

THE NEXT GENERATION OF REFRIGERANTS

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ABSTRACT

This paper reviews the progression of refrigerants, from early uses to the present, and then addresses future directions and candidates. The paper breaks the history into four refrigerant generations based on defining selection criteria. It discusses displacement of earlier working fluids, with successive criteria, and how interest in some early refrigerants re-emerged, for example renewed interest in those now identified as “natural refrigerants.” The paper examines the outlook for current options in the contexts of existing international agreements, including the Montreal and Kyoto Protocols to avert stratospheric ozone depletion and global climate change, respectively. It also examines other environmental concerns and further international and local control measures. The paper illustrates how isolated attention to individual environmental issues or regulatory requirements, in contrast to coordinated responses to the several issues together, can result in unintended environmental harm that almost certainly will require future reversals.

1. REFRIGERANT PROGRESSION

Natural refrigeration goes back to ancient times, using stored ice, vaporization of water, and other evaporative processes. Numerous investigators in different countries studied phase-change physics in the 1600s and 1700s; their fundamental findings set the foundation for “artificial” (man-made) refrigeration. Oliver Evans first proposed the use of a volatile fluid in a closed cycle to freeze water into ice (Evans, 1805). He described a system that produced refrigeration by evaporating ether under a vacuum, and then pumped the vapor to a water-cooled heat exchanger to condense for re-use. While there is no record that he built a working machine, his ideas probably influenced both Jacob Perkins and Richard Trevithick. The latter proposed an air-cycle system for refrigeration in 1828, but again did not build one. Perkins, however, did so with his invention of the vapor-compression machine in the 1830s, and thus introduced actual refrigerants, as we know them. His patent describes a cycle using a “volatile fluid for the purpose of producing the cooling and freezing ... and yet at the same time condensing such volatile fluids, and bringing them into operation without waste” (Perkins, 1834). Many refrigeration experts recognize his landmark contribution with identification of this mechanical vapor-compression approach as the Perkins Cycle. Although designed to use *sulfuric* (ethyl) ether as the refrigerant, the first tests actually used *caoutchoucine*, an industrial solvent that Perkins used and therefore had available in his business as a printer.

Figure 1 depicts the progression of refrigerants from their advent through four generations.

1.1. First Generation — Whatever Worked

The most common refrigerants for the first hundred years were familiar solvents and other volatile fluids; they constituted the *first generation* of refrigerants, effectively including whatever worked and was available. Nearly all of these early refrigerants were flammable, toxic, or both, and some were also highly reactive.

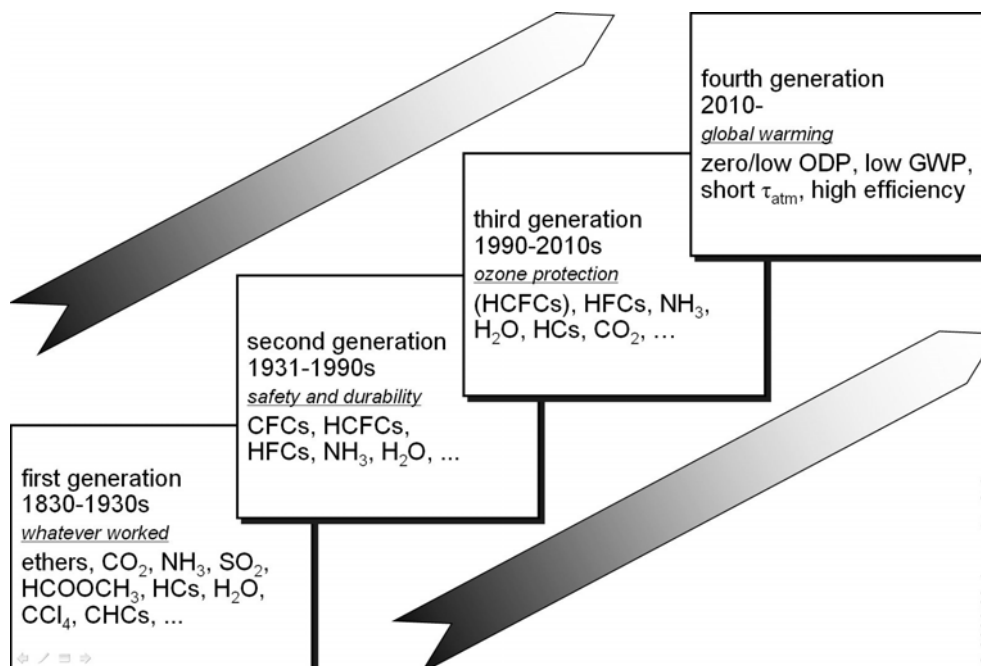


Figure 1. Refrigerant Progression

Accidents were common. For perspective, a number of companies marketed propane (R-290) as the “odorless safety refrigerant” in promoting it over ammonia (R-717) (CLPC, 1922). A telling, historic advertisement claimed that propane “is a neutral chemical, consequently no corrosive action occurs” and “is neither deleterious nor obnoxious and should occasion require, the engineer can work in its vapor without inconvenience” (CLPC, 1922). Continued preference, even today, of ammonia over hydrocarbons in industrial applications suggests that high flammability was and remains a greater concern in large systems.

The first documented, systematic search for a refrigerant offering a practical design with improved performance came in the 1920s, with examination of refrigerants for chillers (Carrier and Waterfill, 1924). Willis H. Carrier, known for his advances in psychrometrics and air conditioning, and R. W. Waterfill investigated a range of candidate refrigerants for suitability in positive displacement and centrifugal compression machines with focus on developing the latter. They concluded (without analysis of trans-critical cycles) that the performance of carbon dioxide (R-744) would depend on the cycle and amount of liquid subcooling, but that it yielded the lowest predicted performance of the fluids analyzed. They also noted that ammonia and water (R-718) would require excessive stages for centrifugal compressors for the conditions sought, and that water “gives a low efficiency of performance.” They rejected sulfur dioxide (R-764) for safety reasons and carbon tetrachloride (R-10) for incompatibility with metals, especially in the presence of water. They finally selected *dielene* (1,2-dichloroethene, R-1130) for the first centrifugal machine, though this selection then required an international search to find a source (Ingels, 1952).

1.2. Second Generation — Safety and Durability

The *second generation* was distinguished by a shift to fluorochemicals for safety and durability. Repeated leaks, of then prevalent methyl formate (R-611) and sulfur dioxide (R-764), retarded early efforts to market domestic refrigerators to replace iceboxes. With direction that “the refrigeration industry needs a new refrigerant if they expect to get anywhere,” Thomas Midgley, Jr., and his associates Albert L. Henne and Robert R. McNary, first scoured property tables to find chemicals with the desired boiling point. They

restricted the search to those known to be stable, but neither toxic nor flammable. The published boiling point for *carbon tetrafluoride* (R-14) drew attention to the organic fluorides, but they correctly suspected the actual boiling temperature to be lower than published. Turning to the periodic table of elements, Midgley quickly eliminated those yielding insufficient volatility. He then eliminated those resulting in unstable and toxic compounds as well as the inert gases, based on their low boiling points. Just eight elements remained, namely carbon, nitrogen, oxygen, sulfur, hydrogen, fluorine, chlorine, and bromine (Midgley, 1937). Within three days of starting, in 1928, Midgley and his colleagues made critical observations regarding flammability and toxicity of compounds consisting of these elements. They also noted that every known refrigerant at the time combined just seven of these elements — all but fluorine. The first publication on fluorochemical refrigerants shows how variation of the chlorination and fluorination of hydrocarbons influences boiling points, flammability, and toxicity (Midgley, 1930).

Commercial production of R-12 began in 1931 followed by R-11 in 1932 (Downing, 1966 and 1984). Chlorofluorocarbons (CFCs) and later — especially starting in the 1950s in residential and small commercial air conditioners and heat pumps — hydrochlorofluorocarbons (HCFCs) dominated the second generation of refrigerants. Ammonia continued as, and remains today, the most popular refrigerant in large, industrial-scale systems especially for food and beverage processing and storage.

1.3. Third Generation — Ozone Protection

Linkage of released CFCs —including CFC refrigerants — to depletion of protective ozone catalyzed the *third generation* with focus on stratospheric ozone protection. The Vienna Convention and resulting Montreal Protocol forced abandonment of ozone-depleting substances (ODSs). Fluorochemicals retained the primary focus, with emphasis on HCFCs for interim (transitional) use and hydrofluorocarbons (HFCs) for the longer term. The shifts sparked renewed interest in “natural refrigerants” — particularly ammonia, carbon dioxide, hydrocarbons, and water — along with expanded use of absorption and other *not-in-kind* (those not using vapor-compression systems with fluorochemical refrigerants) approaches. Public and private research programs systematically examined both additional non-fluorochemical and hydrofluoroether (HFE) candidates, but yielded few promising options.

Manufacturers commercialized the first alternative refrigerants in late 1989 and, within 10 years, introduced replacements for most ozone-depleting refrigerants. Non-Article 5 (mostly-developed) countries phased out CFC refrigerant use in new equipment by 1996, as required by the Montreal Protocol. Article 5 countries will do so by 2010. The “Article 5” distinction relates to the level of prior usage of ozone-depleting substances as defined in the Protocol. Except as restricted by national regulations, continued use and service is allowed for existing equipment employing CFC refrigerants until otherwise retired.

The transition from HCFCs also is underway. The Montreal Protocol limits production of HCFCs in steps in 1996, 2004, 2010, 2015, and 2020 with full production phaseout by 2030 in non-Article 5 countries and imposes a freeze starting in 2016 and cessation of production by 2040 in Article 5 countries. Individual countries adopted different response approaches. Most western- and central-European countries accelerated HCFC phase outs, while the majority of other developed countries set limits by phasing out propellant and blowing agent (especially R-141b) uses early, requiring phaseout of R-22 (the most widely used refrigerant today) by 2010 in new equipment, and then banning all HCFC use in new equipment by 2020. The schedule for Article 5 countries begins with a freeze in 2016 and ends with phaseout by 2040. Again, continued future use and service is allowed for existing equipment employing HCFC refrigerants until

otherwise retired except as restricted by national regulations. Although discussed herein as *production*, the Montreal Protocol actually regulates *consumption*, which it defines as production plus imports less exports and specified destruction. As a result, exports from Article 5 countries into non-Article 5 countries are effectively restricted to meet the more stringent non-Article 5 schedules. To avoid separate domestic and export products and to exploit newer technologies derived from joint ventures and licensing agreements, some products in Article 5 countries incorporate replacements earlier than required.

Three points warrant notice. First, refrigerants historically constituted only a minor fraction of total ODS emissions, but most of the same CFCs and some of the HCFCs in common use as refrigerants also were used in much more emissive applications, including as aerosol propellants, foam blowing agents, and solvents. Second and at least comparable in importance to the refrigerant replacements, the environmental concerns prompted major changes in design, manufacturing, installation, service, and ultimate disposal procedures to reduce avoidable refrigerant emissions (Calm, 2002). Third, the ozone layer is recovering despite episodic reports of record ozone holes in the Antarctic. The size of the annual Antarctic hole results from variable factors such as southern polar winds and oscillations, which induce the polar vortex, and winter temperature severities that regulate the efficiencies of ozone destruction and natural replenishment. International scientific assessments document that both new ODS releases and residual prior emissions are declining (WMO, 2006). Scientists interpret the minimum ozone concentration and minimum ozone area trends depicted in Figure 2 as indicating stabilization in recent years and the start of recovery, since both measures reached their worst levels in 1998. The progress in ozone recovery is even more evident when measured by global mean ozone rather than ozone in the isolated Antarctic vortex.

While increasing ODS emissions could exacerbate ozone depletion and prolong or preclude recovery, opportunities to accelerate ozone layer recovery significantly are much more limited, especially considering the huge influence of previously released CFCs, halons, and other ODSs having long atmospheric lifetimes. This point suggests focal consideration of atmospheric lifetime (τ_{atm}) in selection of alternatives, to avoid a repetition of atmospheric buildup before discovery of new concerns that may arise in the future.

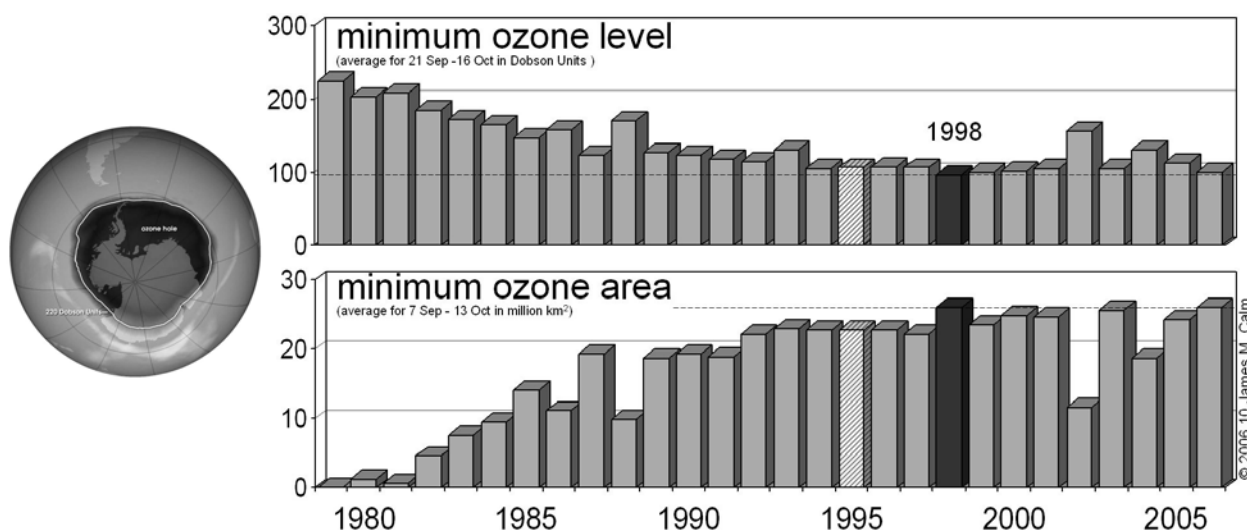


Figure 2. Severity of the Ozone Hole based on NASA data (Newman, 2006): Ozone levels declined and the “ozone hole” (area with a level less than 220 Dobson units) grew until 1998. Both the minimum ozone level and area reflect stabilization or improvement since 1998, but with annual variability (most noticeably in 2002). An orbiting instrument failure precluded measurements for 1995.

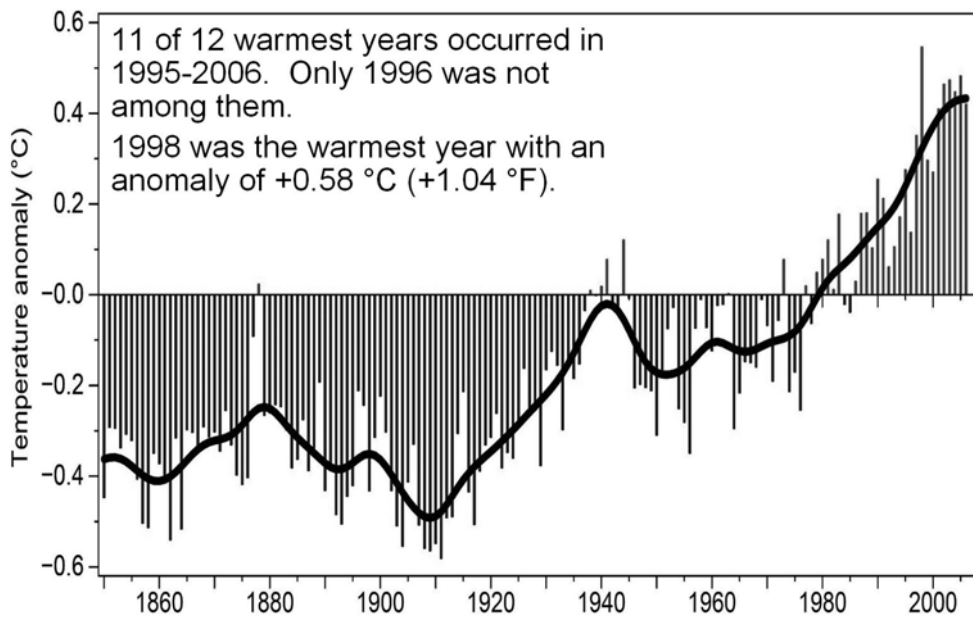


Figure 3. Global Temperature Rise (based on Brohan et al., 2006, and Rayner et al., 2006): Analyses of tree rings, coral reefs, ice cores, and other proxy indicators show the 1990s to be the warmest decade in the last millennium and the 20th century to be its warmest century.

1.4. Fourth Generation — *Global Warming*

The very successful response to ozone depletion stands in sharp contrast to the deteriorating situation with climate change, as depicted in Figure 3. New findings and political debate of global warming have become daily events, especially in recent months. The Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4) reflects the latest scientific consensus, namely that “warming of the climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global average sea level” (IPCC, 2007). The assessment concluded that “most of the observed increase in globally averaged temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations” and that “discernible human influences now extend to other aspects of climate, including ocean warming, continental-average temperatures, temperature extremes and wind patterns” (IPCC 2007).

The Kyoto Protocol, pursuant to the international Framework Convention on Climate Change, sets binding targets for greenhouse gas (GHG) emissions based on calculated equivalents of carbon dioxide, methane, nitrous oxide, HFCs, perfluorocarbons (PFCs), and sulfur hexafluoride. It does not address ODSs covered by the Montreal Protocol, although some also are very potent GHGs. National laws and regulations to implement the Kyoto Protocol differ, but they typically prohibit avoidable releases of HFC and PFC refrigerants and in some countries also control or tax their use. More recent measures (either adopted or proposed) at regional, national, state, and municipal levels are more stringent. These restrictions are forcing shifts to a *fourth generation* of refrigerants defined by attention to global warming.

The European Parliament set the timing with a directive that bans fluorochemical (“F-gas”) refrigerants having GWPs exceeding 150 in air conditioners for new model automobiles effective 2011 and for all new automobiles starting in 2017. The adopted regulations also require periodic inspection of stationary systems using HFCs. The EU Parliament rejected recommended measures that would have banned HFCs as aerosol propellants by 2006, as foam blowing agents by 2009, and as refrigerants in stationary air

conditioners and refrigeration by 2010. The contentious vote on the last item was 262-368, more than 40% in favor. This significant support level invites future reconsideration, especially with recent scientific findings regarding more rapid and more severe onset of climate change. The immediate effect of these measures is a ban on R-134a in its largest and, as a refrigerant, its most emissive application — mobile air conditioners. The adopted GWP limit intentionally allows consideration of low GWP HFCs (notably R-152a even though flammable). The *F-gas* measures also sanction more-stringent national regulations, some of which prohibit HFCs in large systems, explicitly ban HFC use in chillers, or impose GWP-weighted excise taxes on HFC refrigerants. Unions in Europe are pushing for adoption of more stringent measures to curb greenhouse gas emissions. A number of states and cities in the USA have proposed restrictions on GHG emissions, either individually or regionally, though the specific impacts on individual HFCs is uncertain. A frequent bellwether state and the one with the largest population, California passed new legislation in late 2006 imposing a first-in-the-nation emissions cap on utilities, refineries and manufacturing plants, with a goal of cutting greenhouse gas emissions back to 1990 levels by 2020. The law requires the state regulatory body to determine actual requirements, likely to include measures for refrigeration systems and automobile air conditioners. At least eight other states are prone to follow California's lead if it does regulate HFC uses or emissions. A number of Northeastern and Mid-Atlantic states joined in a pact in 2007 to impose caps on power plant emissions and encourage trading of allowances among utilities and the Governors of five states agreed in 2007 to the Western Regional Climate Action Initiative with similar goals.

2. NEXT GENERATION OF REFRIGERANTS

Refrigerant manufacturers quickly responded to the F-Gas directive with announcements of new refrigerants. At least three multinational manufacturers of refrigerants reported proprietary development of innovative refrigerants to meet the GWP limit of 150 (DuPont, 2006; Honeywell, 2006; and INEOS Fluor, 2006). Considering the very large market value of automotive refrigerant sales, it is safe to assume that most refrigerant companies are seeking solutions, especially now that some of the largest companies are on record as expecting to meet the F-Gas mandates. Contacts with representative companies confirm this expectation.

These companies have released preliminary environmental, safety, and performance data, but they are restricting full disclosure of the refrigerant compositions for competitive reasons because final formulations still are being honed and because full data do not exist yet. Some of the underlying patents afford insight into the substances considered, either individually or as blend components (for example Singh et al., 2005, and Minor et al., 2006). Table 1 expands this information with the author's perceptions on candidate components for the next-generation refrigerants. The patents suggest that some candidates and uses may require compatibilizers (such as anti-foam additives or metal-surface deactivators), stabilizers (such as oxidation inhibitors), lubricant solubizers, or other additives.

Some if not all of the manufacturers anticipate that the solutions or variants of the solutions identified to satisfy the F-Gas requirements will have broader application potential. DuPont (2006), Minor et al. (2006), and Singh et al. (2005) specifically identify wider application opportunities, both for refrigerants in stationary air conditioning and refrigeration systems and for foam blowing agent and fire suppression applications. The perceived ease — without apparent compromise in safety, durability, or efficiency — masked enormous investments to develop the third generation refrigerants and associated lubricants, optimize and build manufacturing plants, modify and qualify component (especially compressor) and equipment designs, and train installing, operating, and servicing technicians. The rapid and strongly

Table 1. Candidates Components

candidates	considerations
“natural refrigerants” (NH ₃ , CO ₂ , HCs, H ₂ O, air)	efficiency, for NH ₃ and HCs also flammability
low GWP HFCs (R-32, R-152a, R-161, ...)	flammability; most suppressants have high GWP
HFES	disappointing thus far, still ?
HCs, HEs (R-290, R-600, R-E170, ...)	flammability
unsaturates (olefins) (R-1234yf, ...)	short atmospheric lifetime and therefore low GWP flammability? toxicity? compatibility?
HFICs, FICs (R-311I (CH ₂ FI), R-131I (CF ₃ I), ...)	expensive, ODP>0 but not in MP some are toxic; compatibility?
fluorinated alcohols (-OH) fluorinated ketones (-C=O-)	efficiency? flammability? toxicity? compatibility?
others	??? — <u>no ideal refrigerants</u>

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optimistic responses to the F-Gas GWP limit for automotive refrigerants — the start of the next generation — sends a signal to regulators that refrigerant options exist to meet more sustainable environmental goals than embodied in the current Montreal and Kyoto Protocols.

However, four very important points warrant consideration. First, manufacturers previously had examined and even conducted limited tests of key replacement refrigerants. Records specifically document tests of non-ODS refrigerants to replace CFCs, for example use of R-134a in domestic refrigerators, more than ten years before the Montreal Protocol (Dupont, 1988). Except as blend components (such as R-152a in R-500 and R-23 in R-503), the industry avoided HFC refrigerants based on lubricant considerations prior to ODS phaseout, though recognized as candidates as early as 1928. Second, the replacement refrigerants generally are less efficient than earlier choices. With a few exceptions, the efficiency gains achieved in machinery using the alternative refrigerants derive primarily from improvements in equipment design rather than the properties of newer working fluids. Simply put, better optimization with the old refrigerants would have yielded even higher efficiency in most cases, and the alternative refrigerants reduce margins for further product efficiency improvement. Third, none of the current or candidate refrigerants is ideal, and future discovery of ideal refrigerants is extremely unlikely (Calm and Didion, 1997). The intensifying constraints force new compromises among different environmental, safety, performance, cost, and other goals; they do not expand the finite options available. And fourth, sequential attention to individual environmental issues risks elimination of important or even critical options, for balanced overall solutions, based on minor or even negligible impact on single issues (Wuebbles and Calm, 1997).

3. BALANCE AMONG DIFFERENT ENVIRONMENTAL GOALS

The new refrigerants raise interesting questions on the balance between conflicting environmental targets and between environmental goals and safety or compatibility. ODS phase-outs reduce options to address climate change either from direct consequences or from indirect consequences such as energy-related emissions. Two examples are conflicting goals for R-131I (CF₃I, a fluoro-iodocarbon, FIC) as a potential

component in low-GWP automotive refrigerants (Singh et al., 2005) and R-123 (an HCFC) as a chiller refrigerant (Calm, 2006). These two refrigerants both offer short atmospheric lifetime, very low GWP, low acute inhalation toxicity, and non-flammability; both are effective fire suppressants. However, both have very low, but non-zero ODP — 0.011-0.018 (modeled) depending on the latitude and altitude of release for R-131I and 0.02 semi-empirical (0.012 modeled) for R-123.* R-131I offers potential as a blend component in combination with fluorinated olefins (unsaturated alkenes) to suppress their flammability while minimizing both ODP and GWP. Despite being an ODS, albeit with very low ODP, R-131I is not controlled by the Montreal Protocol since it was not in commercial use in 1992, the last time substances were added to the Protocol. R-123 is the most efficient refrigerant for water chillers other than R-11 and R-141b (UNEP, 2007a), both of which have significantly higher ODP and higher GWP. Still, R-123 already was phased out in Europe as an ODS and is scheduled, barring reconsideration, for similar phaseout in new chillers by 2020 in non-Article 5 countries and by 2040 in Article 5 countries. R-123 has a very low overall impact on the environment because of its low ODP, very low GWP, very short atmospheric lifetime, very low emissions in current chiller designs, and efficiency (UNEP, 2007a). The Montreal Protocol allows limited production for service needs until 2030 in non-Article 5 countries. It imposes no limit anywhere for continued use and service of existing equipment or stockpiled or recovered refrigerant. These examples illustrate clear conflicts in environmental objectives to address ozone depletion and climate change. At least one recent assessment suggests reconsideration of earlier proposals regarding phasing out all ODSs. It indicates that “production and consumption of specific chemicals proved to be harmless to the ozone layer could be permitted after the assessment through an adjustment of the Protocol” (UNEP, 2007b).

Comparing Figure 2 and Figure 3, as well as the options to address and consequences of stratospheric ozone depletion and climate change, suggests both much greater difficulty and more urgency for global warming mitigation. These comparisons challenge rote elimination of the few options having insignificant or even indiscernible influence on stratospheric ozone but significant, or even strong, potential to mitigate global climate change. Both environmental issues are important, but the absence of ideal candidates that solve both concerns jointly, without degrading safety, requires balance among objectives. Although speculative, the framers of the Montreal Protocol probably would have exercised more care in broad elimination of chemicals by class, rather than by individual determination, had there been current awareness of the severity of global warming and recognition of response limitations at the time. Nevertheless, the Protocol provided for future adjustments based on scientific assessments, which offers an option — albeit a difficult one politically — for revisions to address the few but significant cases of this type.

Other issues arise in environmental trade-offs. The primary replacement selected by manufacturers for R-22, currently the most widely used refrigerant, is R-410A (a blend of HFCs R-32 and R-125). While this substitute offers practically zero ODP, it increases the GWP by 16% (from 1810 to 2100 for 100-yr integration) and lowers the attainable efficiency for conventional air conditioners with simple cycles by 6% (Calm and Domanski, 2004). Product refinements enable matching or even improvement of efficiencies at standard rating conditions, especially with exploitation of the blend’s superior heat transfer, but the ultimate opportunity for future performance improvement is lower. In addition, the efficiency of R-410A degrades more rapidly than that of R-22 at increasing ambient temperatures approaching the R-125 critical temperature, so the peak power demand is higher with R-410A for air-cooled systems for the same rated seasonal efficiencies. That drawback is especially significant for consideration of expensive but more sustainable electricity generation. Also, R-32 and some other R-32 blends, although marginally flammable, avoid this concern, and offer both higher efficiencies and lower GWPs (Calm and Domanski, 2004).

Fluoro-olefins, such as those under consideration as low GWP automotive refrigerants, generally are more reactive than compounds with only single carbon-carbon bonds. This reactivity leads to shorter atmospheric lifetime, lower ODP (for those containing chlorine, bromine, or iodine), and lower GWP, but also to decreased stability and higher toxicity. Likewise, chemicals with the lowest GWPs tend to decompose near the surface, often predominantly in proximity to the location of release. Some may be smog progenitors, and others may decompose or contribute directly or catalytically to formation of other chemicals with higher GWPs than the original chemical, hence presenting higher indirect than direct GWP. The indirect GWPs for most small hydrocarbon alkanes and olefins (alkenes) exceed their direct GWPs, and the influences of temperature, latitude, altitude, and even presence of other atmospheric pollutants complicate determination of net GWPs for them. Resolution of such complications is beyond the focus of this paper. The issue is raised only to illustrate the complex interactions and unavoidable trade-offs (compromises) among environmental goals even beyond consideration of ozone depletion and global warming or between the refrigerant-related (“direct effect”) and energy-related (sometimes identified as “indirect effect,” not the same as indirect GWP) emission impacts.

4. CONCLUSIONS

Driven by scientific findings, regulatory requirements, and market pressures, a fourth generation of refrigerants appears imminent, with almost certain introduction by 2010. The governing selection criteria for the new generation will add low GWP — initially 150 or less (determined for 100-yr integration) — to old requirements for suitability, safety, and materials compatibility. With recognition of potential for additional environmental concerns and implicit for fluorochemicals meeting new GWP limits, short atmospheric lifetime should also be a criterion. Most importantly, the new generation must offer high efficiency or the change to address low-GWP will backfire with increased rather than decreased net GHG emissions. While the current regulatory pressures address mobile air conditioners, future extension to other applications is almost certain. Many refrigerants currently viewed as new alternatives, including many HFCs, could become old rejects. Given the scarcity of viable options, future refrigerant selections warrant collective consideration of all environmental issues together, with integrated assessments, rather than piecemeal treatments that risk elimination of good overall options for minor or even indiscernible impacts for individual issues.

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