A THERMODYNAMIC ANALYSIS OF REFRIGERANTS. II. POSSIBILITIES AND TRADEOFFS FOR LOW-GWP REFRIGERANTS

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ABSTRACT

We explore the possibilities for refrigerants having low global warming potential (GWP) by use of two distinct approaches. In a companion paper (Domanski *et al.*, 2013), we evaluate the effect of a refrigerant's fundamental thermodynamic parameters on its performance in the vapor compression cycle; this defines the limits of what is thermodynamically possible for a refrigerant and the optimal thermodynamic parameters needed to approach those limits. In the second approach, presented here, we examine more than 56 000 chemical compounds from a public-domain database. A subset of about 1200 candidate fluids is identified by applying screening criteria to estimates for GWP, flammability, stability, toxicity, and critical temperature. Methodologies for this screening have been presented in earlier works and are summarized here. The fluids with critical temperatures between 300 K and 400 K (*i.e.*, those that could be used in current types of equipment with minor modifications) number 62. The fluids include halogenated olefins; compounds containing oxygen, nitrogen, or sulfur; as well as carbon dioxide. We discuss the tradeoffs presented by these 62 candidates, considering their thermodynamic properties as well as their stability and toxicity characteristics, to the extent that such data are available. No fluid is ideal in all regards—all have one or more negative attributes: poor thermodynamic properties, acute or chronic toxicity, chemical instability, low to moderate flammability, or very high operating pressures.

1. INTRODUCTION

In the search for new refrigerants having a low global warming potential (GWP), a number of other criteria must also be met. As laid out by McLinden and Didion (1987), these include stability within the refrigeration system and a short atmospheric lifetime (which is related to GWP and ozone depletion potential (ODP)), attributes that are often mutually exclusive. Also important are thermodynamic properties matched to the application, low flammability and toxicity, and other practical considerations, including cost and compatibility with the materials of construction. The "optimum" refrigerant depends on the constraints of the day, and so the choice of refrigerants must be reconsidered when those constraints change, as is the case today with the concern of the contribution of HFCs to anthropogenic global warming (Velders *et al.* 2009).

In the present project, we carry out two parallel and complementary approaches to identify refrigerants possessing both low values of GWP and suitable thermodynamic properties. In a companion paper (Domanski *et al.*, 2013), we determine the optimum thermodynamic parameters for refrigerants in the vapor compression cycle, an analysis we have termed the "exploration of thermodynamic space."

In the second approach (presented here), we select from a public-domain database of 100 million chemical compounds a set of 56 000 candidate molecules composing only a limited set of elements and having 15 or fewer atoms in the molecule. For these candidates we estimate the GWP, flammability, critical temperature and other thermodynamic parameters and filter out those molecules having functional groups known to be generally toxic or unstable. This yields a set of about 1200 candidate refrigerants. The details of this analysis are presented by Kazakov *et al.* (2012) and McLinden *et al.* (2012). In the present paper, we examine in some detail the 62 fluids resulting from this screening process that also have critical temperatures between 300 K and 400 K, which is to say critical temperatures suitable for use in common types of refrigeration and air-conditioning equipment.

2. EXPLORATION OF THERMODYNAMIC SPACE

We explore "thermodynamic space" in terms of fundamental fluid parameters, such as critical temperature and vapor heat capacity. By use of evolutionary algorithms, we identify the most important thermodynamic parameters and their optimum values. We use the concept of corresponding states to model the fluid properties; this allows us to simulate fluids in terms of nine property parameters. Thus, this approach is not limited to fluids that are known, although corresponding states calculations are tied to real "reference fluids," so that thermodynamic consistency between properties is maintained.

That work is presented in a companion paper at this conference (Domanski *et al.*, 2013), and we give a brief summary here to establish the context of the integrated study. The simple (ideal) vapor compression cycle and several variations on the simple cycle (liquid-line/suction-line heat exchanger, economizer, and work recovery device) were considered. By use of evolutionary algorithms, the most important thermodynamic parameters and their optimum values were determined. This is illustrated by the so-called "Pareto front" on coordinates of inverse volumetric capacity versus inverse coefficient of performance (COP). An example Pareto front is presented in Figure 1 for the simple vapor compression cycle and temperatures representative of an air-conditioning application.

The Pareto front represents the thermodynamic limit to performance in a given cycle and application. It illustrates a fundamental tradeoff between volumetric capacity and COP (*i.e.*, efficiency): it is not possible to achieve both a high COP and high capacity. Figure 1 also plots several current refrigerants, and this illustrates that better refrigerants (*i.e.*, lying closer to the Pareto front) are at least *allowed* by thermodynamics. The analysis shows that the refrigerant critical temperature T^{crit} is associated with the position on the Pareto front (*i.e.*, capacity versus COP tradeoff). Otherwise, a high value of critical pressure p^{crit} and a low value of the acentric factor ω (a parameter related to the slope of the vapor-pressure curve with temperature) results in the "best" performance, *i.e.*, closest to the Pareto front. The optimum value of the ideal-gas heat capacity C_p° varies with the cycle; low values are optimal for the simple cycle, while cycles with a liquid-line/suction line heat exchanger are better matched with refrigerants having higher values of C_p°. The other thermodynamic parameters have a relatively small effect. We use these results to inform the selection of refrigerants presented in this paper.

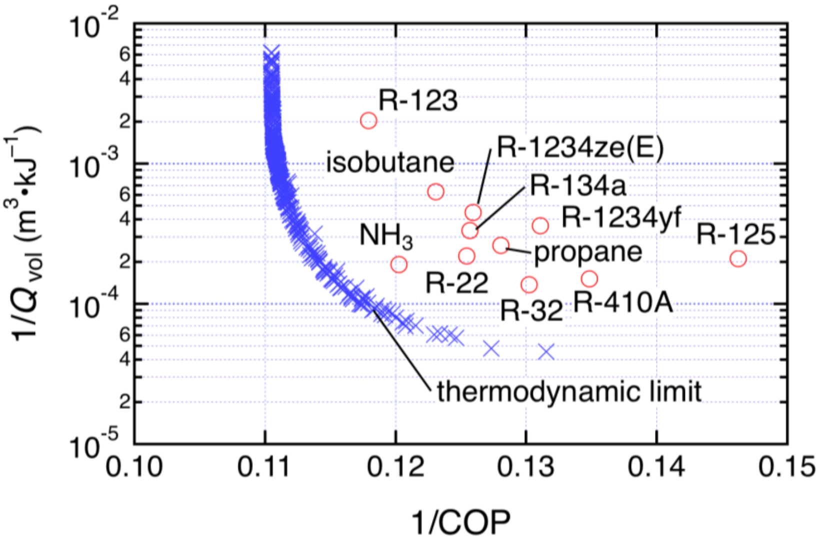

Figure 1. Pareto front (×) and selected current refrigerants (○) for the simple vapor compression cycle.

3. SCREENING OF CANDIDATE MOLECULES

We start with the public-domain PubChem database of the National Institutes of Health (Bolton *et al.*, 2008), which lists more than 100 million compounds. This number is reduced to 56 203 candidates by considering only molecules with 15 or fewer atoms and comprising only the elements C, H, F, Cl, Br, O, N, and/or S. We limit the molecular size to a maximum of 15 atoms, because the refrigerants in current commercial use are all small molecules, and McLinden (1990) provided a thermodynamic basis for preferring small molecules. The choice of elements traces back to Midgley (1937) who observed that only a small portion of the periodic table would form compounds sufficiently volatile to serve as refrigerants. This is confirmed by the ASHRAE (2010) classification standard for refrigerants, where the only exceptions among the listed refrigerants are helium, neon, and argon, which are used in cryogenic refrigeration systems, but which have boiling points and critical temperatures that are too low for normal refrigeration applications. We include chlorine and bromine despite their potential to deplete stratospheric ozone. A compound containing Cl or Br, and having a very short atmospheric lifetime, would have a very small ODP and might be acceptable.

3.1 Estimation of GWP

The global warming potential of a chemical results from the combination of its *radiative forcing* and *atmospheric lifetime*, together with the time frame for evaluation. The radiative forcing is the change in net irradiance at the tropopause due to the change in atmospheric concentration of a trace gas resulting from a pulse release of that gas. The *radiative efficiency* (RE) is the radiative forcing for a unit change in atmospheric concentration.

For the present purpose of screening a large number of compounds, a direct estimation of the GWP was not possible for two reasons. First, GWP is a complex characteristic of a chemical and, second, the “learning set” that was available to develop a direct estimate was very limited and was heavily biased towards present classes of fluids, such as the CFCs, HCFCs, and HFCs. Instead, Kazakov *et al.* (2012) separately estimated the RE and atmospheric lifetimes of the 56 000 candidate compounds.

The concept of GWP has a number of weaknesses, such as the neglect of the effect of reaction products resulting from breakdown and the assumption of a global mean concentration. Our estimation of GWP introduces further uncertainties—in particular, our consideration of reaction only with hydroxyl radicals in the atmosphere yielded estimated values that represent an upper bound on GWP. Reaction with OH is the dominant loss mechanism for most of the compounds considered. A comparison of the GWP values based on a 100-year time horizon (designated GWP_{100}) reported in the literature (which are available for 103 fluids) with values estimated by Kazakov *et al.* (2012) are shown in Figure 2. Overall, there is significant scatter, but the estimated values follow the expected trend, and the logarithmic root mean square deviation (RMSD) corresponds to a factor of 3.0. This is adequate for screening purposes, especially in view of GWP_{100} ranging over four orders of magnitude. The most significant outlier in Figure 2, CF_3I, is a compound that is quickly photolyzed by ultraviolet light, but which reacts slowly with OH; thus the high estimate for GWP_{100} is obtained.

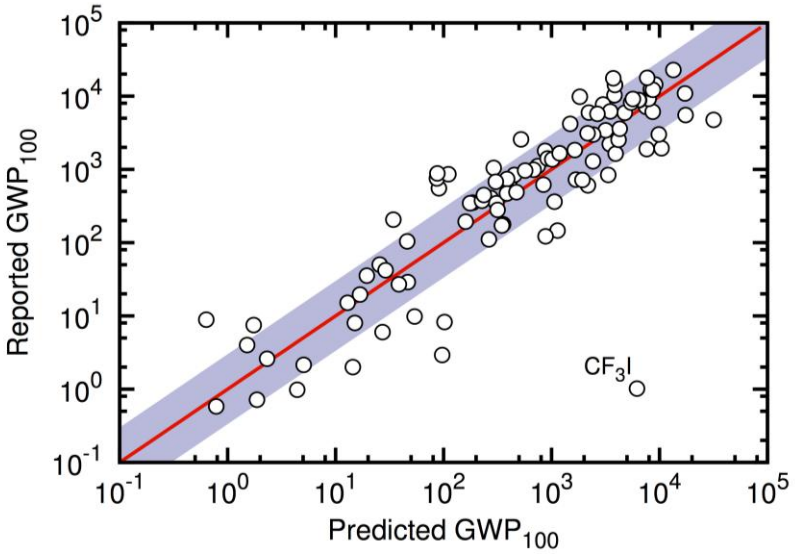

Figure 2. Comparison of estimated and reported values of GWP_{100}; the shaded area represents the RMSD.

3.2 Estimation of Flammability

For the estimation of flammability, Kazakov *et al.* (2012) started with the correlation between the heat of combustion (ΔH_{comb}) and the lower flammability limit (LFL), with both expressed on a mass basis. The heat of combustion is readily calculated given the heats of formation, and these had already been estimated for each of the 56 000 compounds in the course of determining the infrared spectra needed for the RE calculation. To verify the method, heats of combustion for 468 chemicals were calculated by the same methods and compared to experimental values of LFL taken from the DIPPR (2011) compilation, as shown in Figure 3. Although several outliers are present, the estimation method is generally seen to work well, with a logarithmic RMSD corresponding to a factor of 1.24. These results are correlated by the empirical function

$$\mathrm{LFL/kg\cdot m^{-3}} = 2.38 \times \left(\Delta H_{comb} / \mathrm{MJ\cdot kg^{-1}}\right)^{-1.19}. \qquad (1)$$

Note that this method and Eq. 1 apply only to materials with a positive heat of combustion. Materials with ΔH_{comb} lower than about 3 $\mathrm{MJ{\cdot}kg^{-1}}$ (including negative values) are generally nonflammable.

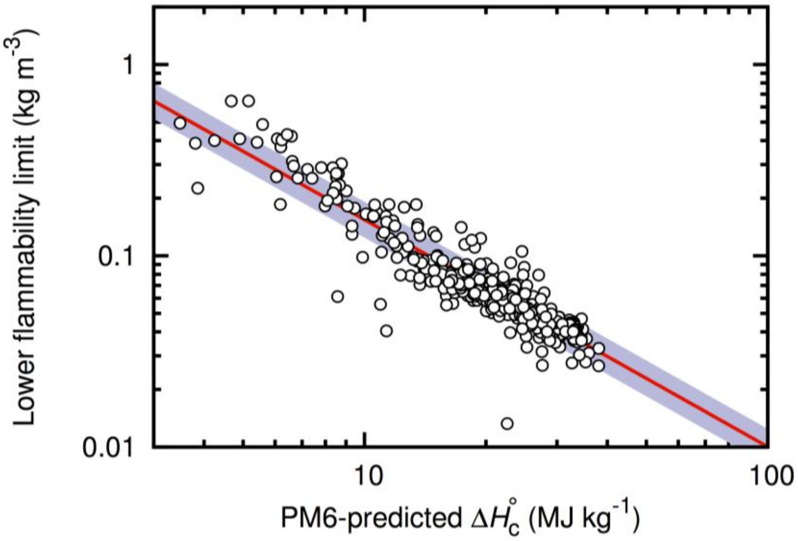

Figure 3. Experimental lower flammability limit (from DIPPR, 2011) versus estimated heat of combustion for 468 chemical compounds; the shaded area represents the RMSD.

3.3 Estimation of Critical Parameters and Other Screening Criteria

The methods for the estimation of critical temperature and critical pressure were described by Kazakov *et al.* (2010). The ideal-gas heat capacity C_p° was estimated from a standard statistical-mechanical, rigid-rotor/harmonic oscillator model (McQuarrie, 1976). This model requires only the vibrational frequencies, and those were taken from the PM6 statistical-mechanical calculations that were done for the RE estimation. (PM6 refers to the level of theory employed.) C_p° is a function of temperature, and we base the screening on its value at 298.15 K.

A cursory toxicity filtering was performed based on a list of markers and associated rules for the elimination of compounds that contain them, compiled by Lagorce *et al.* (2008). Although this test is by no means comprehensive, it allows elimination of some obviously toxic compounds (such as cyanide compounds), and could be performed very rapidly.

An additional screening was applied to eliminate unstable fluids (Kazakov *et al.*, 2012). While some degree of instability is required for reaction in the atmosphere and low GWP, excessive instability would not be acceptable for a refrigerant expected to operate for many years in a sealed system, and so we screened out a number of generally unstable functional groups. This screening was based on bond dissociation energies (BDE). For example, the incremental BDE of a carbon-carbon double bond dissociating to a single bond is 83 $\mathrm{kJ{\cdot}mol^{-1}}$ compared to 38 $\mathrm{kJ{\cdot}mol^{-1}}$ (Luo, 2007) for a carbon-carbon triple bond dissociating to a double bond. Thus, from a strictly thermodynamic viewpoint (*i.e.*, neglecting reaction kinetics), double bonds are generally more stable than triple bonds. We postulate that if a double bond provides sufficient instability to give an acceptable GWP, then there is little reason to prefer a compound with a triple bond. We recognize that counterexamples to this general rule exist, and if no suitable candidates are found, the fluids eliminated by this screen should be reexamined (and we do this in Section 4.7). Compounds with any of the following functional groups were eliminated: (1) triple bond, (2) nitro ($-NO_2$) group, (3) peroxide (–O–O–) group, (4) 3- and 4-member rings, (5) disulfide (–S–S–) group, (6) –C=S group, (7) linear diene (–C=C–C=C–), (8) NO and NN groups (any bond order), (9) N–X and O–X groups, where X = F, Cl, or Br, (10) =C= group, and (11) groups exhibiting keto-enol tautomerism.

4. RESULTS

Of the 56 203 compounds screened by Kazakov *et al.* (2012), 52 565 (93.5 %) had GWP_{100} values less than 200. The majority of these compounds, including those with zero or near-zero GWP_{100}, were not suitable for use as refrigerants because of very low or very high critical temperatures or stability or toxicity problems. Thus, a screening based solely on GWP_{100} does not provide a sufficient constraint for selecting candidate refrigerants, and the additional filters discussed in Section 3 were applied. We postulated that a refrigerant with low or no flammability would be desirable, and thus we filtered out fluids with a LFL less than $0.10\ \mathrm{kg{\cdot}m^{-3}}$. This was also in recognition that among flammable fluids, a number of excellent refrigerants are well known and readily available, namely the simple hydrocarbons, such as propane and isobutane, as well as dimethyl ether. The primary thermodynamic constraint was a critical temperature in the range of 300 K to 550 K. The upper limit is substantially above current refrigerants in most applications. (For example, R-123, which is used in low-pressure centrifugal systems, has one of the highest values of T^{crit} among current refrigerants at 456.8 K.) This generous constraint on the critical temperature would also encompass working fluids for high-temperature heat pumps and organic Rankine-cycle power systems.

The result of the screening was a set of about 1200 candidate fluids. (The full list is presented in the Supporting Information of Kazakov *et al.*, 2012.) These fluids are presented on T^{crit}–GWP_{100} coordinates in Figure 4, which is subdivided into several chemical classes. The vast majority of the candidates are halogenated because of the flammability constraint. Of the 1200 compounds, only six did not contain one or more halogens. Over 60 % of the halogenated candidates contain only fluorine, because the addition of heavier chlorine or bromine atoms, while also suppressing flammability, generally increases the critical temperature, often exceeding the constraint on T^{crit}.

This large number of candidates might suggest that finding alternative fluids with low GWP is easy. But only a small percentage (62 candidates) have critical temperatures in the range $300\ \mathrm{K} < T^{\mathrm{crit}} < 400\ \mathrm{K}$, which is the range required for use in the majority of current types of refrigeration equipment. Use of a refrigerant outside this range would require extensive redesign of the equipment. A high-critical-temperature refrigerant would result in a low volumetric capacity, while a low-critical-temperature fluid would most likely involve a transcritical cycle and increased expansion losses. There are also other tradeoffs that must be considered. The 62 candidates are presented in Table 1, which lists their chemical names and structures and several key thermodynamic parameters. The values listed are those estimated by Kazakov *et al.* (2012), except where noted. The uncertainties in the estimated values of GWP_{100} and LFL correspond to logarithmic RMSD of 3.0 and 1.24, respectively. For T^{crit} and the $T^{\mathrm{crit}}/p^{\mathrm{crit}}$ ratio, the estimation method of Kazakov *et al.*, 2010 gives errors of less than 10 K and 3 %, respectively, for 90 % of the compounds considered in the development of the method. The estimated uncertainty for the C_p° values is 3 %. Also included is the identifying number in the PubChem database; this allows access to further data on each candidate (U.S. NIH, 2013).

We discuss the 62 candidates and some of their tradeoffs in the following sections. Candidates of similar chemical class are discussed together, and the order of discussion parallels the ordering in Table 1. We focus on the thermodynamic characteristics, but also comment on toxicity and reactivity where data are available. Toxicity data are drawn from a variety of sources, including safety standards, compilations of toxic industrial chemicals, regulatory filings, and material safety data sheets (MSDS) of chemical manufacturers. Among the various sources, we apply a hierarchy. Refrigerant safety classifications are based largely on health effects resulting from chronic (long-term) exposures, and we reference data on chronic exposures where available. Chronic toxicity is often characterized by allowable workplace exposure limits (based on a 40-hour work week); such limits can be assigned by regulatory agencies, but also include values recommended by chemical manufacturers. They include Recommended Exposure Limits (REL) of the U.S. National Institute for Occupational Safety and Health (U.S. NIOSH, 2007).

Numerous metrics for acute (short-term) exposures are available. The U.S. NIOSH (2007) defines “IDLH” (immediately dangerous to life and health) levels; for flammable compounds, the IDLH is set to 10 % of the lower flammability limit. ASHRAE Standard 34 (ASHRAE, 2010) defines an “acute toxicity exposure limit” (ATEL), which is an approximation to IDLH values for fluids lacking an IDLH. We also refer to “protective action criteria” (PAC) values compiled by the U.S. Department of Energy (2012). These values are for acute (short-term) exposure and are available for 3387 chemicals (mostly those in current industrial use). Three PAC values are compiled: PAC-1 is the level (expressed in parts per million (ppm) in air) resulting in “mild, transient health effects,” PAC-2 levels result in “irreversible or other serious health effects that could impair the ability to take protective action," and PAC-3 is the level for "life-threatening health effects." In the absence of other chronic or acute measures, we reference the concentration lethal to 50 % of the test animals (LC_{50}); often these are reported for four-hour exposures on rats. The LC_{50} will be a higher value than the IDLH or PAC-3 levels. Finally, sometimes only limited data, meant only for initial screening or not taken in accordance with current protocols, are available.

This discussion is not meant to be complete or authoritative; we present it to point out known safety hazards with chemicals that might otherwise have promising thermodynamic characteristics. For comparison, the REL for CO_2 is 5 000 ppm, with PAC-1, PAC-2, and PAC-3 levels of 30 000 ppm, 30 000 ppm, and 50 000 ppm, respectively. R-134a has a REL of 1000 ppm, an ATEL of 50 000 ppm, and PAC-1, PAC-2, and PAC-3 levels of 8 000 ppm, 13 000 ppm, and 27 000 ppm, respectively. Ammonia has a REL of 25 ppm, IDLH of 300 ppm, and PAC-1, PAC-2, and PAC-3 levels of 30 ppm, 160 ppm, and 1100 ppm, respectively.

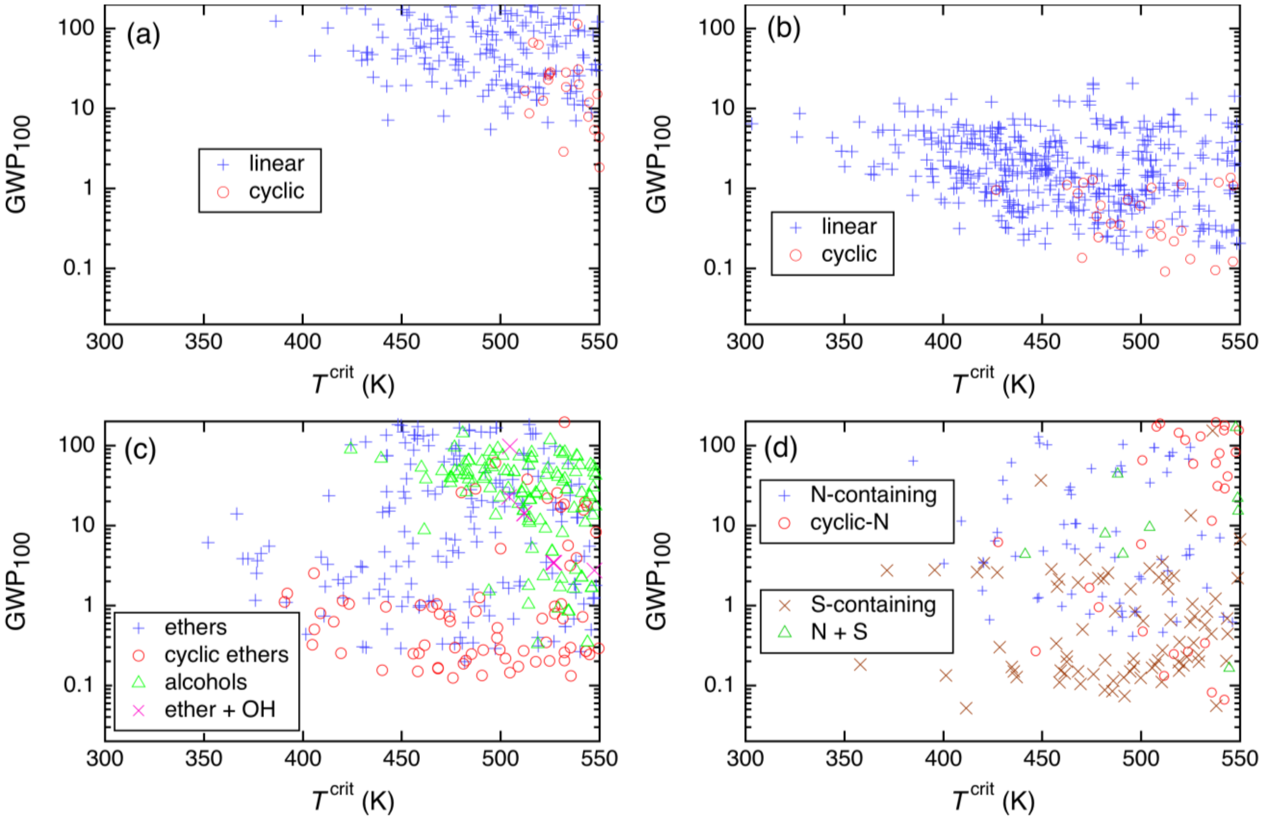

Figure 4. Compounds remaining after applying all filters and grouped by chemical class:
(a) alkanes; (b) olefins; (c) compounds containing oxygen; (d) compounds containing N and/or S.

4.1 Halogenated Alkanes

The halogenated alkanes are saturated, that is, they contain only single bonds. This group includes the familiar HFC refrigerants. While a large number of candidates are indicated in Figure 4a, only one of these has a critical temperature less than 400 K, namely R-152a; this fluid has an LFL = 0.11 $kg{\cdot}m^{-3}$, which is just within the cutoff for this parameter. Other familiar fluids, such as R-32, R-134a and R-143a, for example, have values of GWP_{100} greater than the somewhat arbitrary screening cutoff of 200. (See, for example, Brown (2013) for a discussion of what constitutes "low GWP.").

4.2 Fluorinated Olefins

The olefins contain at least one carbon-carbon double bond, and this group includes the hydrofluoroolefins (HFOs), which are the focus of considerable current interest in the industry. All of the fluids in this class have predicted GWP_{100} values less than ten.

We start with the propenes (compounds with three carbon atoms and one double bond) and proceed from fully fluorinated to less fluorinated. R-1216 has fairly low toxicity on acute exposure (PAC-1 of 480 ppm), but it is highly toxic upon chronic exposure. Its workplace exposure limit is 0.5 ppm to 2.0 ppm (ECETOC,

Table 1. Summary of the candidates passing the screening filters and also having 300 K < T^{crit} < 400 K.

PubChem no.	IUPAC name	Formula	Structure	ASHRAE designation	GWP_{100}	LFL ($kg \cdot m^{-3}$)	T^{crit} (K)	p^{crit} (MPa)	C_p° (298 K) ($J \cdot mol^{-1} \cdot K^{-1}$)
Halogenated Alkanes									
6368	1,2-difluoroethane	$C_2F_2H_2$	CHF_2-CH_3	R-152a	124	0.11	386.4§	4.52§	66.5§
Halogenated Alkenes (Fluorine only)									
6369	1,1-difluoroethene	$C_2F_2H_2$	CF_2=CH_2	R-1132a	4.4	0.130	302.7*	4.43*	57.8
8301	1,1,2,2-tetrafluoroethene	C_2F_4	CF_2=CF_2	R-1114	6. 5	0.360	307.3*	3.94*	80.5
69647	1,1,3,3,3-pentafluoropropene	C_3F_5H	CF_2=CH-CF_3	R-1225zc	4.3	0.319	343.9	3.39	106.9
5708673	(Z)-1,2,3,3,3-pentafluoro-1-propene	C_3F_5H	CHF=CF-CF_3	R-1225ye(Z)	2.9	0.296	348.6	3.85	108.8
5365501	(E)-1,2-difluoroethene	$C_2F_2H_2$	CHF=CHF	R-1132(E)	1.9	0.124	350.1	6.77	58.1
6329539	(E)-1,2,3,3,3-pentafluoroprop-1-ene	C_3F_5H	CHF=CF-CF_3	R-1225ye(E)	2.9	0.296	353.8	3.74	108.7
594043	1,1,2,3,3-pentafluoroprop-1-ene	C_3F_5H	CF_2=CF-CHF_2	R-1225yc	6.8	0.282	357.6	3.74	108.0
8302	1,1,2,3,3,3-hexafluoroprop-1-ene	C_3F_6	CF_2=CF-CF_3	R-1216	8.7	0.441	359.0*	3.13*	119.9
5462921	(Z)-1,2-difluoroethene	$C_2F_2H_2$	CHF=CHF	R-1132(Z)	1.5	0.123	365.1	5.32	58.1
67745	1,1,2,3,3,4,4,4-octafluorobut-1-ene	C_4F_8	CF_2=CF-CF_2-CF_3	R-1318cycm	5. 1	0.452	367.1	2.71	162.7
2776731	2,3,3,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CH_2=CF-CF3	R-1234yf	1.5	0.207	367.8§	3.38§	101.5§
61109	1,1,3,3,3-pentafluoro-2-(trifluoromethyl)prop-1-ene	C_4F_8	CF_2=C(-CF_3)$_2$		5.4	0.517	369.4	2.47	158.9
21096859	1,1,3,3,4,4,4-heptafluorobut-1-ene	C_4F_7H	CF_2=CH-CF_2-CF_3	R-1327czcm	2.0	0.353	369.5	2.56	149.7
14310966	1,1,2-trifluoroprop-1-ene	$C_3F_3H_3$	CF_2=CF-CH_3	R-1243yc	5.4	0.135	375.3	3.65	92.7
21731865	1,1,3,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CF_2=CH-CHF_2	R-1234zc	3.5	0.203	375.8	3.88	95.9
11855995	1,1,2,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CF_2=CF-CH_2F	R-1234yc	2.8	0.190	377.4	3.88	98.6
12672	3,3,3-trifluoroprop-1-ene	$C_3F_3H_3$	CH_2=CH-CF_3	R-1243zf	0.82	0.144	378.6*	3.61*	88.2
5708720	(E)-1,3,3,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CHF=CH-CF_3	R-1234ze(E)	1.7	0.212	382.5§	3.64§	99.3§
12543097	(Z)-1,2,3,3,4,4,4-heptafluorobut-1-ene	C_4F_7H	CHF=CF-CF_2-CF_3	R-1327eycm(Z)	1.4	0.333	386.1	2.73	161.1
2775851	(E)-1,1,1,2,3,4,4,4-octafluorobut-2-ene	C_4F_8	CF_3-CF=CF-CF_3	R-1318myym(E)	5.3	0.480	386.1	3.08	151.6
3034116	(Z)-1,1,1,2,3,4,4,4-octafluorobut-2-ene	C_4F_8	CF_3-CF=CF-CF_3	R-1318myym(Z)	5.3	0.477	390.1	2.88	161.3
21096848	1,1,2,3,4,4,4-heptafluorobut-1-ene	C_4F_7H	CF_2=CF-CHF-CF_3	R-1327cyem	4.1	0.334	390.5	3.03	149.7
23237196	(E)-1,2,3,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CHF=CF-CHF_2	R-1234ye(E)	2.3	0.193	391.7	4.45	97.0
20496975	2-(difluoromethyl)-1,1,3,3,3-pentafluoroprop-1-ene	C_4F_7H	CF_2=C(-CHF_2)(-CF_3)		5.0	0.357	393.7	2.69	147.6
5708514	(Z)-1,1,1,2,4,4,4-heptafluorobut-2-ene	C_4F_7H	CF_3-CF=CH-CF_3	R-1327myzm(Z)	1.8	0.367	393.8	2.92	148.6
11116025	(Z)-1,3,3,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CHF=CH-CF_3	R-1234ze(Z)	1.4	0.211	394.6	3.86	96.1
22956412	1,1,3-trifluoroprop-1-ene	$C_3F_3H_3$	CF_2=CH-CH_2F	R-1243zc	1.2	0.135	395.0	4.01	87.3
12633094	(E)-1,3,3,4,4,4-hexafluorobut-1-ene	$C_4F_6H_2$	CHF=CH-CF_2-CF_3	R-1336ezcm(E)	0.74	0.258	398.9	3.03	140.2
88954	1,1,2,3,4,4,4-heptafluoro-3-(trifluoromethyl)but-1-ene	C_5F_{10}	CF_2=CF-CF(-CF_3)$_2$		3.7	0.472	399.1	2.16	204.6
12576087	1,1,3,3,4,4,4-heptafluoro-2-(trifluoromethyl)but-1-ene	C_5F_{10}	CF_2=C(-CF_3)CF_2-CF_3		2.9	0.510	399.9	2.03	201.9
23237197	(Z)-1,2,3,3-tetrafluoroprop-1-ene	$C_3F_4H_2$	CHF=CF-CHF_2	R-1234ye(Z)	2.2	0.194	400.0	4.23	97.0
Halogenated Alkenes (Fluorine plus Chlorine or Bromine)									
6594	1-chloro-1,2,2-trifluoroethene	C_2ClF_3	CClF=CF_2	R-1113	12.	0.427	378.9*	4.06*	82.8

102335	2-chloro-1,1,3,3,3-pentafluoroprop-1-ene	C_3ClF_5	$CF_2=CCl-CF_3$	R-1215xc	9.2	0.522	380.6	2.93	122.2
521001	3-chloro-1,1,3,3-tetrafluoroprop-1-ene	C_3ClF_4H	$CF_2=CH-CClF_2$	R-1224zc	4.7	0.347	382.4	3.19	110.0

Table 1. Summary of the candidates passing the screening filters and also having 300 K < T^{crit} < 400 K (continued).

PubChem no.	**IUPAC name**	**Formula**	**Structure**	**ASHRAE designation**	**GWP$_{100}$**	**LFL** ($kg\cdot m^{-3}$)	T^{crit} (K)	p^{crit} (MPa)	C_p° **(298 K)** ($J\cdot mol^{-1}\cdot K^{-1}$)
Halogenated Alkenes (Fluorine plus Chlorine or Bromine) (continued)									
13717712	(Z)-1-chloro-1,2,3,3,3-pentafluoroprop-1-ene	C_3ClF_5	$CClF=CF-CF_3$	R-1215yb(Z)	9.2	0.491	387.1	3.22	122.8
5463105	(E)-1-chloro-1,2-difluoroethene	C_2ClF_2H	$CClF=CHF$	R-1122a(E)	4.3	0.258	394.1	5.12	71.2
22714818	(E)-1-chloro-1,2,3,3,3-pentafluoroprop-1-ene	C_3ClF_5	$CClF=CF-CF_3$	R-1215yb(E)	9.6	0.489	394.9	3.38	122.9
9664	2-chloro-1,1-difluoroethene	C_2ClF_2H	$CF_2=CHCl$	R-1122	3.9	0.269	397.6	4.50	70.5
14047952	3-bromo-1,1,2,3,3-pentafluoroprop-1-ene	C_3BrF_5	$CF_2=CF-CF_2Br$	R-1215ycB1	9.1	0.543	399.0	3.22	126.8
Halogenated Oxygenates									
14474	1,1,2-trifluoro-2-(trifluoromethoxy)ethene	C_3F_6O	$CF_2=CF-O-CF_3$		6.1	0.682	352.0	3.37	135.9
2783163	1,1,2,3,3-pentafluoro-3-(trifluoromethoxy)prop-1-ene	C_4F_8O	$CF_2=CF-CF_2-O-CF_3$		14.	0.700	366.6	2.25	176.7
14875812	(E)-1,2,3,3,3-pentafluoro-1-(trifluoromethoxy)prop-1-ene	C_4F_8O	$CF_3-CF=CF-O-CF_3$		3.9	0.696	372.3	2.32	176.4
21940994	1-fluoro-1-(trifluoromethoxy)ethene	$C_3F_4H_2O$	$CH_2=CF(-O-CF_3)$		1.2	0.310	376.0	3.41	114.0
14617222	1,1,3,3,3-pentafluoro-2-(trifluoromethoxy)prop-1-ene	C_4F_8O	$CF_2=C(-CF_3)(-O-CF_3)$		2.5	0.696	376.6	2.44	175.3
45075659	(Z)-1,2,3,3,3-pentafluoro-1-(trifluoromethoxy)prop-1-ene	C_4F_8O	$CF_3-CF=CF-O-CF_3$		3.6	0.695	376.9	2.37	176.3
82672	1,1,1,2,2-pentafluoro-2-(1,2,2-trifluoroethenoxy)ethane	C_4F_8O	$CF_2=CF-O-CF_2-CF_3$		4.5	0.615	378.8	2.39	178.7
21325449	1-(difluoromethoxy)-1,2,2-trifluoroethene	C_3F_5HO	$CF_2=CF-O-CHF_2$		5.5	0.414	382.9	3.33	123.8
11744752	2,2,4,5-tetrafluoro-1,3-dioxole	$C_3F_4O_2$	$c-CF_2-O-CF=CF-O-$		1.1	0.515	390.6	3.94	114.1
22292402	1,1-difluoro-2,2-bis(trifluoromethoxy)ethene	$C_4F_8O_2$	$CF_2=C(-O-CF_3)_2$		1.1	1.036	391.7	4.45	97.0
12140230	2,2,3,3,4,5-hexafluorofuran	C_4F_6O	$c-CF_2-CF_2-CF=CF-O-$		1.4	0.383	392.2	3.05	140.4
Halogenated Nitrogen Compounds									
10220269	1,2,2-trifluoro-N,N-bis(trifluoromethyl)ethenamine	C_4F_9N	$(CF_3)_2-N-CF=CF_2$		11.	0.663	373.2	2.28	190.7
10214404	N-(difluoromethyl)-N,1,1,1-tetrafluoromethanamine	C_2F_5HN	$CF_3-NF(-CHF_2)$		49.	0.624	382.6	3.60	122.4
144610	N-(difluoromethyl)-1,1,1-trifluoro-N-(trifluoromethyl)methanamine	C_3F_8HN	$CHF_2-N-(CF_3)_2$		64.	1.014	384.8	2.44	163.2
141139	N,N,1,1-tetrafluoromethanamine	CF_4HN	CHF_2-NF_2		20.	0.383	398.9	5.06	80.6
Halogenated Sulfur Compounds									
30555	trifluoromethanethiol	CF_3SH	CF_3-SH		0.18	0.517	358.0	2.86	78.1
136206	trifluoro(trifluoromethylsulfanyl)methane	C_2F_6S	CF_3-S-CF_3		2.8	0.964	376.8*	2.59	127.4
19779344	1,1,1,2,2-pentafluoro-2-(trifluoromethylsulfanyl)ethane	C_3F_8S	$CF_3-S-CF_2-CF_3$		2.8	0.798	395.6	2.07	170.2
Inorganic Compounds									
280	carbon dioxide	CO_2	CO_2	R-744	1.000	n/a	304.1§	7.38§	37.1§
222	ammonia	NH_3	NH_3	R-717	<1		405.4§	11.33§	35.6§
Other									
136491	1,2-difluoroethyne	C_2F_2	$FC\equiv CF$		0.2	0.107	322.6	5.38	61.1
69578	3,3,3-trifluoroprop-1-yne	C_3F_3H	$CF_3-C\equiv CH$		1.4	0.144	366.0	3.67	80.8
69654	1,1,1,4,4,4-hexafluorobut-2-yne	C_4F_6	$CF_3-C\equiv C-CF_3$		0.25	0.275	374.8	2.82	131.5

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§Literature values taken from NIST REFPROP (Lemmon, *et al.*, 2010).

*Literature values taken from NIST TDE (Frenkel *et al.*, 2011).

2005), and this would rule out its use as a refrigerant, even in industrial settings. This illustrates that the toxicity screen discussed in Section 3.3 was a rough filter for only the most toxic functional groups, and that some toxic compounds will have passed that screen.

All four possible isomers of R-1225, including stereo isomers, are listed in Table 1, with predicted critical temperatures ranging from 343.9 K to 357.6 K. This range of critical temperatures makes these fluids interesting as replacements in air-conditioning equipment currently using R-410A ($T^{\mathrm{crit}} = 344.45$ K). Their range of critical pressures fall in a fairly narrow range of (3.4 to 3.8) MPa, which are similar to current refrigerants. Their ideal-gas heat capacities (C_p°) range from (106.9 to 108.8) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$; these are higher than optimal for the simple vapor compression cycle, and these fluids may benefit from a liquid-line/suction-line heat exchanger or other cycle modifications (Domanski *et al.*, 2013). Initial (acute) toxicology testing on R-1225ye(Z) was encouraging. Lindley and Noakes (2010) report a $\mathrm{LC_{50}} > 50\,000$ ppm for R-1225ye(Z), based on four-hour inhalation tests with rats; 28-day, sub-chronic testing on rats showed toxicological effects at a concentration of 10 000 ppm. The conclusion was that such toxicity “prevented its use as an industrial refrigerant.” Similar conclusions were reported for R-1225ye(E) (Lindley and Noakes, 2010). However, Schuster (2009) summarized confidential internal company reports showing an $\mathrm{LC_{50}}$ between 10 430 ppm and 20 200 ppm, and results from 28-day testing showing toxic effects at 1000 ppm, and reproductive effects at 500 ppm. He reported that “development of … HFO-1225yeZ as foam blowing agent has been discontinued after the observation of several adverse effects in the test animals.” The discrepancy in these reports can not be resolved at this time.

R-1225zc has a four-hour rat ALC (approximate lethal concentration) of 851 ppm; it also was positive for genetic effects (Lindley and Noakes, 2010). They mention the “$=\mathrm{CF_2}$ structural alert” in regards to R-1225zc; this is the observation that the $=\mathrm{CF_2}$ group has a high reactivity that is often associated with toxic effects. This leaves R-1225yc, but this compound also possesses a $=\mathrm{CF_2}$ group. Powrie *et al.* (2007) present results of *in vitro* testing of the glutathione metabolic pathway and report strong positive results (*i.e.*, toxic effects) for R-1225zc and R-1225yc. By contrast, R-1225ye(E) and R-1225ye(Z) showed small effects in the same test.

All seven possible stereo isomers of R-1234 are listed in Table 1; these have predicted critical temperatures ranging from 363.4 K (R-1234yf) to 400.0 K (R-1234ye(Z)). Two of these—R1234yf and R1234ze(E)—have received a safety classification of A2L under ASHRAE Standard 34, meaning that they are of “lower toxicity” and are only marginally flammable, defined as having a flame speed less than 10 $\mathrm{cm{\cdot}s^{-1}}$. Both are in limited commercial production. (We reference the ASHRAE Standard; the analogous ISO Standard 817 (ISO, 2012) is very similar in its nomenclature and classifications, but ISO 817 is currently a “final draft international standard” and is not yet adopted.) The values of C_p° for the R-1234 isomers range from (95.9 to 101.5) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, and these fluids may benefit from a liquid-line/suction-line heat exchanger or other cycle modifications (Domanski *et al.*, 2013). Their critical pressures range from 3.8 MPa to 4.5 MPa, which is in the range of most current refrigerants.

Among the R-1234 isomers, besides the now-familiar R-1234yf and R-1234ze(E), R1234ze(Z) is being actively investigated (see, for example, Brown *et al.*, 2009; Higashi *et al.*, 2013). R-1234ye(E) has the highest critical pressure (4.45 MPa) of the R-1234 isomers, and this is associated with good cycle performance. R-1234zc and R-1234yc contain the $=\mathrm{CF_2}$ group that was noted as problematic in connection with the toxicity of R-1225zc. In view of this and thermodynamic properties that are very similar to the now-commercialized R-1234ze(E), these two isomers would be of a lower priority for further investigation.

Table 1 includes three of the eight possible stereo isomers of R-1243. (The other five possible R-1243 isomers were included in the screening but have predicted critical temperatures between 406.6 K and 429.9 K, and so are not listed in Table 1.) All of the R-1243 isomers would be expected to be more flammable than the R-1234 isomers due to their higher hydrogen content; they would likely receive a “2” flammability classification under ASHRAE Standard 34 (as opposed to the “2L” classification for R-1234yf and R-1234ze(E)). Brown (2012) noted that R-1243zf was cited in a number of patents between 2010 and 2012, and detailed property data are starting to become available for it (for example, see Brown *et al.*, 2013). In 28-day sub-chronic toxicity testing on rats (Huntington Life Sciences, 2010) myocardial (heart) effects were observed at concentrations ≥ 4967 ppm. No value was established for the NOAEL (no observed adverse effect level). It is worthwhile to note that concentrations of up to 50 000 ppm were tested in this same program, and none of the test rats died, indicating that R-1243zf has low acute toxicity. Both R-1243yc and R-1243zc contain the $=CF_2$ group and so might be expected to have higher toxicity, although no toxicity data on these isomers was found. These two isomers have been cited in a number of patents, but only in the context of broad claims listing many possible fluorinated olefins (*e.g.*, Sievert *et al.*, 2010).

The propenes with one or two fluorines (*i.e.*, isomers of R-1261 and R-1252) were predicted to have LFL < $0.10\ \mathrm{kg{\cdot}m^{-3}}$, and so did not pass our flammability screen.

The fluorinated ethenes (compounds with two carbons joined by a double bond) offer interesting thermodynamic properties in light of the results of Domanski *et al.* (2013), although, as a group, they have serious safety issues or unknown risks. R-1114 is also known as tetrafluoroethylene, and it is the precursor to the polymer polytetrafluoroethylene (PTFE). It is a flammable and unstable compound; it is toxic with a workplace exposure limit of 2 ppm (Matheson Tri-Gas, 2008). Its critical temperature of 307.3 K is similar to that of carbon dioxide and so would present the same challenges of operating in a transcritical cycle for most applications while also having significant safety issues. R-1132a is also known as vinylidene fluoride, and it is the precursor to the polymer polyvinylidene fluoride. It is toxic, with a REL of 1 ppm.

R-1132(E) and R-1132(Z) have critical temperatures (350.1 K and 365.1 K, respectively) which would result in relatively high volumetric capacity in a refrigeration cycle. Their high critical pressures (6.8 MPa and 5.3 MPa) and low ideal-gas heat capacities ($58.1\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ for both) are correlated with good cycle efficiency. These compounds have LFL values slightly above our cutoff of $0.10\ \mathrm{kg{\cdot}m^{-3}}$, and are thus predicted to be moderately flammable. Very little information is available on these compounds, and no commercial source for them was found. The analogous chlorinated compounds (1,1-dichloroethene, both (E) and (Z)) “do not polymerize” (Eberhard-Ludwig, 2011) suggesting that R-1132 (both (E) and (Z)) might also be stable.

Ten fluorinated butenes (four carbon atoms) with $T^{\mathrm{crit}} < 400$ K passed all of the screens. Their critical pressures are in a relatively low range from (2.5 to 3.0) MPa and their ideal-gas heat capacities are relatively high, and range from (140.2 to 162.7) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. The values of these parameters suggest that the cycle efficiencies will be relatively low. The two fluorinated pentenes (five carbon atoms) have even more extreme values of p^{crit} and C_p°. While such fluids cannot be ruled out *a priori* on the basis of these thermodynamic parameters, simpler fluids should be investigated first. At least one fluorinated butene (1,1,1,4,4,4-hexafluoro-2-butene) has low toxicity and is being commercialized as a foam-blowing agent for polyurethane and polyisocyanurate foams (DuPont, 2011); its critical temperature is too high for inclusion in Table 1, although with a normal boiling point of 33 ˚C, it may be applicable for centrifugal chillers and/or organic Rankine-cycle power systems. It should be noted that 1,1,3,3,3-pentafluoro-2-(trifluoromethyl)prop-1-ene (also known as perfluoroisobutylene) is an extraordinarily toxic compound (PAC-3 = 0.33 ppm), again emphasizing that the toxicity screen should be viewed with caution.

4.3 Halogenated Olefins—Fluorine plus (Chlorine or Bromine)

Table 1 lists eight alkenes containing chlorine or bromine in addition to fluorine. These have estimated GWP_{100} values ranging from 3.9 to 12—slightly higher than the fluorinated olefins. Chlorine- and bromine-containing compounds typically have non-zero ozone depletion potential, but might be acceptable if the atmospheric lifetime were sufficiently short. For example, the U.S. Environmental Protection Agency has approved the use of R-1233zd(E) ($C_3H_2ClF_3$, $T^{\mathrm{crit}} = 438.8$ K, ODP = 0.00024 – 0.00034) in chiller applications (U.S. EPA, 2012).

As with the fluorine-only alkenes, the two-carbon compounds show the most promising thermodynamic parameters: critical pressures range from (4.0 to 5.1) MPa and C_p° from (70.5 to 82.8) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, although the relatively high critical temperatures of these three fluids (377.8 to 397.6) K would imply relatively low volumetric capacities. R-1113 is known as chlorotrifluoroethylene; it is commercially produced as the precursor to certain specialty fluoropolymers. Toxicity data are available (U.S. EPA, 2008), and the PAC-1, PAC-2, and PAC-3 levels are 16 ppm, 86 ppm, and 420 ppm, respectively.

The propenes in this category have LFL values that range from (0.35 to 0.54) $\mathrm{kg{\cdot}m^{-3}}$, indicating limited to no flammability. They have fairly low critical pressures (2.9 to 3.4 MPa) and fairly high C_p°, ranging from (111 to 127) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. Very little stability or toxicity information was found. In view of thermodynamic parameters that indicate low cycle performance, these would be a low priority for further investigation unless other fluids with similar T^{crit} cannot be found and/or low flammability is an absolute requirement.

4.4 Halogenated Oxygenates

The 11 oxygen-containing compounds in Table 1 are ethers (compounds with a –O– group). They all have a carbon-carbon double bond, and so share the reaction mechanism for atmospheric degradation that gives the olefins their short atmospheric lifetimes and low GWP_{100} values. There has been past interest in fluorinated ethers as refrigerants, as summarized by Bivens and Minor (1998), but those earlier candidates did not posses double bonds. As a class, the fluorinated ethers (without double bonds) have GWP_{100} of the same magnitude as the HFCs. The lowest T^{crit} for a low-GWP ether without a double bond is 413 K for $CF_3OCH_2CH_3$. A number of halogenated alcohols (compounds with an –OH group) also appear in Figure 4c, but these tend to have high critical temperatures and relatively high GWP_{100}. (Bivens and Minor (1998) also discussed fluorinated alcohols.) The lowest T^{crit} among the alcohols was 424 K for CF_3OH.

The ethers identified in the screening generally have low critical pressures and high vapor heat capacities. Two of these (2,2,4,5-tetrafluoro-1,3-dioxole and 1,1-difluoro-2,2-bis(trifluoromethoxy)ethene), however, have values of these parameters more indicative of better cycle efficiency. Both of these are di-ethers (containing two oxygen atoms) and both are fully fluorinated and have LFL values that would indicate very low flammability. The dioxole is a cyclic compound and is described as “a useful monomer, which polymerizes” (Squires, 1985).

4.5 Halogenated Nitrogen and Sulfur Compounds

Four halogenated nitrogen compounds are listed in Table 1; all are amines (compounds with three groups attached to a central nitrogen atom). These compounds have estimated GWP_{100} values in the range of 11 to 64; these are higher than the GWP_{100} of virtually all the other candidates in Table 1 and suggest higher stability. The relatively high LFL values indicate low flammability. Unfortunately, these have low values of critical pressure and relatively high values of C_p°.

Sulfur-containing compounds comprise thiols (–SH, also known as mercaptans) and thiol ethers (–S–). Three sulfur compounds have $300\ \text{K} < T^{\text{crit}} < 400\ \text{K}$. At least two of these, trifluoro(trifluoromethylsulfanyl)-methane and 1,1,1,2,2-pentafluoro-2-(trifluoromethylsulfanyl)ethane, have been investigated for refrigeration uses (Minor and Shealy, 1994). These have low values of critical pressure, although their values of C_p° are lower than the halogenated nitrogen compounds. It should be noted, however, that compounds with N or S are often viewed as problematic due to materials compatibility concerns (amines and thiols are generally corrosive) or other issues, such as odor in the case of thiols.

4.6 Inorganic Compounds

Among the fluids passing the screening criteria only two are inorganic compounds. Carbon dioxide is a well-known fluid with excellent thermodynamic, safety, and environmental properties. It operates in a transcritical cycle in many applications, and the operating pressures in refrigeration systems are very high. Considerable effort has been expended in recent years to mitigate these drawbacks. It is the only fluid listed in Table 1 that currently has an “A1” safety classification under ASHRAE Standard 34 (ASHRAE, 2010). Ammonia has been used as a refrigerant for more than a century. Its toxicity classification of “B” under ASHRAE Standard 34 has limited its use mostly to very large refrigeration systems (*e.g.*, breweries and refrigerated warehouses), although there is much recent interest in applying it to smaller systems. Its critical temperature exceeds 400 K, but we include it in Table 1 because its very high critical pressure results in a normal boiling point typical of fluids with critical temperatures near 375 K. In view of the results of Domanski *et al.* (2013), ammonia’s very high critical pressure (11.3 MPa) and low C_p° ($35.6\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) are seen to be consistent with its reputation for high efficiency.

4.7 Other Compounds

In view of the limited number of candidates that passed all of our screens and also having favorable toxicity results, particularly for $T^{\text{crit}} < 375\ \text{K}$, we reconsidered the 494 compounds that were initially screened out on the basis of having generally unstable functional groups in the molecule. Of this group, 15 had $300\ \text{K} < T^{\text{crit}} < 375\ \text{K}$. These included eight compounds with the –OF group, two with the =C= group, one with a three member ring, and a ketene; these compounds would be expected to be unstable for the reasons outlined in Section 3.3. The –OF group is analogous to the –OH group that defines an alcohol. The bond dissociation energy of the O–F bond, however, is less than one-half that of the O–H bond in an alcohol (Luo, 2007), and the fluorine would likely be reactive with water, forming HF (hydrofluoric acid). Compounds based on the =C= group are known as allenes, and these have been traditionally characterized as "difficult to prepare and very reactive" (Brummond, 2011), although this source also notes that "great advances in the chemistry of allenes have been made [in recent years]." The cyclic compound (tetrafluorocyclopropene, R-C1214) is a three-member ring with a double bond. Sargeant and Krespan (1969) describe it as "remarkably stable" in the absence of an ignition source but went on to describe explosions in pure tetrafluorocyclopropene at a pressure of 0.1 MPa and reactions with water generating HF; they characterized it as "probably toxic" based on lethality to fruit flies at a concentration of 3300 ppm. The fluorinated ketene (2,2-difluoroethenone, $F_2C{=}C{=}O$, $T^{crit} = 308.2$ K) is interesting because it represents another functional group. However, ketenes are generally extremely reactive, and the unfluorinated analogue (ethenone, $H_2C{=}C{=}O$) was described as having the "same order of toxicity as phosgene and hydrogen cyanide" (Wooster *et al.,* 1947).

Three compounds contain a carbon-carbon triple bond, and these are listed in Table 1. These are fluorinated derivatives of ethyne, propyne, and butyne (two, three, and four carbons, respectively), and these are listed in Table 1 under "other." Compounds with a carbon-carbon triple bond tend to be relatively unstable, and readily available information can quickly eliminate two of them. Difluoroethyne has a relatively low T^{crit} (322.6 K), and Lentz and Michael (1988) describe it as "an extremely unstable molecule." The fluorinated butyne (1,1,1,4,4,4-hexafluorobut-2-yne) has a T^{crit} in the range where other promising candidates are found, and it is described as "highly toxic by inhalation" (Sigma-Aldrich, 2012a).

The 2,2,2-trifluoropropyne has $T^{crit} = 366$ K, and this would make it a potential replacement for R-404A or R-410A. Its values of critical pressure and C_p° would indicate thermodynamic performance similar to current refrigerants. This compound is commercially available in small quantities. Although limited hazard information is available, it is described as "stable under recommended storage conditions" (Sigma-Aldrich, 2012b). It is likely to be highly polar, increasing the possibility that it would form highly non-ideal mixtures, including azeotropes.

5. DISCUSSION AND CONCLUSIONS

Starting from the universe of known chemical compounds (as represented by the 100 million compounds in the PubChem database), the list of fluids that might be suitable low-GWP refrigerants was progressively pared down to 56 000 to 1200 to 62 candidates as ever more restrictive criteria were applied. The list of 62 was further reduced because of thermodynamic parameters suggesting mediocre efficiency or known chemical instability or toxic effects; many of the candidates also present additional unknown risks.

Remaining are a number of promising candidates, although no fluid is ideal in all regards. Included are two HFOs already classified "A2L" (low toxicity and mild flammability), namely R-1234yf and R-1234ze(E), along with HFOs that have low acute toxicity, but may be toxic on chronic exposure (R-1225ye(Z) and R-1225ye(E)) or that are flammable (R-1243zf). R-1234ye(E) has a critical pressure suggesting better cycle efficiency than the other R-1234 isomers. These are all fluorinated propenes (three carbon atoms). The fluorinated ethenes (two carbon atoms with a double bond) generally offer better thermodynamic properties compared to the propenes. Some of these are known to be toxic or unstable. The two R-1132 isomers have unknown risks, but would be interesting for further study.

The fluorinated butenes (four carbon atoms) and pentenes (five carbon atoms) have thermodynamic parameters that suggest mediocre performance in the most common types of refrigeration equipment; they cannot be dismissed *a priori*, but would be a lower priority for investigation. The olefin-based compounds that also contain chlorine or bromine have thermodynamic parameters that make them a lower priority for further study; they would also have a small, but non-zero, ozone depletion potential.

Among the oxygen-containing candidates there are two that have thermodynamic parameters that suggest refrigeration cycle performance similar to that of the propene-based HFOs. None of the compounds containing nitrogen or sulfur have remarkable thermodynamic characteristics.

Given the dearth of good candidates with critical temperatures in the range of R-410A, we reexamined compounds that we initially screened out because of stability concerns. Most of the candidates in this group were toxic and/or likely to be highly reactive. However, among the fluorinated alkynes (compounds with a carbon-carbon triple bond), at least one, 3,3,3-trifluoroprop-1-yne, warrants further investigation.

We have not attempted to estimate the cost or manufacturability of any new refrigerant. Cost of the refrigerant has heretofore not been a major consideration, but this was against a background of inexpensive fluids that would account for only a tiny fraction of the total system cost. HFOs are more difficult molecules to manufacture than most HFCs and will inevitably be more costly; the synthesis of R-1234yf, for example, involves six steps compared to a single-step process for R-134a (Calm, 2012). No publically disclosed prices for either of the two commercialized HFOs (R-1234yf and R-1234ze(E)) could be found, but anecdotal accounts indicate prices for R-1234yf as much as an order of magnitude higher than R-134a (*e.g.*, Calm, 2012). However, the price advantage for the HFCs has been reduced or nullified in some countries by a tax levied on greenhouse gases, based on their GWP. For R-134a such taxes range from approximately USD 26/kg (€20/kg) in Denmark, to USD 30/kg (€23/kg) in Australia, to USD 44/kg (€34/kg) in Norway. The first cost of either an expensive new fluid or a highly-taxed HFC could, instead, be applied to safety measures that might allow the use of a flammable fluid.

The results presented here may be disappointing in that only a few promising fluids are identified. Nothing presented here has contradicted the prevailing view that tradeoffs are inevitable (*e.g.*, McLinden and Didion, 1987; Calm and Didion, 1997). But have we missed any fluids? We do not claim to have considered every possibility, but we do note as an example that of the 31 possible fluorinated propene isomers, 30 were considered in the screening. Based on thermodynamic arguments, we restricted our search to small molecules, and there are a finite number of possible combinations allowed by the rules of chemistry. But while the number of promising new candidates is not large, the majority of current refrigeration and air-conditioning applications are met with a limited set of fluids, namely the HFCs R-134a, R-32, R-125, R-143a and their blends, along with several hydrocarbons (notably propane and isobutane), ammonia, and carbon dioxide. It may be sufficient to have a similar number of low-GWP fluids to supplement (and eventually replace) the high-GWP HFCs.

The present project is ongoing. In future tasks, we will relax the screening criteria to include flammable fluids and those with moderate values of GWP_{100}; this will allow a comparison of a wider range of candidates on a consistent basis. We will estimate additional thermodynamic properties of the 1200 candidate fluids, so that we can carry out simulations in the vapor compression cycle. This will allow cycle efficiency to be an additional screening parameter. A subset of a few dozen compounds will be selected and studied in more detail, including the estimation of transport properties. A new cycle model is in development that will account for both thermodynamic and transport properties, including a representation of the heat transfer processes in heat exchangers with optimized refrigerant mass flux. This will address the tradeoff between the pressure drop penalty and refrigerant heat transfer enhancement. This model will allow a more realistic screening of different refrigerants than the present model involving thermodynamic properties alone.

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NOMENCLATURE

ALC = approximate lethal concentration
ATEL = acute toxicity exposure limit
CFC = chlorofluorocarbon
COP = coefficient of performance
C_p° = heat capacity in the limit of $p \to 0$
GWP = global warming potential
GWP_{100} = global warming potential for a time horizon of 100 years
HCFC = hydrochlorofluorocarbon
HFC = hydrofluorocarbon
HFO = hydrofluoroolefin
IDLH = immediately dangerous to life and health
LC_{50} = lethal concentration
LFL = lower flammability limit
MSDS = material safety data sheet

NOAEL = no observed adverse effect level
ODP = ozone depletion potential
OH = hydroxyl radical
p = pressure
PAC = protective action criteria
Q_{vol} = volumetric heating or cooling capacity
RE = radiative efficiency
REL = recommended exposure limit
RMSD = root mean square deviation
T = temperature
ΔH_{comb} = heat of combustion
ω = acentric factor

Superscripts

crit = critical point value
o = ideal-gas state

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