

# Options for Low-GWP Refrigerants in Small Air-Conditioning Systems<sup>†</sup>

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## Abstract

We summarize a systematic examination of possible low-GWP (global warming potential) replacements for the HFC (hydrofluorocarbon) refrigerants currently used in small air-conditioning systems. The methodology identified the optimal thermodynamic parameters for a refrigerant; this was based on an ideal-cycle analysis, which indicated a tradeoff between efficiency (COP) and refrigeration capacity depending largely on the refrigerant critical temperature. A more realistic analysis, which included an optimization of the heat exchangers, however, revealed that there was a maximum in COP at a relatively high refrigeration capacity, corresponding to refrigerants with a relatively low critical temperature and operating at moderately high pressures. A search in an exhaustive chemical database for fluids having the identified thermodynamic parameters as well as acceptable chemical stability, toxicity, and GWP identified a list of 29 candidate refrigerants. But none of these are a direct, nonflammable, low-GWP replacement for the R-410A currently used in the majority of small air-conditioning systems.

## Introduction

The Kigali Amendment to the Montreal Protocol, which phases down the production and consumption of hydrofluorocarbon (HFC) refrigerants, entered into force January 1, 2019. But even before this milestone was reached numerous regional and national regulations concerning the use of HFCs were already in place. For example, the “F-gas” regulations in the European Union<sup>1</sup> mandate maximum values of GWP (global warming potential) for refrigerants in various applications, as well as specifying training and reporting requirements. In the United States, the Significant New Alternatives Program (SNAP) of the U.S. Environmental Protection Agency<sup>2</sup> prohibits or allows specific refrigerants in various applications. The need to identify alternative fluids is obvious.

This paper starts with a brief perspective on the environmental impacts of the HFCs and other refrigerants. The main discussion considers options for low-GWP fluids. First, the methodology of our search for replacement fluids is summarized, and the resulting candidate fluids are presented. Some of the limitations and tradeoffs inherent with replacement fluids are discussed. Finally, brief conclusions are presented. Much of the present paper is drawn directly from our previous works<sup>3,4,5,6,7,8,9,10,11</sup>, and the reader is referred to those references for complete details.

## Background—Environmental Properties of Refrigerants

Emissions of HFCs currently account for only a small fraction of anthropogenic climate change—about 1 % of the total radiative forcing due to all greenhouse gases, including CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, according to the 2018 Scientific Assessment of Ozone Depletion.<sup>12</sup> The Kigali Amendment and other regulations are driven by estimated large increases in future emissions predicted under “business as usual” scenarios as laid out by Velders *et al.*<sup>13,14</sup> With the HFC phasedown of the Kigali Amendment, Velders<sup>15</sup> estimates that the surface temperature increase from HFCs will be limited to 0.06 K by the end of the century compared to (0.3 to 0.5) K with “business as usual.”

The environmental characteristics of selected refrigerants, as compiled by the WMO,<sup>12</sup> are listed in Table 1. The GWP parameter was first presented by the Intergovernmental Panel on Climate Change<sup>16</sup> in 1990 as a simple

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metric for comparing the impact of different gases on the climate system. The GWP of a gas is relative to that of carbon dioxide; furthermore, it is calculated over some time interval, or “time horizon.” A time horizon of 100 years is most commonly used (including in regulations) and is referred to as GWP<sub>100</sub>. Other time horizons are sometimes used, and Table 1 also lists the GWP<sub>20</sub>—the value for a 20-year time horizon. For long-lived gases, such as R-12, the GWP<sub>100</sub> and GWP<sub>20</sub> are similar. For gases with lifetimes on the order of a few decades or less (*e.g.*, the HFCs), however, the GWP<sub>20</sub> is substantially higher than the GWP<sub>100</sub> because the climate impact of such gases is concentrated in the initial years following their release into the atmosphere. When calculating over a longer time horizon, the impact in the later years is small, and the GWP<sub>100</sub> basically “averages out” the impacts. This indicates that the short-term climate impact of the HFCs can be understated by their GWP<sub>100</sub>. But this also underlies an opportunity for a positive impact on the climate by mid-century by phasing down the HFCs: CO<sub>2</sub> is long-lived in the atmosphere, and so the benefits of any reduction in its emissions are damped by its existing concentration in the atmosphere. A phase-down of HFC emissions, on the other hand, has much more immediate benefits.

**Table 1. Environmental characteristics of selected refrigerants.<sup>†</sup>**

R-number	Formula	$T_{\text{NBP}}$ (°C)	Lifetime (years)	ODP	GWP <sub>20</sub>	GWP <sub>100</sub>
<b>CFCs and HCFCs</b>						
R-12	CCl <sub>2</sub> F <sub>2</sub>	−29.8	102	0.73–0.81	10800	10300
R-22	CHClF <sub>2</sub>	−40.8	11.9	0.024–0.034	5310	1780
R-123	CHCl <sub>2</sub> CF <sub>3</sub>	27.8	1.3	0.01	290	80
<b>HFCs</b>						
R-32	CH <sub>2</sub> F <sub>2</sub>	−51.7	5.4	0	2530	705
R-125	CHF <sub>2</sub> CF <sub>3</sub>	−48.1	30	0	6280	3450
R-134a	CH <sub>2</sub> FCF <sub>3</sub>	−26.1	14	0	3810	1360
R-152a	CH <sub>3</sub> CHF <sub>2</sub>	−24.0	1.6	0	545	148
<b>HFOs and HCFOs</b>						
R-1233zd(E)	CF <sub>3</sub> CH=CHCl	18.3	0.071	<0.0004	13.5	3.7
R-1234yf	CF <sub>3</sub> CF=CH <sub>2</sub>	−29.5	0.029	0	1	<1
R-1234ze(E)	CF <sub>3</sub> CH=CFH	−19.0	0.045	0	4	<1
<b>Natural fluids</b>						
R-290	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> (propane)	−42.1	0.041	0	<1	<1
R-717	NH <sub>3</sub> (ammonia)	−33.3	“few days”	0	<1	<1
R-744	CO <sub>2</sub> (carbon dioxide)	−56.6 <sup>‡</sup>	–	0	1.00	1.00

<sup>†</sup>Environmental data from WMO<sup>12</sup>;  $T_{\text{NBP}}$  from REFPROP<sup>17</sup>; table from ref<sup>10</sup>.

<sup>‡</sup>Triple-point temperature

While the many of the HFCs do have high values of GWP it must be kept in mind that they were developed and implemented to replace substances with high ozone-depletion potential (ODP), the so-called ozone-depleting substances or ODSs, primarily the CFCs and HCFCs. Many of the CFCs and HCFCs also have high values of GWP (see Table 1); for example, the GWP<sub>100</sub> of the most common refrigerant in automotive systems was reduced by a factor of 7.5 (10300 to 1360) when R-12 was replaced with R-134a. Thus, the Montreal Protocol, which was originally targeted at stratospheric ozone protection, has already had a tremendously positive effect on climate, as reported by Velders *et al.*<sup>18</sup> In that analysis, Velders *et al.* consider a scenario in which the 1987 Montreal Protocol (and subsequent amendments) was not implemented. Without any action, the radiative forcing (*i.e.*, impact on climate) of the ODSs would have been comparable to CO<sub>2</sub> emissions by 2010. Instead, the actual yearly GWP-weighted emissions of the ODSs peaked in 1988 at an equivalent equal to 43 % of that of CO<sub>2</sub>. By

2010, the Montreal Protocol had avoided emissions of approximately 10 Gt CO<sub>2</sub>[eq] (*i.e.*, emissions with a warming impact equivalent to 10 gigatonnes of CO<sub>2</sub>) per year; by comparison, global CO<sub>2</sub> emissions from fossil fuels and industrial processes were 32 Gt per year in 2010.<sup>19</sup> Put another way, the Montreal Protocol has delayed climate change by 7–12 years, according to Velders *et al.*<sup>18</sup>

Thus, by rapidly phasing out the CFCs and other ODSs in the 1990s, the refrigeration industry has already avoided significant climate impacts, and with the HFC phasedown called out in the Kigali Amendment to the Montreal Protocol the industry will make further substantial contributions.

## The Search for Replacement Fluids

The present paper summarizes the results of a comprehensive search for the best single-component, low-GWP replacement fluids for use in small air-conditioning systems, as presented by McLinden *et al.*<sup>9</sup> We searched for suitable replacement fluids by applying thermodynamic and environmental screening criteria to a comprehensive chemical database. The fluids passing these screens were then simulated in an air-conditioning system, with the calculated volumetric refrigeration capacity and COP (*i.e.*, energy efficiency) serving as additional screens.

A refrigerant is the essential working fluid in a vapor-compression refrigeration cycle; it absorbs heat at a relatively low temperature in the evaporator (*e.g.*, the cooling coil in an air conditioner) and releases it at a higher temperature in the condenser (*e.g.*, the outside coil). To identify replacement refrigerants one must first consider the characteristics required of any refrigerant and then also consider the optimal properties for the particular application of interest.

**General requirements of a refrigerant.** The requirements of a replacement refrigerant have been considered by numerous authors including McLinden and Didion,<sup>20</sup> Calm and Didion,<sup>21</sup> and Kujak and Schultz.<sup>22</sup> Always at the top of the list is the need for chemical stability within the sealed refrigeration system; next are health and safety considerations. Existing safety codes (*e.g.*, ASHRAE Standard 15<sup>23</sup>) require nonflammable refrigerants for many applications, but that requirement is being reconsidered. Environmental considerations (*e.g.*, ODP and GWP) are obviously important—they are the reason new fluids are currently under consideration. Practical requirements such as cost and materials compatibility also factor in.

A refrigerant must also possess certain thermodynamic characteristics for it to function. Since a refrigerant absorbs and releases heat primarily through evaporation and condensation, a high latent heat of vaporization might seem to be desirable. A boiling-point temperature low enough that air will not leak into a system is desirable; but the boiling point should not be so low that the system pressures are “too high.” A high discharge temperature upon compression will lower the efficiency of the cycle, but conversely, “wet compression” must be avoided in most types of compressors.

**The “Exploration of Thermodynamic Space.”** But how are these seemingly disparate thermodynamic characteristics related, and how is one to identify a refrigerant satisfying them? McLinden *et al.*<sup>4</sup> and Domanski *et al.*<sup>5</sup> approached this problem by defining fluids in terms of a small number of fundamental thermodynamic characteristics and then searching for optimal values of those parameters. Thus, they considered the full range of possible thermodynamic behaviour, rather than scanning a finite number of known fluids (which would reveal no new fluids). They termed this approach the “exploration of thermodynamic space.”

The fluid thermodynamic properties were modeled by the “extended corresponding states” (ECS) approach laid out by Huber and Ely.<sup>24</sup> Corresponding states is the observation that the properties of fluids are similar when scaled by their critical point parameters,  $T_{\text{crit}}$  and  $p_{\text{crit}}$ , where the critical point is the state where the saturated liquid and saturated vapor approach one another. Key to this method is a “reference fluid” to which the properties of the unknown fluid are scaled. This method is “extended” by additional parameters; the most significant were the heat capacity of the vapor ( $C_p^0$ ) and the acentric factor,  $\omega$ , which is related to the slope of

the vapor pressure curve. The range of the parameters considered is given in Table 2. The critical temperature is not as familiar as the normal boiling point temperature,  $T_{\text{NBP}}$ , but the two are related, and here both are used here. (Other parameters were considered, but they were found to be of minor importance.<sup>5</sup>)

**Table 2. Fluid parameters varied in the optimization runs and their ranges.**

Parameter	Range
reference fluid	propane –or– R-32
$T_{\text{crit}}/\text{K}$	305 – 650
$p_{\text{crit}}/\text{MPa}$	2.0 – 12.0
$\omega$	0.0 – 0.6
$C_p^0(300 \text{ K})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	20.8 – 300

**Optimum Thermodynamic Characteristics.** Any optimization requires objective function(s), and here the coefficient of performance (COP) and volumetric capacity ( $Q_{\text{vol}}$ ) were selected for a cycle operating between an evaporation temperature of 10 °C and a condensation temperature of 40 °C. The hypothetical fluids were simulated in three cycles (shown in Figure 1): (a) the simple (basic) four-component vapor-compression cycle, (b) a cycle with a liquid-line/suction-line heat exchanger (LL/SL HX), and (c) a two-stage economizer cycle. All three cycles were modelled assuming isentropic compression, no pressure drop in the heat exchangers, and saturated liquid and vapor exiting the condenser and evaporator, respectively. Sets of thermodynamic parameters within the ranges defined in Table 2 defined a series of hypothetical fluids. By varying these parameters according to an evolutionary algorithm, optimal values were determined; see McLinden *et al.*<sup>4</sup> and Domanski *et al.*<sup>5</sup> for details.

This exploration of thermodynamic space indicated a trade-off between efficiency and volumetric capacity. Refrigerants with a high critical temperature gave high efficiency, but low capacity; fluids with a relatively low  $T_{\text{crit}}$  resulted in the converse. A critical pressure at the upper limit of the range resulted in both higher efficiency and increased capacity, while an acentric factor near the lower limit was optimal. The optimum value of the vapor heat capacity varied with the cycle; a relatively low value was best for the simple vapor-compression cycle, while a higher value was optimal for a cycle with internal heat exchange between the condenser outlet and compressor inlet. These results are presented in Figure 2; a clear efficiency-versus-capacity tradeoff is seen for all three cycles. Figure 2 also shows the “Pareto front” comprising the set of hypothetical fluids having thermodynamic parameters offering the highest COP for a given  $Q_{\text{vol}}$  and vice-versa; this defines the upper limit of performance that is allowed by thermodynamics. (The inverse of COP and  $Q_{\text{vol}}$  are plotted to yield a minimization, which is the convention for this type of problem.) For selected “real” refrigerants, the cycle with the LL/SL heat exchanger (Figure 2(b)) shows a much smoother variation of COP versus  $Q_{\text{vol}}$  compared to the simple cycle (Figure 2(a)); some refrigerants, notably ammonia and R-32, have a lower COP with the LL/SL HX. The economizer cycle (Figure 2(c)) shows a higher COP for both the Pareto front and the current refrigerants compared to the simple vapor-compression cycle. The relative benefit of the LL/SL heat exchanger cycle versus the economizer cycle compared to the simple cycle varied with the fluid.

**Database Screenings.** Having defined a desired set of thermodynamic parameters, we next set out to identify fluids having those characteristics. Our search relied on screening a comprehensive database of molecules by applying filters representing different refrigerant selection criteria. The search was carried out in the PubChem database—a listing with more than 60 million chemical structures.<sup>25</sup> A first screening of this database is described by Kazakov *et al.*<sup>3</sup>; we summarize here a second screening.<sup>9</sup> All current refrigerants are small molecules, and McLinden<sup>26</sup> provides a thermodynamic basis for this. Thus, we limited our search to molecules with 18 or fewer atoms and comprising only the elements C, H, F, Cl, Br, O, N, or S. The choice of elements follows the observation by Midgley<sup>27</sup> that only a small portion of the periodic table would form compounds

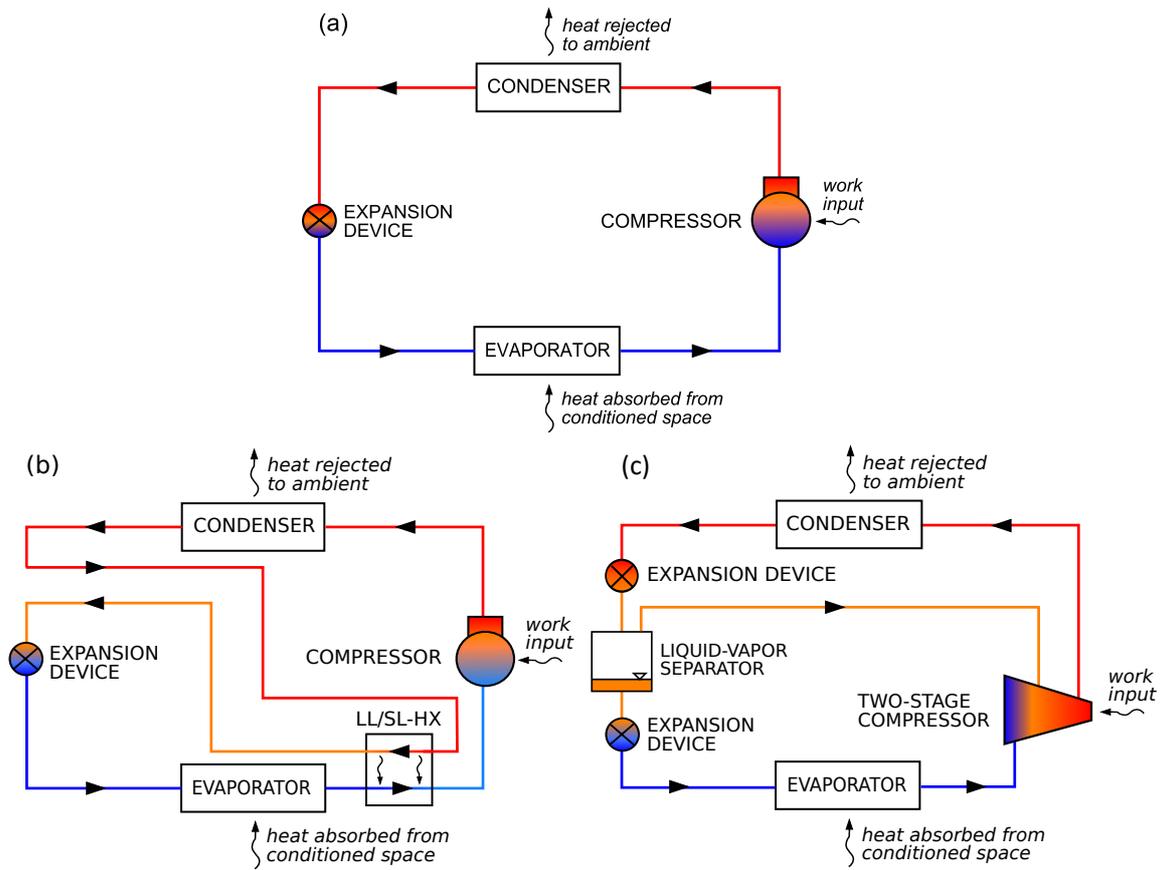


Figure 1. Cycles simulated: (a) simple vapor-compression cycle; (b) cycle with 100 % effective LL/SL heat exchanger; (c) economizer cycle; figure from ref <sup>9</sup>.

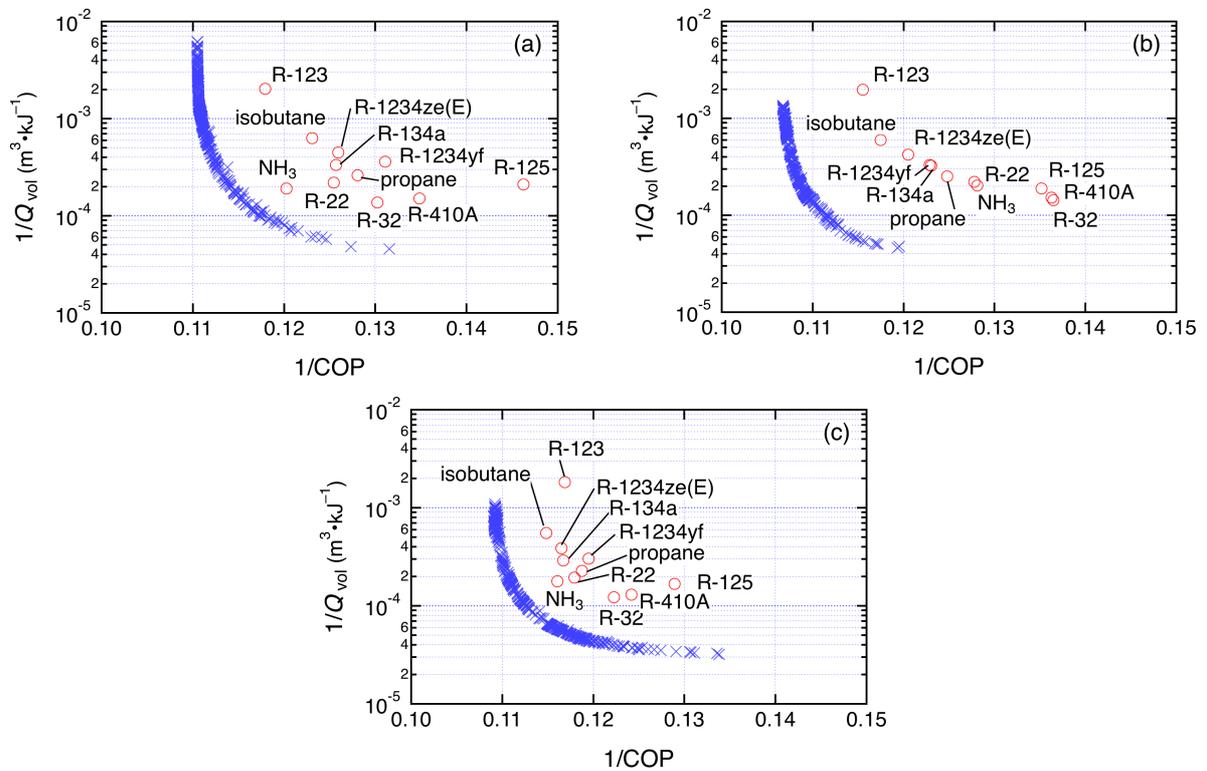


Figure 2. Pareto front (x) and selected current refrigerants (o) for different cycle options: (a) simple vapor-compression cycle; (b) cycle with 100 % effective LL/SL heat exchanger; (c) economizer cycle; figure from ref <sup>4</sup>.

volatile enough to serve as refrigerants. Despite their ability to deplete stratospheric ozone, chlorine and bromine were included since molecules including Cl or Br might have a negligible ODP and might be acceptable if they had a very short atmospheric lifetime. These restrictions on elements and molecular size resulted in 184 000 molecules to be considered further.

Further screens for  $320\text{ K} < T_{\text{crit}} < 420\text{ K}$  and  $\text{GWP}_{100} < 1000$  yielded 138 fluids. The PubChem database does not provide  $T_{\text{crit}}$  and  $\text{GWP}_{100}$  values for the vast majority of the compounds, so they were estimated using methods based solely on molecular structure; these estimations constituted a major effort of the project.<sup>28,3,4,29</sup> The limits on critical temperature correspond to fluids usable in small AC systems, with an allowance for the uncertainty in the estimated values of  $T_{\text{crit}}$ . While refrigerants with values of GWP as low as possible are obviously desirable, fluids with  $\text{GWP}_{100} < 750$  are, for example, permitted under E.U. regulations in AC systems with less than 3 kg of refrigerant.<sup>30</sup> (The full list of 138 fluids is given in the Supplementary Information of McLinden *et al.*<sup>9</sup>, which also lists the estimated  $T_{\text{crit}}$  and  $\text{GWP}_{100}$  for each fluid.)

The next screens were for chemical stability and toxicity. Compounds with generally unstable functional groups were dropped from further consideration. For example, peroxides (compounds with the  $-\text{O}-\text{O}-$  group) are unstable. Ketenes (compounds with the  $-\text{C}=\text{C}=\text{O}$  group) are generally very reactive, and three such compounds were dropped. Allenes have the  $-\text{C}=\text{C}=\text{C}-$  group and are characterized as “difficult to prepare and very reactive.”<sup>31</sup> Compounds with a carbon-carbon triple bond are generally less stable than those with a double bond; for example, fluoroethyne ( $\text{FC}\equiv\text{CH}$ ) is described as “treacherously explosive in the liquid state.”<sup>32</sup> There are exceptions, however, and trifluoropropyne was retained.

Attempts to automate the screening of toxicity were not successful. Fortunately, at this point, the number of compounds was sufficiently small to allow a “manual” examination of toxicity data. We considered published toxicity data, where available, making use of a variety of sources, including safety standards, compilations of toxic industrial chemicals, regulatory filings, and safety data sheets of chemical manufacturers. We also dropped compounds with two specific groups. Molecules that included the  $=\text{CF}_2$  group were deemed “not viable candidates” on the basis of Lindley and Noakes<sup>33</sup> who discuss the “ $=\text{CF}_2$  structural alert” in regards to R-1225zc ( $\text{CF}_3\text{CH}=\text{CF}_2$ ); this is the observation that the  $=\text{CF}_2$  group has a high reactivity which is often associated with toxic effects. The presence of a  $=\text{CF}_2$  group does not assure that a molecule is toxic, but we are aware of only one possible counterexample of R-1123 ( $\text{CHF}=\text{CF}_2$ ), which has an acute toxicity similar to that of the commercialized refrigerant R-1234ze(E).<sup>34</sup> (The chronic toxicity of R-1123 has not been reported in the public literature.) The absence of a  $=\text{CF}_2$  group does not, however, imply that a molecule is of low toxicity. Fluids having the  $-\text{OF}$  group were also dropped. The  $-\text{OF}$  group is analogous to the  $-\text{OH}$  group that defines an alcohol. The bond dissociation energy of the  $\text{O}-\text{F}$  bond, however, is less than one-half that of the  $\text{O}-\text{H}$  bond in an alcohol,<sup>35</sup> and the fluorine would likely be reactive with water, forming HF (hydrofluoric acid—a highly toxic compound).

**Performance in the Ideal Vapor-Compression Cycle.** The 138 candidates identified in the database screening were simulated in the simple (ideal) vapor-compression cycle. For the representation of refrigerant properties we used detailed equations of state (EOS) implemented in the NIST REFPROP database<sup>36</sup> where available. However, for a majority of fluids we used the extended corresponding states (ECS) model,<sup>4,24</sup> as discussed above. This screening proceeded in two rounds. The first round of cycle simulations made use of the theoretical CYCLE\_D model<sup>37</sup> and provided a first estimate of volumetric capacity and COP.<sup>7</sup> These simulations assumed an ideal cycle with 100 % compressor efficiency and no pressure drops. At this stage, we dropped fluids with a volumetric capacity less than one-third that of R-410A or a  $\text{COP} < 5$ . (For R-410A in the ideal cycle  $Q_{\text{vol}} = 6.62\text{ MJ}\cdot\text{m}^{-3}$  and  $\text{COP} = 7.41$ .)

## Candidate Fluids

The database search combined with the performance simulation in the ideal cycle resulted in a list of 27 fluids with the assertion that it would be “highly unlikely that any better-performing fluids will be found.”<sup>9</sup> The list already included several fluids that failed the stated screening criteria, but were added because of commercial

interest. These included R-1123, which was identified as unstable by Tanaka *et al.*<sup>38</sup>, but a blend with R-32 may be stable.<sup>39</sup> Have any additional fluids been identified in the intervening time? Domanski *et al.*<sup>8</sup> added R-1132a to the list. This fluid was among the 138 fluids passing the original screening but was rejected based on an indication of high toxicity<sup>40</sup>; later data resulted in a “class A” toxicity rating.<sup>41</sup>

The iodine-containing CF<sub>3</sub>I has generated considerable interest recently as a low-GWP option that might be used to suppress the flammability of blends (see, for example, McGowan<sup>42</sup>). CF<sub>3</sub>I was recently classified as “A1” (low-toxicity, nonflammable) under ASHRAE Standard 34 and designated as R-1311.<sup>43</sup> This fluid was considered early on by Kazakov *et al.*<sup>3</sup> The C–I bond is very weak and is readily photolyzed by UV light; thus, it did not fit within the estimation scheme for GWP developed by Kazakov. CF<sub>3</sub>I and other iodine-containing compounds were investigated in the 1990s during the search for CFC replacements (see Calm<sup>44</sup> and Nimitz and Lankford<sup>45</sup>) and again in the early 2000s in the program sponsored by the Society of Automotive Engineers to identify replacements for R-134a in automotive air-conditioning systems.<sup>46</sup> Interest waned in the iodine-containing compounds on both occasions because of stability and toxicity concerns. Thus, iodine was not included in the list of eight elements making up the fluids in the database searches of Kazakov *et al.*<sup>3</sup> and McLinden *et al.*,<sup>6,9</sup> but we include it here.

The final list of 29 candidates is given in Table 3. This list is a subset of the 138 candidates having  $320\text{ K} < T_{\text{crit}} < 420\text{ K}$  and  $\text{GWP}_{100} < 1000$ , with the deletion of those that have low  $Q_{\text{vol}}$ , low COP, or are unstable or toxic. The list comprises four hydrocarbons and the closely related dimethylether; five fluorinated alkanes (*i.e.*, HFCs); ten fluorinated alkenes and an alkyne; two fluorinated oxygen-containing molecules; three fluorinated nitrogen or sulfur compounds; CF<sub>3</sub>I; and two inorganic molecules (ammonia or NH<sub>3</sub> and carbon dioxide). The list includes a small number of novel molecules that have not been previously considered as refrigerants (at least publicly), but a majority of the fluids are well known, including ammonia (R-717) and propane (R-290), or are the focus of current research in the refrigeration industry, *i.e.*, the fluorinated alkenes (also known as hydrofluoroolefins or HFOs).

Refrigerant blends are currently in common use, and the fluids in Table 3 also constitute the components of future blends. Several of the fluids have low critical temperatures and would operate in a transcritical cycle for our investigated conditions; thus, they were not simulated. These fluids might, however, be useful as a component in a refrigerant blend, and they were included in Table 3 for this reason. The table also includes an additional four current HFCs and HCFCs for comparison purposes. Despite their high values of  $\text{GWP}_{100}$  R-134a and R-125 might also find use as blend components. Some of the reasons behind this paucity of candidates are discussed below.

**Simulations in an Optimized Cycle.** The second round of simulations made use of a more advanced “optimized” cycle model that provided a more realistic representation of an air conditioner employing typical forced-convection, air-to-refrigerant heat exchangers, which were optimized for a particular refrigerant.<sup>47</sup> In this type of heat exchanger, the refrigerant undergoes a phase change as it flows down the inside of a tube and exchanges heat with air on the outside of the tube. Specifically, the model accounted for the effect of optimized refrigerant mass flux, which enhances the refrigerant heat transfer coefficient at an acceptable penalty of the pressure drop. These simulations included the effects of the transport properties (thermal conductivity and viscosity) on the heat transfer coefficient and pressure drop, which were not included in the ideal cycle simulations. The simulation model maintained the same heat flux in the evaporator through all simulations, which is a prerequisite for a fair rating of competing refrigerants.<sup>48</sup> The isentropic efficiency of the compressor was a function of the refrigerant properties and averaged 70%.<sup>49</sup> Here, the relative ranking of fluids differs from a ranking based only on thermodynamic properties; it is, however, more representative of a fluid’s performance in an AC system in commercial production, which would be optimized for the refrigerant being used.

The COP and  $Q_{\text{vol}}$  of the candidate fluids, based on the optimized model, are presented in Table 3 and Figure 3. Unlike the COP versus  $Q_{\text{vol}}$  tradeoff observed for the ideal analysis (Figure 2), the results of the optimized cycle simulations in the simple cycle (Figure 3) show a maximum in COP corresponding to  $Q_{\text{vol}}$  of approximately 60%

**Table 3. COP and volumetric capacity of selected low-GWP fluids and current HFC and HCFC fluids.** Results are presented for the basic, liquid-line/suction-line heat exchanger (LL/SL), and economizer (Econ.) cycles. Values are for the “optimized” cycle model and are relative to the performance of R-410A in the basic cycle.  $GWP_{100}$  are from WMO<sup>12</sup> or E.U. regulation<sup>30</sup> unless noted. The fluids are grouped by chemical class and, within classes, listed in order of increasing critical temperature; table adapted from ref<sup>9</sup>.

IUPAC Name	Structure	ASHRAE Designation	$GWP_{100}$	COP/COP <sub>R-410A</sub> *			$Q_{vol}/Q_{vol,R-410A}$ *		
				Basic	LL/SL	Econ.	Basic	LL/SL	Econ.
<b>Hydrocarbons and dimethylether</b>									
ethane	CH <sub>3</sub> -CH <sub>3</sub>	R-170	6	§					
propene (propylene)	CH <sub>2</sub> =CH-CH <sub>3</sub>	R-1270	<1	1.033	1.053	1.073	0.689	0.694	0.770
propane	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	R-290	<1	1.014	1.042	1.058	0.571	0.579	0.640
methoxymethane (dimethylether)	CH <sub>3</sub> -O-CH <sub>3</sub>	R-E170	1	0.996	1.002	1.035	0.392	0.389	0.427
cyclopropane	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	R-C270	86†	1.018	1.021	1.045	0.472	0.467	0.510
<b>Fluorinated alkanes (HFCs)</b>									
fluoromethane	CH <sub>3</sub> F	R-41	116	§					
difluoromethane	CH <sub>2</sub> F <sub>2</sub>	R-32	705	1.038	1.026	1.070	1.084	1.057	1.191
fluoroethane	CH <sub>2</sub> F-CH <sub>3</sub>	R-161	6	1.026	1.031	1.062	0.601	0.594	0.658
1,1-difluoroethane	CHF <sub>2</sub> -CH <sub>3</sub>	R-152a	148	0.981	0.989	1.022	0.399	0.396	0.435
1,1,2,2-tetrafluoroethane	CHF <sub>2</sub> -CHF <sub>2</sub>	R-134	1135	0.967	0.991	1.024	0.348	0.352	0.385
<b>Fluorinated alkenes (HFOs) and alkyne</b>									
1,1-difluoroethene	CF <sub>2</sub> =CH <sub>2</sub>	R-1132a	<1	§					
fluoroethene	CHF=CH <sub>2</sub>	R-1141	<1	0.968	0.977	1.014	1.346	1.336	1.547
1,1,2-trifluoroethene	CF <sub>2</sub> =CHF	R-1123	3‡	0.956	0.988	1.014	1.054	1.074	1.230
3,3,3-trifluoroprop-1-yne	CF <sub>3</sub> -C≡CH	n.a.	1.4†	0.988	1.023	1.042	0.545	0.557	0.616
2,3,3,3-tetrafluoroprop-1-ene	CH <sub>2</sub> =CF-CF <sub>3</sub>	R-1234yf	<1	0.954	1.006	1.020	0.414	0.431	0.474
(E)-1,2-difluoroethene	CHF=CHF	R-1132(E)	1†	1.016	1.019	1.051	0.591	0.585	0.646
3,3,3-trifluoroprop-1-ene	CH <sub>2</sub> =CH-CF <sub>3</sub>	R-1243zf	<1	0.964	0.997	1.019	0.372	0.379	0.417
1,2-difluoroprop-1-ene‡	CHF=CF-CH <sub>3</sub>	R-1252ye‡	2†	0.973	0.996	1.021	0.355	0.358	0.392
(E)-1,3,3,3-tetrafluoroprop-1-ene	CHF=CH-CF <sub>3</sub>	R-1234ze(E)	<1	0.939	0.977	1.004	0.320	0.329	0.360
(Z)-1,2,3,3,3-pentafluoro-1-propene	CHF=CF-CF <sub>3</sub>	R-1225ye(Z)	<1	0.922	0.972	0.986	0.273	0.285	0.310
1-fluoroprop-1-ene‡	CHF=CH-CH <sub>3</sub>	R-1261ze‡	1†	0.975	0.983	1.018	0.353	0.351	0.385
<b>Fluorinated oxygenates</b>									
trifluoro(methoxy)methane	CF <sub>3</sub> -O-CH <sub>3</sub>	R-E143a	540	0.957	0.992	1.017	0.366	0.374	0.411
2,2,4,5-tetrafluoro-1,3-dioxole	-O-CF <sub>2</sub> -O-CF=CF-	n.a.	1†	0.936	0.984	0.998	0.337	0.349	0.376
<b>Fluorinated nitrogen and sulfur compounds</b>									
N,N,1,1-tetrafluormethaneamine	CHF <sub>2</sub> -NF <sub>2</sub>	n.a.	20†	0.965	1.007	1.027	0.807	0.831	0.937
difluoromethanethiol	CHF <sub>2</sub> -SH	n.a.	1†	1.010	1.019	1.054	0.582	0.580	0.642
trifluoromethanethiol	CF <sub>3</sub> -SH	n.a.	1†	0.977	0.997	1.026	0.418	0.421	0.464
<b>Iodine compound</b>									
trifluoroiodomethane	CF <sub>3</sub> I	R-131I	<1	0.913	0.927		0.310	0.310	
<b>Inorganic compounds</b>									
carbon dioxide	CO <sub>2</sub>	R-744	1.00	§					
ammonia	NH <sub>3</sub>	R-717	<1	1.055	1.028	1.080	0.746	0.721	0.791
<b>Current HFCs and HCFCs</b>									
pentafluoroethane	CF <sub>3</sub> -CHF <sub>2</sub>	R-125	3450	0.913	0.979	0.995	0.746	0.784	0.889
R-32/125 (50.0/50.0)	blend	R-410A	2078	1.000	1.012	1.049	1.000	0.997	1.130
chlorodifluoromethane	CHClF <sub>2</sub>	R-22	1780	1.007	1.008	1.043	0.666	0.658	0.732
1,1,1,2-tetrafluoroethane	CF <sub>3</sub> -CH <sub>2</sub> F	R-134a	1360	0.968	0.993	1.027	0.433	0.439	0.485

\*Values are relative to those for R-410A in the basic cycle; COP<sub>R-410A</sub> = 5.35 and  $Q_{vol,R-410A}$  = 6.93 MJ·m<sup>-3</sup>.

†Value estimated by the method of Kazakov *et al.*<sup>3</sup>

‡This fluid has cis (Z) and trans (E) isomers; the predicted values of both were the same.

§Fluid would be near-critical or supercritical in the condenser and was not simulated.

to 110 % that of R-410A. Although there is considerable scatter, a polynomial curve fitted to the fluids shown in Figure 3 indicates the general trend. Relative to fluids with low values of  $Q_{vol}$ , the high- $Q_{vol}$  fluids have lower values of  $T_{crit}$  and operate at higher pressures; the result is that the cycle operates near the critical point and suffers increased irreversibilities in the expansion process. This effect applies to both the ideal and more-detailed analyses. However, the ideal analysis neglects the fact that the pressure drop in the heat exchangers

(condenser and evaporator) extracts a smaller COP penalty on the high- $Q_{vol}$  (*i.e.*, high-pressure) fluids when the heat exchangers are optimized. An additional effect is that the low- $Q_{vol}$  fluids tend to be more complex molecules. For example, R-32 (one of the best fluids in Figure 3) is based on a single carbon atom, and R-410A is a blend of the single-carbon R-32 and two-carbon R-125. In contrast most of the fluids with  $Q_{vol} < 0.4 \cdot Q_{vol,R-410A}$  are three-carbon compounds; greater molecular complexity is associated with higher values of viscosity, which would increase the pressure drop and lower the COP.

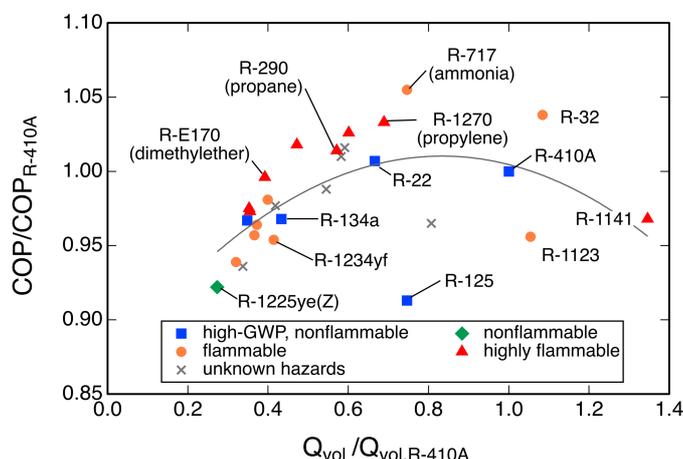


Figure 3. COP and  $Q_{vol}$  of selected low-GWP fluids relative to R-410A in the basic vapor-compression cycle including pressure drop and heat-transfer limitations; the curve indicates the general trend; figure adapted from ref <sup>9</sup>.

The COP ranged from  $-7.8\%$  to  $+5.5\%$  relative to that of R-410A in the basic vapor-compression cycle. Ammonia showed the highest COP, better than that for R-410A by  $5.5\%$ . Beyond ammonia, which is toxic, mildly flammable, and presents materials compatibility issues, the COPs of R-32, propene (R-1270), R-161, R-1132(E), propane (R-290), cyclopropane (R-C270) and difluoromethanethiol are also above the R-410A baseline. The COPs of the remaining fluids are lower. Mildly flammable R-32 has a COP and  $Q_{vol}$  higher than that of R-410A, but this advantage comes with a  $GWP_{100}$  of 705. R-134 and R-E143a have  $GWP_{100}$  values of 1135 and 540, respectively. Three fluids have GWPs within the 80 to 150 range, and GWPs for the remaining fluids do not exceed 20. Except for R-32, R-1123, and R-1141 the listed fluids have  $Q_{vol}$  lower than R-410A and would thus require a larger compressor—by at least  $25\%$  and, for a majority of the candidates, more than twice as large—to provide the same capacity as R-410A. Table 3 does not provide COP and  $Q_{vol}$  for carbon dioxide, ethane, R-41, and R-1132a because their  $T_{crit}$  are low and they may require a different (*i.e.*, transcritical) cycle, depending on operating conditions. We list them because they may be suitable as a component of a blend. In general, fluids with a low  $T_{crit}$  (corresponding to high  $Q_{vol}$ ) suffer performance degradation at high ambient temperatures.

The results for the LL/SL-HX and economizer cycles are qualitatively similar to the basic cycle and are listed in Table 3. The LL/SL-HX cycle provides a performance benefit to fluids with a high vapor heat capacity and degrades the performance of fluids with a low vapor heat capacity (which are best performers in the basic cycle). Consequently, the spread of COP values is smaller than that shown in Figure 3. The economizer cycle increases the COP for all refrigerants, although the increase is larger for the fluids having a high vapor heat capacity.

**Refrigerant Blends.** Given the lack of an obvious low-GWP, nonflammable, pure-fluid candidate with a volumetric capacity similar to R-410A there is considerable interest in refrigerant blends; see, for example, Schultz<sup>50</sup> and Spletzer *et al.*<sup>51</sup> Mixing high-GWP, but non-flammable fluid(s) with low-GWP, but flammable fluid(s) can yield a mildly flammable refrigerant with a  $GWP_{100}$  on the order of 500 or, with a different composition, a non-flammable fluid with a higher  $GWP_{100}$ .

Bell, *et al.*<sup>11</sup> considered the problem of finding a nonflammable replacement for R-134a in an air-conditioning application. They considered blends composed from a slate of 13 candidate fluids with a range of pressure,

flammability, and GWP values that might produce a blend with the desired characteristics of a R-134a replacement. The blend components included hydrofluoroolefins (HFOs), which have very low GWP values ( $\approx 1$  relative to  $\text{CO}_2$ ), but that are mildly flammable; hydrofluorocarbons (HFCs) with moderate-to-high GWP values that were nonflammable and thus, might serve to suppress the flammability of a blend; additional mildly flammable HFCs; and carbon dioxide ( $\text{CO}_2$ ), which is nonflammable with  $\text{GWP} \equiv 1$ , but which would raise the working pressure of a blend and may produce a large two-phase temperature glide in the heat exchangers. All the selected fluids were of low toxicity, *i.e.*, having an “A” classification under ASHRAE Standard 34.<sup>52</sup> Additional considerations were the commercial availability of the fluid and the availability of property data (in the form of an accurate equation of state), so that cycle simulations could be carried out with some measure of confidence. The blend components were the HFCs: R-134a, R-227ea, R-125, R-143a, R-32, R-152a, R-134, and R-41; the HFOs: R-1234yf, R-1234ze(E), R-1234ze(Z), and R-1243zf; and R-744 ( $\text{CO}_2$ ). Hydrocarbons were not included because the objective was to find a nonflammable blend, and a blend containing only a few percent of a hydrocarbon would be flammable.

A simplified cycle model was used, but it did include the effects of compressor efficiency, pressure drop in the condenser and evaporator, subcooling at the condenser outlet, and superheat at the evaporator outlet. The basic cycle conditions were an evaporator dew-point temperature of  $10^\circ\text{C}$  and condenser bubble-point temperature of  $40^\circ\text{C}$ . In contrast to the exploration of thermodynamic space, which employed an optimization based on an evolutionary algorithm, Bell *et al.*<sup>11</sup> simulated all possible combinations of the 13 components, for a total of 100 387 binary and ternary mixtures to be evaluated. All possible four-component mixtures were also considered, for an additional 1.4 million evaluations (although none of the four-component blends were superior to the binary or ternary blends). The flammability of the blends was estimated with a new scheme developed by Linteris *et al.*<sup>53</sup> which yields a “normalized flammability index”  $\bar{\Pi}$ , which varies from  $\bar{\Pi} = 100$  for highly-flammable hydrocarbons (*i.e.*, containing no fluorine);  $\bar{\Pi} = 0$  at the limit of flammability (*i.e.*, the boundary of the ASHRAE “1” (nonflammable) and “2L” (mildly flammable) classes); and  $\bar{\Pi} < 0$  for nonflammable fluids. Note that  $\bar{\Pi}$  is based on the ASTM E-681 test method<sup>54</sup> specified in the ASHRAE standard,<sup>52</sup> and its estimates of flammability versus nonflammability may differ for other test methods.

Figure 4 provides an overview of the results for the binary and ternary blends. Here the COP is plotted versus  $\text{GWP}_{100}$  and sorted into four “bins” of estimated flammability; each dot represents one blend composition. Starting at the right-most bin, which includes blends which are predicted to be clearly nonflammable, all of the blends have substantially lower COP compared to the R-134a baseline, indicated with the red dashed line. (Note that only blends with  $\text{GWP}_{100}$  less than or equal to R-134a are plotted.) The next bin to the left shows the blends that are predicted to be nonflammable, but near the flammability limit (*i.e.*,  $-10 < \bar{\Pi} < 0$ ). Here, only blends with  $\text{GWP}_{100} > 535$  have COPs within a few percent of R-134a, and the upper bound of the COPs increases with  $\text{GWP}_{100}$ , approaching the COP of R-134a at high values of  $\text{GWP}_{100}$ . The second bin from the left contains blends that are estimated to be slightly flammable (*i.e.*,  $0 < \bar{\Pi} < 10$ ). (For comparison,  $\bar{\Pi} = 4.8$  for R-1234yf and  $\bar{\Pi} = -10.5$  for R-134a.) This bin “fills in” the upper-left quadrant of the bin to the right, that is, blends with  $\text{GWP}_{100} < 535$  and COP approaching that of R-134a. Only the left-most bin, comprising blends that are somewhat more flammable, but still estimated to be in the “2L” flammability classification, contains fluids which have both low values of  $\text{GWP}_{100}$  and COPs equal to, or greater than, the R-134a baseline.

The yellow boxes in the middle two bins indicate the relatively small number of blends that would be of interest in the search for a nonflammable R-134a replacement, *i.e.*, those with COPs similar to that of R-134a and that are nonflammable or only mildly flammable. The blends identified in this study are applicable only for its specific objectives, but it hints at the difficulty of finding a suitable blend.

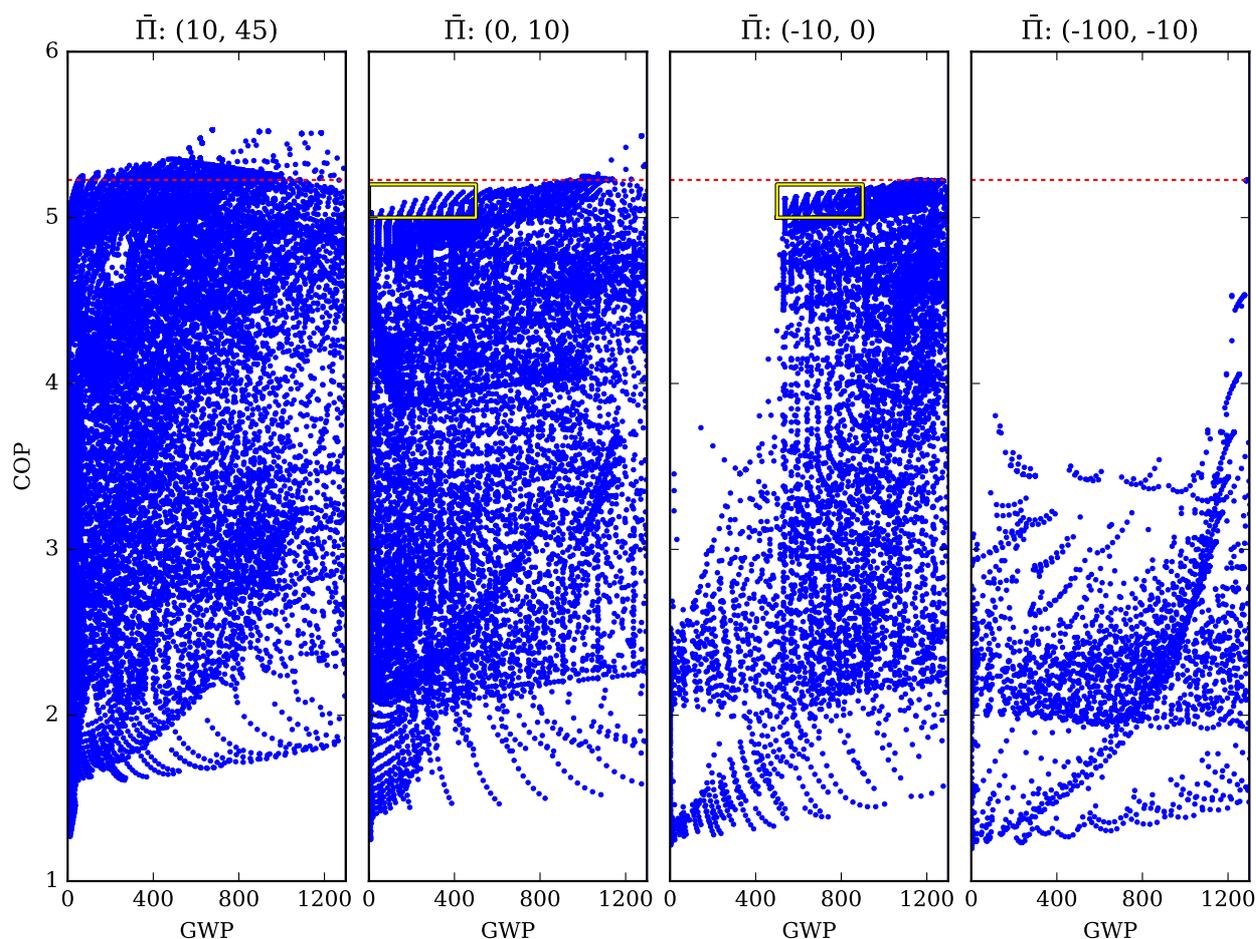


Figure 4. Overview of cycle simulation results sorted into bins of estimated flammability. The flammability decreases moving from left to right; the two right-most bins are predicted to be non-flammable. The red dashed line indicates the COP of the R-134a baseline system, and the yellow boxes indicate the blends of greatest interest. Figure from Bell *et al.*<sup>11</sup>

## Limitations and Tradeoffs

When Midgley famously introduced R-12 at the 1930 meeting of the American Chemical Society by inhaling a lungful of the refrigerant and using it to extinguish a burning candle,<sup>55,56</sup> it seemed that the perfect refrigerant had been found. It was nonflammable, of low toxicity, and was simple and cheap to manufacture. It had good thermodynamic properties, and, in fact, its properties were nearly a perfect match to the simple vapor-compression cycle.<sup>26</sup> But, of course, it was later found to deplete stratospheric ozone and have a high GWP. Even today, R-12 remains the fourth-most powerful greenhouse gas, behind CO<sub>2</sub>, methane, and N<sub>2</sub>O because of past emissions.<sup>12</sup> Since the mid-1970s the task of identifying suitable refrigerants has faced an increasing list of constraints. And, while these constraints have restricted the choice of fluids (*e.g.*, CFCs and HCFCs are no longer available), they have also opened up interest in other fluids. The phaseout of the ozone-depleting fluids, for example, sparked a resurgence of interest in the long-known natural fluids (*e.g.*, ammonia, hydrocarbons). Likewise, the lack of an obvious low-GWP, nonflammable, high-pressure replacement for some of the HFCs has opened a discussion on how fluids with at least some degree of flammability might be safely implemented in a wider variety of systems.

**Constraints on molecular structure.** As environmental regulations became ever more restrictive, the constraints on the molecules suitable for use as refrigerants correspondingly increased. When the CFCs were first introduced in the 1930s, the constraints were to find a molecule that was nonflammable, of low toxicity, cheap to manufacture and with suitable thermodynamic characteristics. The halogenated alkanes can be represented on

a triangular grid, with a separate grid for molecules based on one, two, etc. carbons. The base hydrocarbon (methane, ethane, etc.) is at the top of the triangle, and the bottom corners represent molecules with the hydrogens fully substituted with either chlorine or fluorine. With no environmental constraints, CFCs and HCFCs based on methane (one carbon), namely R-12 and R-22, were available to meet a variety of applications, as shown in Figure 5(a). There was no need to search further. With the discovery that the CFCs and HCFCs depleted stratospheric ozone, the entire lower-left (chlorine-containing) portion of the triangle was eliminated (Figure 5(b)). For the one-carbon molecules, this left only R-32 (difluoromethane) with a boiling point suitable for typical refrigeration and air-conditioning applications; but R-32 is flammable. The industry turned to the two-carbon HFCs, and settled primarily on R-134a and R-125, plus blends (Figure 5(c)).

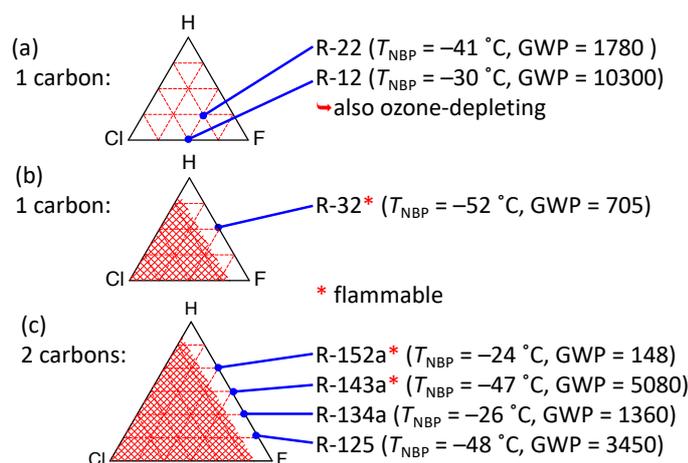


Figure 5. Depiction of constraints on CFCs, HCFCs, and HFCs on triangular composition diagrams; (a) one-carbon compounds with no constraints: R-12 and R-22 are widely used; (b) one-carbon compounds with ODP constraint: only R-32 remains; (c) two-carbon compounds with ODP constraint: several HFCs are candidates for A/C systems.

With the additional constraint, imposed by the Kigali Amendment, of reducing the GWP of refrigerants it seems unlikely that even the  $\text{GWP}_{100} = 1360$  of R-134a will be an acceptable long-term refrigerant, except perhaps in niche applications. This would leave only R-32 and R-152a remaining among the HFCs. The “A2” rating for R-152a represents a greater degree of flammability than many in the industry are comfortable with. R-32 is less flammable (rating of “A2L”), but it has a moderately high  $\text{GWP}_{100}$ , which may limit its long-term viability as a candidate. Once again, the search was on. But, even as the HFCs were being commercialized in the 1990s and before GWP was an explicit concern, the search for alternative fluids continued, and a wide variety of chemical classes were considered (see, for example, Bivens and Minor<sup>57</sup>). Concerns over global warming, and, specifically the E.U. F-gas regulations<sup>1</sup>, reignited the search, and ultimately, the hydrofluoroolefins (HFOs) were deemed to have the best combination of characteristics.

The presence of a carbon-carbon double bond defines the chemical class of “olefin,” and it is the reactivity of the double bond to the atmospheric hydroxyl radical that results in the very low atmospheric lifetimes and GWP values of the HFOs. The reactivity of the olefins, both in the atmosphere and in refrigeration equipment, is discussed by Kujak and Sorenson.<sup>58</sup> The most-common HFC refrigerants (R-134a, R-125, R-32, etc.) are based on one or two carbon atoms. The two-carbon HFOs, on the other hand, have normal boiling point temperatures that are too low for most refrigeration applications, as shown in Figure 6(a). Thus, most of the development efforts are focused on the three-carbon HFOs, and here there are a number of fluids with  $-40\text{ }^{\circ}\text{C} < T_{\text{NBP}} < -20\text{ }^{\circ}\text{C}$ ; see Figure 6(b). But a three-carbon HFO is a more complicated molecule than a one- or two-carbon HFC, and this results in a higher vapor molar heat capacity and a vapor dome that is “skewed” to the right, as discussed by McLinden.<sup>10</sup>

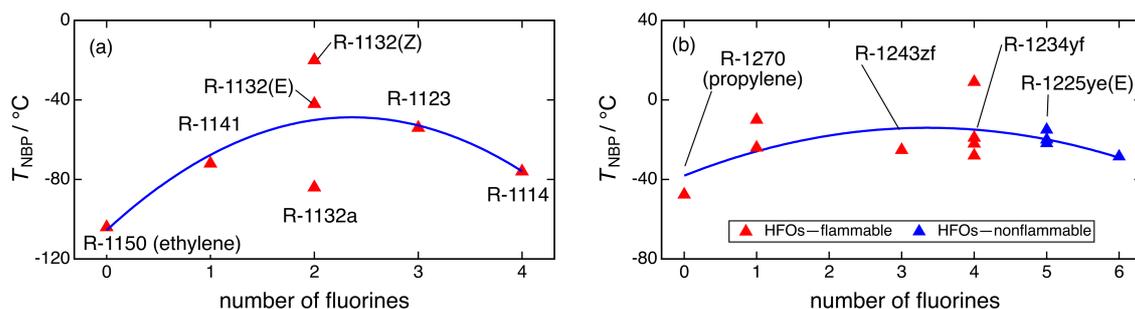


Figure 6. Variation of normal boiling point temperature  $T_{\text{NBP}}$  with the number of fluorines on the molecule; (a) two-carbon HFOs; (b) three-carbon HFOs. The curves indicate the general trends in  $T_{\text{NBP}}$ . Flammability is indicated with a color code.

**Flammability versus GWP.** The best-known HFO is R-1234yf, and this fluid is “marginally flammable” with an ASHRAE Standard 34 flammability classification of “2L”. There is often the perception that some degree of flammability is inevitable with the HFOs. Figure 6 indicates flammability and shows that this is not true, but that, compared to the HFCs, additional fluorines are needed with the HFOs to offset the reactivity of the carbon-carbon double bond. For example, the four fluorines of R-134a are sufficient to yield a nonflammable fluid, while the four fluorines on R-1234yf are not; the three-carbon HFOs require five fluorines for nonflammability (*e.g.*, R-1225ye(E)). For the two-carbon HFOs, even the fully fluorinated R-1114 is flammable.

Among the HFCs, on the other hand, a tradeoff between flammability and GWP is somewhat inevitable. The C–F bond in the HFCs absorbs infrared radiation, and this is the root of the radiative forcing (*i.e.*, high GWP) seen with the HFCs. As the number of fluorines on the molecule increases the infrared absorption increases, but also the number of hydrogens must decrease, and it is the reaction of hydrogen with atmospheric hydroxyl that degrades HFCs in the atmosphere. This combined effect results in  $\text{GWP}_{100}$  values increasing from <1 for R-170 (ethane)<sup>59</sup> to 11 100 for R-116.<sup>12</sup> The HFOs also have C–F bonds and also absorb infrared radiation, but their much, much shorter atmospheric lifetimes result in very low GWP values. Thus, the HFOs can sidestep the flammability versus GWP tradeoff—except that the flammability versus fluorine-number relationship discussed above means that there are a smaller percentage of possible HFOs that are nonflammable.

**How Reliable Was the Screening? Did We Miss Promising Fluids?** The reliability and completeness of the screening could have been compromised by a number of factors. First, we considered that the PubChem database was a complete listing of the small molecules that we were interested in. While there is no guarantee that this is the case, we note that of the 31 possible three-carbon HFO isomers, 30 were listed in PubChem; it is unlikely that the missing molecule would possess significantly different properties.

Did the restricted list of eight elements and maximum molecular size of 18 atoms exclude viable candidates? To explore this, we also carried out a search in the DIPPR database<sup>60</sup> of 2000 industrial chemicals based solely on  $300 \text{ K} \leq T_{\text{crit}} \leq 400 \text{ K}$  (see McLinden *et al.*<sup>7</sup> for details). That search revealed 33 fluids not listed in Table 3, but these included the high-GWP CFCs and HCFCs (the DIPPR database does not tabulate GWP values) and highly toxic fluids, such as HCl, HBr, and  $\text{H}_2\text{S}$ . Eight fluids included elements not in our restricted set, but these included radon (a radioactive gas); arsine ( $\text{AsH}_3$ ), which is highly toxic and pyrophoric (ignites spontaneously on contact with air); phosphine ( $\text{PH}_3$ ), which is toxic; and two silanes— $\text{SiH}_3\text{Cl}$  and  $\text{CH}_3\text{SiH}_3$ , which are both flammable, with  $\text{SiH}_3\text{Cl}$  also being toxic. None of the molecules identified in the DIPPR search had more than 18 atoms. In other words, none of these fluids brought into question our decision to limit our search to the eight elements (C, H, F, Cl, Br, O, N, and S), although, as noted above, there is renewed interest in  $\text{CF}_3\text{I}$ . In the end, the DIPPR database did not expand the list of candidate fluids obtained from our screenings of the PubChem database.

We searched on specific ranges for the properties, and given that most of the properties were estimated from molecular structure, what was the effect of uncertainties in those estimates? The estimated uncertainty in the

critical temperature was 16.5 K, but the range of  $T_{crit}$  in the screening was expanded to accommodate this uncertainty. The uncertainty in the estimate of  $GWP_{100}$  was a factor of three, and while this might seem large, it was unlikely to exclude any viable candidates—even if a candidate with an estimated  $GWP_{100} = 10$ , say, was actually 3 or 30, it would still be considered “very low GWP.”

Finally, there is the possibility of incorrect data in the literature. We noted above that R-1132a was originally excluded from the original list of 27 fluids<sup>9</sup> based on an indication of toxicity from a reliable source.<sup>40</sup> Based on newer data, it was later added to the list. There is no way to avoid this situation except to periodically check for updated data.

**Other fluids?** But why are there so few other fluids? In chemistry, molecules are categorized by the functional group(s) they possess. The HFCs belong to the fluorinated alkane category. The alkanes comprise one or more carbon atoms with hydrogens attached to each carbon as needed to satisfy the requirement that each carbon atom be bonded to four neighbors. In the fluorinated alkanes, some of the hydrogens are simply replaced by fluorine. The alkenes (also known as olefins) are a variation on the alkanes with one or more of the carbon-carbon bonds replaced with a double bond, with each double bond “counting” as two neighbors.

Many other functional groups are well known, and some of these are shown in Figure 7. These are, for the most part, not suitable as refrigerants in moderate-to-high pressure systems because the normal boiling points for even the simplest examples are too high. The simplest alcohol, for example, is methanol with  $T_{NBP} = 65$  °C. Acetone is the simplest ketone with  $T_{NBP} = 56$  °C. Substitution of hydrogen with other atoms generally increases the boiling point. Functional groups with  $T_{NBP}$  low enough to serve as the basis for moderate-to-high-pressure refrigerants include the ethers (C-O-C) and the amines (comprising a central nitrogen with three attached groups). All such compounds were included in the database searches, but apart from dimethyl ether, ammonia, and a very few others, they were rejected because of high  $GWP_{100}$ , high  $T_{crit}$ , or other factors.

Name	Functional Group	Simplest Example	$T_{NBP}/^{\circ}C$
alcohol		methanol	 65
ether		dimethylether	 -25
aldehyde		acetaldehyde	 20
ketone		acetone	 56
thiol		methylmercaptan	 6
thioether		dimethylsulfide	 38
amine		ammonia	 -33

Figure 7. Selected functional groups containing oxygen, sulfur, or nitrogen, with the simplest example of each also shown; R, R', R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> indicate attached hydrogens or alkyl groups.

## Conclusions

In this paper we have summarized the results of a thorough and systematic examination of possible low-GWP replacements for the HFC refrigerants currently used in small air-conditioning systems. The significant elements of this effort were (1) an optimization of fundamental thermodynamic parameters for a refrigerant; this approach was not restricted to known fluids, but encompassed all possible fluids allowed by thermodynamics (an approach we dubbed the “exploration of thermodynamic space”); (2) a search in an exhaustive chemical database for fluids having the identified thermodynamic parameters as well as acceptable chemical stability, toxicity, and GWP; and (3) simulation of the candidate fluids and a final screening based on the COP and capacity in the vapor-compression cycle. The identified list of 29 candidate refrigerants includes well-known fluids as well as fluids being actively investigated by industry; several novel fluids were also identified. But none of these are a direct, nonflammable, low-GWP replacement for the R-410A currently used in the majority of small air-conditioning systems.

The present study was focused on the medium-to-high-pressure refrigerants used in most small systems. Different equipment types may yield a different list of candidates. In particular, chillers with centrifugal compressors (which typically employ low-pressure refrigerants) were not considered, nor were high-temperature heat pumps or very-low-temperature systems. Application of the present methodology to such systems would be worthwhile.

Calm<sup>61</sup> introduced the concept of “refrigerant generations,” and he characterizes the current, fourth generation of refrigerants as driven by “attention to global warming.” Later, Calm<sup>44</sup> posited that, in view of limited options, a fifth generation, which would “re-examine previously discarded candidates”, may be forthcoming as the full range of tradeoffs are considered. But the results of McLinden *et al.*<sup>9</sup> indicate (as summarized here) that there are no fundamentally new classes of chemicals available for use in vapor-compression refrigeration systems. While the “re-examination” discussed by Calm<sup>44</sup> may well occur, the situation may be to return (recycle?) to earlier generations, such as the ammonia, CO<sub>2</sub>, and hydrocarbons of the first generation of “whatever works.” Let us hope that we are not forced back to a “generation zero” of harvesting ice from frozen lakes.

## Acknowledgements

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