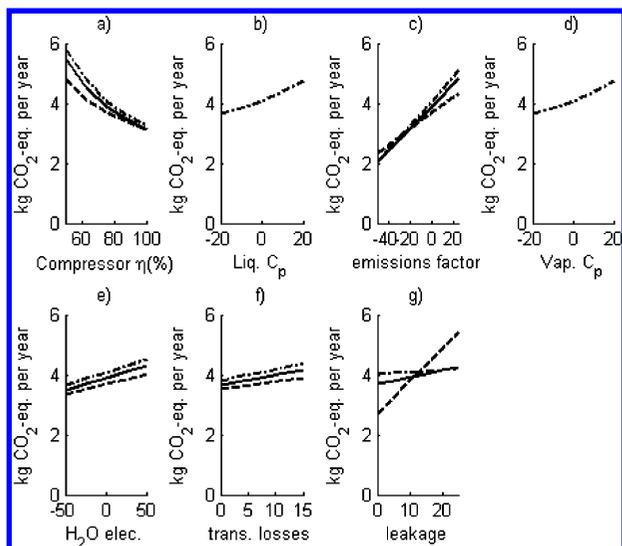

FIGURE 2. Sensitivity analyses results where annual CO_2 emissions equivalents are shown as key parameters are varied. The solid line represents the current HFC (R-134a), the dashed line represents the phased out CFC (R-12), and the dash-dot line represents the likely HFE replacement (CF_3OCH_3). Indirect and direct emissions have been summed together in these plots and the y-axes are in 10^5 kg/year. Panel (a) has the compressor efficiency on the x-axis, panel (f) has the percent electricity losses during transmission of electricity, while all other panels (b−e, g) have a percent change in the respective parameter on the x-axes.

vaporization fraction across the valve due to the Joule−Thomson effect. This leads to a larger required mass of refrigerant that must be transported throughout the refrigeration loop, which increases the overall work duty of the compressor. In fact, the work per mole is lower for the HFE but the need for higher flow rates to meet the cooling requirements leads to higher electricity usage.

Sensitivity analyses were performed to investigate whether trends in CO_2 emissions would change as parameters were varied and the results are shown in Figure 2. The figures are shown in the order of largest variation in emissions to lowest variations. Figure 2a shows how total CO_2-equiv. emissions vary with the compressor efficiency. Compressor efficiencies are typically around 75%, but one can see that emissions would become very similar for the three chemicals if a compressor efficiency of 100% could be obtained. The emissions vary because of the dependence of the work requirement on the efficiency, which also changes the compressor outlet temperature which then changes the water required for cooling, leading to additional changes in electricity needs.

Figure 2b shows how the results change as the liquid HFE heat capacity is varied. In the absence of experimental liquid C_p data for the HFE, the values used in this work were based on corresponding states equations. The equations were validated for the other two refrigerants but the HFE heat capacity may not follow the same trends. If the heat capacity of the liquid were lower, less of the refrigerant would vaporize across the valve, which would lead to reduced refrigerant charge and thus lead to reduced electricity needs for both the compressor and cooling water. A comparison of the results at the lowest point on Figure 2b compared to the basecase analyses shows that the HFE would perform slightly better than the HFC. However, errors using the corresponding states equations compared to experimental data for R-12 and R-134a were less than 2%.

As discussed earlier, the results are sensitive to the value used to evaluate the CO_2-equiv emissions assumed per kWh for power generation. One can see in Figure 2c that the HFE and HFC have equal emissions if the emissions factor was 50% of our assumed value. This indicates that HFEs would be desired in some regions of the world where renewable or nuclear power sources are prevalent. In regions where coal is predominant, the current HFC is more desirable from a CO_2-equiv emissions perspective. Results like these suggest that CO_2 emissions reduction scenarios may be different in different regions of the world, which may lead to different regulatory options.

Figure 2d shows how results would vary for the HFE if the predicted gas-phase heat capacity were different from that used based on our prior work (23). If the predicted heat capacity were lower, impacts would be lower due to both the reduced energy requirement and the reduced material flow that would occur due to the lower liquid phase heat capacity, as discussed earlier. Emissions of CO_2-equiv would be slightly lower than the HFC basecase if the heat capacity were overestimated by 20%. However, our prior computations (23) showed that our error in heat capacity for similar species was only about 3%, so this parameter is unlikely to change the results.

Electricity needs for water preparation and delivery were available in only one reference obtained in the peer reviewed literature so this is an important parameter to investigate and the results are shown in Figure 2e. The figure shows that varying the electricity needed for water does not impact the trends in the results. This is very similar to the results shown in Figure 2f for transmissions losses across the energy grid.

Figure 2g shows how the leakage rate of the refrigerant, due to fugitive emissions or losses during maintenance, affects the results. The current HFC would become less attractive as leakage rates become larger due to the direct CO_2-equiv for the higher GWP refrigerant. One can see that R-12, the phased out CFC, would require even less emissions to become the least attractive refrigerant regarding CO_2-equiv emissions.

Taking into account the U.S. EPA's imminent regulation of HFCs, the results show that consideration of only the direct GWP contribution for refrigerants would lead to an incorrect prediction that global climate change would be curtailed if HFEs are used as the replacement refrigerants unless indirect emissions from electricity were less than half the values

assumed in this work. HFEs are specifically excluded from the current U.S. EPA considerations because their total global radiative forcings are unknown. However, the results here show that the total CO_2-equiv released per year increases when the HFE is used versus the HFC. In contrast, the Montreal Protocol had a significant positive environmental impact by eliminating the ozone-depleting R-12 from use over time, even though the CO_2 emissions increased moderately as the HFC replacement was introduced. Future changes in energy sources will change these results but they are robust under the current worldwide energy generation scenario.

Supporting Information Available

Figures, extensive engineering calculations, expanded justification of correlative methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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