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LOW-GWP REFRIGERANTS FOR MEDIUM AND HIGH-PRESSURE APPLICATIONS*

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Abstract

The merits of an alternative refrigerant are established based on many attributes including environmental acceptance, chemical stability in the refrigeration system, low toxicity, flammability, efficiency and volumetric capacity. In an earlier work, these criteria were used to screen a comprehensive database to search for refrigerants with low global warming potentials (GWP). The present paper summarizes the screening process and presents the performance of the ‘best’ replacement fluids for small and medium-sized air-conditioning, heating, and refrigeration applications. In addition to considering cycle calculations based only on thermodynamic properties, a simulation model that included transport properties and optimized heat exchangers was used to assess the performance potentials of the candidate fluids. The need for this more detailed modeling approach is demonstrated for systems relying on forced-convection evaporation and condensation. The study shows that the low-GWP refrigerant options are very limited, particularly for fluids with volumetric capacities similar to those of R 410A or R-404A. The identified fluids with good COP and low toxicity are at least mildly flammable. Refrigerant blends can be used to increase flexibility in choosing tradeoffs between COP, volumetric capacity, flammability, and GWP. The probability of finding ‘ideal’, better-performing low-GWP fluids is minimal.

Keywords

Air Conditioning; COP; Global Warming Potential; Refrigerants; Volumetric Capacity

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1. INTRODUCTION

As anticipated for some time, an amendment to the Montreal Protocol adopted in October 2016 requires a significant reduction of the weighted value of global warming potential (GWP) of fluids used in air-conditioning and refrigerant equipment (UNEP, 2016). Consequently, hydrofluorocarbon (HFC) refrigerants having a high GWP will be eliminated or their use will be significantly reduced. Hence, new replacement fluids with a low GWP must be found. This paper presents results of our multiyear study, in which we searched for low-GWP replacement refrigerants for small and medium-sized air-conditioning (AC), heat pumping, and refrigeration equipment. Such systems are comprised of a positive-displacement compressor, air-to-refrigerant condenser and evaporator, expansion device, and associated fans and controls. R-410A (a blend of the HFCs R-32 and R-125) is the dominant refrigerant in this equipment category, with the exception of commercial refrigeration applications where R-404A (a blend of the HFCs R-32, R-143a, and R-134a) is very common. R-22, a hydrochlorofluorocarbon refrigerant (HCFC), was most commonly used prior to the introduction of HFCs, and is still used in Article 5 countries of the Montreal Protocol (UNEP, 2016).

Our search for low-GWP replacement fluids involved multiple phases. Here we briefly summarize those phases and some of the intermediate results and reference the papers presenting the details. First, we investigated the characteristics of the “ideal” refrigerant. These include safety and environmental factors, but the focus of our study was on the thermodynamic characteristics. We explored “thermodynamic space” by simulating the coefficient of performance (COP) and volumetric capacity of different fluids in several variations of the vapor compression cycle. The key point was that known fluids were not simulated, but rather fluids were described in terms of fundamental thermodynamic parameters; this allowed a simulation of virtually all possible fluids. It revealed that the refrigerant critical temperature was the most important parameter. Other parameters that were significant (but of lesser importance) were the molar heat capacity of the vapor, the critical pressure, and the acentric factor (a parameter related to the slope of the vapor pressure curve). The methods for describing the thermodynamic characteristics were presented in McLinden *et al.* (2012).

Furthermore, this approach was amenable to optimization, which revealed a fundamental tradeoff between efficiency (*i.e.*, COP) and volumetric capacity: refrigerants with a high critical temperature tended to have a high COP but low capacity, and *vice versa*. This tradeoff was presented in terms of Pareto front, which is a set of refrigerants (with their COPs and volumetric capacities) for which it is impossible to find a single refrigerant from the universe of refrigerant options that would have a better COP without sacrificing volumetric capacity, and vice versa. Significantly, it also revealed that the current refrigerants were placed away from the Pareto front on the COP versus volumetric capacity chart, implying that better fluids were at least allowed by thermodynamics. Domanski *et al.* (2014) discussed these performance limits of the vapor compression cycle.

The second major thrust of the project was to identify actual fluids having the ideal characteristics identified in the first phase. This was done by applying screening criteria (or

“filters”) to the molecules in an exhaustive, public-domain PubChem database (Kim *et al.*, 2016). We carried out two separate screenings of this database. The result was a list of the 27 “best” low-GWP refrigerants. We summarize the results of this phase in Section 2.

In the final phase of the project we simulated the performance (COP and volumetric capacity) of the fluids “passing” the screening process in the basic vapor compression cycle and two variations on the basic cycle. A first round of simulations assumed ideal behavior (*e.g.*, zero pressure drop and 100 % efficient compression), and a second round of more-detailed simulations included pressure drop and heat-transfer effects in the condenser and evaporator and compression efficiency. Results for heating and refrigeration applications are presented here in Sections 3 and 4. Previous results for air-conditioning are also summarized.

2. DATABASE SCREENING

The merits of a candidate replacement fluid are established based on many attributes including GWP (low value desired), ozone depletion criteria (ODP, zero or very low), chemical stability in the refrigeration system, toxicity (low value desired), flammability (low value desired), and cycle performance parameters, *i.e.*, COP and volumetric capacity (Q_{vol}). Practical attributes include compatibility with the system materials, although this consideration is typically considered in the later phase of the refrigerant selection process.

To search for the most suitable low-GWP refrigerants, we used the PubChem database listing over 60 million unique chemical molecules (Kim *et al.*, 2016). The concept of our study relied on establishing filters representing different refrigerant selection criteria and applying them to the molecules listed in PubChem. We accepted the thermodynamic argument that viable refrigerants are restricted to small molecules (McLinden, 1990), and we considered PubChem to be exhaustive for such molecules.

The effectiveness of database screening processes depends on the quality of established filters and the sequence in which they are applied. The results of the first screening (McLinden *et al.*, 2014) provided us insights, based on which we changed the sequence of filters for a second screening. For this second (and final) database screening, 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, following the observation by Midgley (1937) that only a small portion of the periodic table would form compounds volatile enough to serve as refrigerants, as presented by McLinden *et al.* (2015). Also excluded were ions, radicals, and molecules enriched in specific isotopes. Despite their ability to deplete stratospheric ozone, we included Cl and Br since molecules including Cl or Br might have a negligible ODP and might be acceptable if they have a very short atmospheric lifetime. These restrictions reduced the pool of molecules for further consideration to 184 000.

The next two filters involved GWP_{100} and T_{crit} . The PubChem database does not provide these data for the vast majority of the compounds, so they had to be estimated using novel methods developed within this study (Kazakov *et al.*, 2012, Carande *et al.*, 2014, Carande *et al.*, 2016); the development and application of these estimation methods constituted a major

effort. These methods were based solely on the molecular structure. The prediction of GWP_{100} combined estimates of the radiative efficiency and atmospheric reactivity with the hydroxyl radical. The tradeoff of computational efficiency versus accuracy was a major consideration given the large number of compounds to screen. The method achieved a logarithmic root mean square deviation of 3.0 for the GWP_{100} estimates compared to available literature values, and this accuracy was considered adequate for screening purposes. The estimates of critical temperature were done using the method presented in Kazakov *et al.*, (2010).

The applied filters of $GWP_{100} < 1000$ and $320\text{ K} < T_{\text{crit}} < 420\text{ K}$ reduced the pool of candidates to 138 fluids, as listed in McLinden *et al.* (2017). The limits on T_{crit} were based on experience with refrigerants used in small AC systems, with an allowance for the uncertainty in the T_{crit} estimation method. The limit of 1000 for GWP_{100} also provided an allowance for the estimation uncertainty and considered that, for example, refrigerants with $GWP_{100} < 750$ are permitted under EU regulations in AC systems with refrigerant charge under 3 kg (EU, 2014).

The next filters were for chemical stability and toxicity; both were applied manually. Compounds with generally unstable functional groups were dropped from further consideration. These included peroxides (compounds with the $-\text{O}-\text{O}-$ group), ketenes (compounds with the $-\text{C}=\text{C}=\text{O}$ group), and allenes (compounds with the $-\text{C}=\text{C}=\text{C}-$ group). Compounds with a carbon-carbon triple bond were generally dropped as less stable than those with a double bond; for example, fluoroethyne ($\text{FC} \dots \text{CH}$) is described as “treacherously explosive in the liquid state.” (Middleton and Sharkley, 1959). There were exceptions, however, and trifluoropropyne was retained.

For the toxicity filter, in addition to considering functional groups, *e.g.*, $=\text{CF}_2$ and $-\text{OF}$, the analysis involved a manual examination of toxicity data from a variety of sources, such as safety standards, material safety data sheets (MSDS), compilations of toxic industrial chemicals, and regulatory filings. McLinden *et al.* (2017) provide more detailed discussion.

In this second (final) screening, we did not apply the flammability filter but rather used flammability as an attribute to be considered as a tradeoff in the final refrigerant selection. We opted for this approach because the first screening (McLinden *et al.*, 2014) did not reveal compelling nonflammable candidates, and the flammability filter rejected a large number of fluids, some of which perhaps could be used in certain applications after implementing appropriate hazard mitigation measures.

3. PERFORMANCE EVALUATION

Performance merits of refrigerants include COP and Q_{vol} obtained at specified operating conditions. When considering only the thermodynamic properties, there is an inherent tradeoff between COP and Q_{vol} , which can be related to the refrigerant critical temperature; fluids with a high T_{crit} tend to have a high COP and low Q_{vol} , and vice versa (Domanski *et al.*, 2014). In this sense, the applied filter $320\text{ K} < T_{\text{crit}} < 420\text{ K}$ ensured that the accepted 138 low-GWP fluids had the COP and Q_{vol} in a general range of those of currently used

refrigerants. The imposed T_{crit} range corresponded to air-conditioning applications, and we carried out a further refrigerant selection process using operating conditions representative of air conditioning (AHRI, 2008). Accurate estimations of COP and Q_{vol} of candidate fluids required thermodynamic cycle simulations. To manage the level of effort of the selection process, we performed two rounds of simulations at different levels of detail. Our final simulations included the basic thermodynamic cycle, a cycle with a liquid-line/suction-line heat exchanger (LL/SL-HX), and a two-stage economizer cycle (Figure 1).

3.1 Simplified cycle simulations

In the first round, we simulated the performance of candidate fluids in an air-conditioning application in the basic thermodynamic cycle (Figure 1(a)), as implemented in the CYCLE_D model (Brown *et al.*, 2015), with an imposed evaporating temperature of 10 °C and condensing temperature of 40 °C, and with the ideal assumptions of zero pressure drop in the heat exchangers and a 100 % efficient compression process. These simulations involved only thermodynamic properties. To better elucidate thermodynamic trends, we performed these simulations on the complete list of 138 low-GWP candidates (i.e., including the unstable or toxic fluids), and also included an additional eight currently-used refrigerants. For the representation of refrigerant properties, we used the detailed equations of state (EOS) implemented in the NIST REFPROP database (Lemmon *et al.*, 2013), where available. However, for a majority of the fluids we used the extended corresponding states (ECS) model (McLinden *et al.*, 2012), where available.

Figure 2 presents COPs and volumetric capacities obtained from these simplified simulations. The figure clearly shows the COP versus Q_{vol} tradeoff, which results from an ideal analysis based only on thermodynamic properties (McLinden, 1988). The figure also includes a Pareto Front, which represents the COP limit for ‘ideal’ hypothetical fluids allowed by thermodynamics (Domanski *et al.*, 2014). At this stage, we dropped fluids with a volumetric capacity less than one-third that of R-410A ($Q_{\text{vol, R-410A}} = 6.62 \text{ MJ}\cdot\text{m}^{-3}$) or a $\text{COP} < 5$ ($\text{COP}_{\text{R-410A}} = 7.41$). The volumetric capacity of R-22 is 66 % that of R-410A, so this would correspond to dropping fluids with a capacity less than one-half that of R-22. These criteria yielded a set of less than 30 low-GWP fluids for evaluation in the second round of more detailed simulations.

3.2 Detailed cycle simulations

The second round of simulations used a more advanced cycle model, which is referred to as CYCLE_D-HX (Brignoli *et al.*, 2017). The CYCLE_D-HX model builds on the concept of using temperature profiles of the heat sink and heat source, and the mean effective temperature differences between the refrigerant and heat transfer fluids (T_{hx}) in the evaporator and condenser (Domanski and McLinden, 1992). This modeling approach facilitates accounting for pressure drop and heat transfer, i.e., effects related to the transport properties of viscosity and thermal conductivity, and also the effect of drop in saturation temperature with pressure, dT_{sat}/dp (Brown *et al.*, 2002a and 2002b). Most importantly, it provides a more realistic representation of an air conditioner employing typical forced-convection, air-to-refrigerant heat exchangers, which are optimized for a particular refrigerant. 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. CYCLE_D-HX accounts for the effect of optimized refrigerant mass flux, which enhances the refrigerant heat transfer coefficient at an acceptable penalty of pressure drop, as described by Brown *et al.* (2002b).

To examine the importance of the optimization of refrigerant circuitry, consider that a pressure drop in the evaporator or condenser causes a decrease in the saturation temperature and results in increased mean effective temperature differences T_{hx} in the heat exchangers. The refrigerant heat-transfer coefficient h also affects T_{hx} ; a higher h yields a lower T_{hx} . A decrease in condenser and evaporator T_{hx} lowers the temperature lift seen by the compressor and subsequently lowers the compressor work, which improves the COP. The heat-transfer coefficient h and pressure drop p are both a function of the refrigerant mass flux G , where h approximately increases proportionally to $G^{0.8}$, while p increases proportionally to G^2 (Collier and Thome, 1994). There is an optimum value of G that provides the best compromise between the opposite effects that h and p have on the system COP.

Figure 3 shows the dependency of h and p on the mass flux in evaporation at $T_{sat} = 0\text{ }^{\circ}\text{C}$ for R-32, R-1234yf, and R-717 (ammonia). We used correlations by Wojtan *et al.* (2005a and 2005b) and Muller-Steinhagen and Heck (1986) for generating data for h and p , respectively. The results shown are normalized by nominal h and p values for R-32 at $G_{nom} = 100\text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, $h_{nom} = 3.16\text{ kW}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ and $p_{nom} = 1.26\text{ kPa}$, respectively. All values are average values calculated by Eq. (1):

$$F = \frac{1}{x_{end} - x_{start}} \int_{x_{start}}^{x_{end}} f(x) \quad (1)$$

where $f(x)$ is h or p , x_{start} is the quality corresponding to the isenthalpic expansion from a condenser saturation temperature of $45\text{ }^{\circ}\text{C}$ and 3 K subcooling to evaporator conditions of $T_{sat} = 0\text{ }^{\circ}\text{C}$, and $x_{end} = 1$.

Figure 3 shows the G^2 dependence of the pressure drop and the weaker $G^{0.8}$ dependence of the heat-transfer coefficient. For example, in comparing R-32 (a high-pressure fluid) and R-1234yf (a medium-pressure fluid), we see that R-1234yf has a lower heat-transfer coefficient and a higher pressure drop than R-32 at the same mass flux, and the rate of increase of heat-transfer coefficient in relation to pressure drop is less favorable for R-1234yf than for R-32. Also, the drop of saturation temperature of R-1234yf is greater than that of R-32 for the same pressure drop. For example, at $T_{sat} = 0\text{ }^{\circ}\text{C}$, $dT_{sat}/dp = 0.0934\text{ K}\cdot\text{kPa}^{-1}$ for R-1234yf and $dT_{sat}/dp = 0.0384\text{ K}\cdot\text{kPa}^{-1}$ for R-32, which leads to a 2.4 times greater decrease in saturation temperature for R-1234yf than for R-32 at the same pressure drop. Similar trends take place in condensing flows. Brown *et al.*, (2012) and Cavallini *et al.*, (2010), who studied heat transfer and pressure drop of refrigerants in flow boiling and flow condensation, respectively, concluded that lower pressure refrigerants have a lower forced-convection heat transfer potential than higher pressure refrigerants.

The optimum refrigerant mass flux G is different for each refrigerant and depends on the thermodynamic and transport properties of the refrigerant. Ammonia, for example, which has a very high thermal conductivity and moderate saturation temperature drop due to its low vapor density, will realize the best compromise between heat-transfer coefficient and pressure drop at a low mass flux, i.e., at a high number of parallel tube circuits. On the other hand, R-32, being a higher-pressure fluid (higher vapor density) and having lower liquid thermal conductivity than ammonia, will realize the best compromise between heat transfer and pressure drop at a higher mass flux, i.e., at a lower number of circuits.

Among other modeling considerations, CYCLE_D-HX maintained the same heat flux in the evaporator through all simulations, which is a prerequisite for a fair rating of competing refrigerants (Domanski and McLinden, 1992). The isentropic efficiency of the compressor was at about the 70 % level, and it differed between the fluids as it was a function of refrigerant thermodynamic properties (Brignoli *et al.*, 2017). The more detailed cycle analysis implemented in CYCLE_D-HX yielded fluid COP and Q_{vol} that are different from those obtained from CYCLE_D simulations based on thermodynamic properties alone (Figures 4a and 4b). The CYCLE_D results show refrigerants with a low Q_{vol} having a higher COP than high-capacity fluids. This COP-versus-capacity tradeoff is not maintained in the CYCLE_D-HX results; the maximum COP corresponds to Q_{vol} of approximately 60% to 110% of that of R-410A.

It is important to understand the disparity in the COP-versus-capacity trends between CYCLE_D and CYCLE_D-HX simulations. With the same (imposed) saturation temperatures in the evaporator and condenser, CYCLE_D-type simulations tend to yield higher COPs for low-pressure refrigerants compared to high-pressure refrigerants because low-pressure fluids operate far below their critical point and tend to exhibit lower irreversibilities resulting from the superheated vapor horn and throttling process (Domanski and Didion, 1993). However, this thermodynamic advantage of low-pressure fluids can be erased in systems using heat exchangers that implement refrigerant forced-convection evaporation and condensation (*e.g.*, air-to-refrigerant coils) because low-pressure fluids have low vapor density and therefore exhibit relatively large pressure drops and decreases in saturation temperature in forced-convection coils. These irreversibilities may render high-pressure refrigerants more efficient, particularly when refrigerant circuitries (and therefore mass fluxes) in these heat exchangers are optimized, which was done in the CYCLE_D-HX simulations.

The COP-versus-capacity trends obtained from CYCLE_D-HX simulations were also noted in an earlier work, which studied the performance of a range of fluids (R-600a, R-134a, R-290, R-22, R-410A, and R-32) using a detailed air-to-air heat pump model with a heat exchanger optimization capability (Domanski and Yashar, 2006). These performance trends are also reflected in the engineering practice of selecting low-pressure refrigerants for water chillers with shell-and tube heat exchangers, which have a low pressure drop, and applying higher-pressure refrigerants in systems with forced-convection heat exchangers. Consequently, we can conclude that the more-detailed simulation methodology used by CYCLE_D-HX is preferable for screening refrigerants for systems with forced-convection

heat exchangers over the simpler CYCLE_D-type simulation models using imposed saturation temperatures in the evaporator and condenser.

4. SCREENING RESULTS AND TRADEOFFS

Following CYCLE_D-HX simulations we completed our screening process and generated a list of 27 fluids we deemed to be the best single-component low-GWP replacements for small AC systems [see Table 1 in McLinden *et al.* (2017)]. This list is a subset of the 138 fluids, i.e., those with $320\text{ K} < T_{\text{crit}} < 420\text{ K}$, after unstable or toxic fluids were removed along with those having low Q_{vol} or COP. However, this list of 27 includes R-1225ye(Z) with low acute toxicity and low capacity, and R-1123 with low acute toxicity based on evidence of some commercialization interest, R-134 ($\text{GWP}_{100} = 1120$) since it may be considered as a blend component, and three high-pressure fluids: carbon dioxide (R-744), ethane (R-170), fluoromethane (R-41). R-744 is the only low-toxicity and nonflammable fluid that was identified, but it would operate in a transcritical cycle because of its low T_{crit} . R-170 and R-41 would also operate near the critical point and were not simulated in our study. Being highly flammable, R-170 and R-41 do not seem to be attractive as single-component refrigerants, but may be considered as blend components. These additional fluids were included with the intent to produce a “complete” list of refrigerant options for small AC applications. The fluorinated alkenes—also known as hydrofluoroolefins (HFOs)—is the largest group in the list. The other fluids are halogenated alkanes, halogenated oxygenates, hydrocarbons, halogenated nitrogen and sulfur compounds, and inorganic compounds.

Table 1 of the present paper provides COP and Q_{vol} values for heating and refrigeration applications for the fluids listed in Table 1 in McLinden *et al.* (2017) with the addition of 1,1-difluoroethene (R-1132a), bringing the current list to 28 fluids. R-1132a was not included in the final list in McLinden *et al.* (2017) because of a published exposure limit of 1 ppm from an authoritative source (NIOSH, 2007), which would indicate that R-1132a is highly toxic. Other source (ACGIH, 2008), however, lists an exposure limit of 500 ppm, and an ASHRAE Standard 34 classification of A2 is pending (ASHRAE, 2017). This fluid is potentially unstable in contact with certain materials, and it is normally supplied with a stabilizer that would not be suitable for use in a refrigeration system. Thus, R-1132a is a possible blend component, but not a pure refrigerant. Having $T_{\text{crit}} = 324.2\text{ K}$, R-1132a would operate near the critical point and was simulated in this study.

Figures 4, 5, 6, and 7 present COP and Q_{vol} for 24 of the above-discussed fluids (without R-744, R-170, R-41, and R-1132a) for air-conditioning, heating, and refrigeration applications for different cycles. Four currently used refrigerants were included for comparison purposes. The figures allow for a few general observations. The majority of fluids are known and have ASHRAE designations (ASHRAE, 2016). Some of them are considered by industry for application as single-component refrigerants or blend components. The figures include six novel molecules that have not been previously considered as refrigerants (at least in the public domain).

All low-GWP fluids in the figures are at least mildly flammable, except R-1225ye(Z). The refrigerant classification standard assigns refrigerants to one of three classes (1, 2, 3),

progressing from nonflammable to highly flammable based on the lower flammability limit and heat of combustion, with one optional subclass (2L) based on the burning velocity (ASHRAE, 2016). Figures 4, 5, 6 and 7 show fluids in class 2 (including subclass 2L) using the color yellow, and denote class 3 fluids with red. Current air-conditioning systems predominantly use class 1 (nonflammable) refrigerants; switching to flammable refrigerants requires the examination of involved risks and the development of safety measures. A significant amount of research in this area has been undertaken by industry already and is still ongoing. We may note that the only nonflammable low-GWP refrigerant in the figures, R-1225ye(Z), has a capacity only of about 25 % of R-410A and a substantially lower COP. It has a low acute toxicity (Lindley and Noakes, 2010) but showed toxic effects for longer exposures at 500 $\mu\text{L/L}$ 1000 $\mu\text{L/L}$ (500 ppm – 1000 ppm) by volume in air (Schuster, 2009).

4.1 Air conditioning

The reference operating conditions for the R-410A air conditioner corresponded to an evaporating temperature of 10 °C and a condensing temperature of 40 °C. The discussion presented here follows McLinden *et al.*, (2017) where these results were first reported, including Figures 4(b), 5(a), 5(b) and the list of the ‘best’ fluids with numerical values for COP and Q_{vol} . From Figure 4(b), which presents results for the basic cycle, the maximum COP corresponds to Q_{vol} of approximately 60 % to 110 % of that of R-410A, however, a significant agglomeration of fluids occurs for Q_{vol} smaller than 60 %. These are the lower-pressure fluids on the list. They tend to achieve low COPs in systems with forced-convection evaporators and condensers (Figure 4(b)), although they would have a performance advantage in systems with shell-and-tube heat exchangers (Figure 4(a)). The COP of the basic vapor compression cycle ranges from –7.8 % to +5.5 % relative to that of R-410A (13.3 % range). Ammonia shows 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-270), 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 GWP₁₀₀ of 677. R-134 and R-E143a have GWP₁₀₀ values of 1120 and 523, 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.

The list of 28 fluids includes six novel molecules: tetrafluorodioxole, trifluoromethanethiol, trifluoropropyne, difluoromethanethiol, (E)-1,2-difluoroethene (R-1132(E)), and tetrafluoromethanamine. Few data are available on these fluids so their risks are unknown. Furthermore, their performance does not stand out and does not provide a compelling reason for a substantial research effort. Difluoromethanethiol and (E)-1,2-difluoroethene, for example, have predicted COPs slightly higher than R-410A, but Q_{vol} values that are about 40 % lower than that of R-410A. They are flammable (in addition to possible other hazards), and their COP and Q_{vol} are very similar to propane (R-290). It does not seem reasonable to

take on the unknown risks of these fluids when one could use the somewhat more flammable, but well-known propane.

In addition to the basic cycle, the cooling mode simulations included a cycle with a LL/SL-HX and a two-stage economizer cycle. These two advanced cycles can be used to improve a refrigerant's performance by minimizing throttling irreversibilities. Figures 5(a) presents COP and Q_{vol} of the selected fluids in a cycle with a LL/SL-HX. The results are given with a reference to the R-410A values for the basic cycle. The addition of the LL/SL-HX to the cycle benefits fluids with a large molar heat capacity but may degrade the performance of fluids with a small molar heat capacity (Domanski, 1995). For example, the COP of R-410A improved with respect to the COP in the basic cycle by 1.2 %. A significant improvement (up to 5.4 %) of COP is noted for most HFOs, which are larger molecules and tend to have larger molar heat capacities. On the other hand, ammonia and R-32 (best performers in the basic cycle), which are small molecules with smaller molar heat capacities, achieved lower COPs in the LL/SL-HX cycle than in the basic cycle. Since the LL/SL-HX penalized the better performers and improved the lesser performers, the range of observed COPs is reduced to 8.1 % for the LL/SL-HX cycle, from 13.3 % for the basic cycle.

The application of the two-stage economizer cycle improves the performance of all fluids, with the fluids performing worse in the basic cycle achieving a greater improvement than the better performers. Here, R-410A improved by 4.9 %, the COP of R-32 and ammonia is about 3.2 % and 2.5 % better than in the basic cycle, but others *e.g.*, R-1234ze(E) improved by over 6 %. Except for R-1225ye(Z) and tetrafluorodioxole, the COP of each fluid in the economizer cycle exceeded the COP of R-410A in the basic cycle, but only six fluids had a higher COP if compared to that of R-410A in the same economizer cycle.

4.2 Heating

We simulated the selected fluids for the heating application with reference to a heat pump using R-410A. The reference operating conditions corresponded to an evaporating temperature of $-10\text{ }^{\circ}\text{C}$ and a condensing temperature of $30\text{ }^{\circ}\text{C}$. The general pattern for the heating operation is similar to the pattern we discussed for the cooling operation, i.e., the agglomeration of low-GWP fluids occurs for low values of Q_{vol} , and the fluids with low values of Q_{vol} have low COPs. One difference may be noted that COPs of refrigerants with a low Q_{vol} (Figure 6(a)) are a few percentage points lower with respect to R-410A than those for the cooling operation (Figure 4(b)). Two reasons can be given for this observation:

1. The lower evaporation temperature during heating operation ($-10\text{ }^{\circ}\text{C}$ for heating vs. $10\text{ }^{\circ}\text{C}$ for cooling) results in lower refrigerant density in the evaporator for the heating operation, which effects a larger refrigerant pressure drop and saturation temperature drop during the heating mode; the low-pressure (low- Q_{vol}) fluids are more sensitive to this penalty.
2. The lower condensing temperature in heating operation ($30\text{ }^{\circ}\text{C}$ for heating vs. $40\text{ }^{\circ}\text{C}$ for cooling) moves the high-pressure side of the thermodynamic cycle away from the refrigerant's critical temperature, and this move is of more benefit for the high-pressure (high- Q_{vol}) fluids, such as R-410A.

The above statement applies to a comparison of heating versus cooling in the economizer cycles as well (Figures 5(b) and 6(b)).

4.3 Refrigeration

We simulated the selected fluids for the refrigeration application with the reference to a system using R-404A (Figure 7). The reference operating conditions corresponded to an evaporating temperature of $-20\text{ }^{\circ}\text{C}$ and a condensing temperature of $30\text{ }^{\circ}\text{C}$. The general pattern for the refrigeration operation is similar to the pattern we discussed for the cooling and heating cycles. Specifically, the low-pressure (low- Q_{vol}) refrigerants have substantially lower COPs in the basic cycle than does R-404A. The COP spread between the low- Q_{vol} and high- Q_{vol} is over 30 %, the largest of the three operating conditions simulated. For the economizer cycle, the COP spread is reduced to 17.2 %, although this is still substantial. R-1270 showed the best COP, the same result as for the heating operation.

4.4 GWP versus flammability tradeoff

Why are there no low-GWP fluids that are also nonflammable and with high volumetric capacity? The classic way to suppress flammability is to replace hydrogens on a molecule with halogens (fluorine, chlorine, or bromine). But there is a trade-off with respect to adding halogens—as more halogens are added the flammability decreases, but the GWP increases, because it is the hydrogens that are primarily responsible for reaction with atmospheric hydroxyl radicals and a resulting short atmospheric lifetime. For example, R-125 (with five fluorines and one hydrogen on a two-carbon backbone) is nonflammable, but it has a GWP_{100} of 3170, while R-152a (with two fluorines and four hydrogens) is flammable (ASHRAE flammability classification of 2) and has $\text{GWP}_{100} = 138$. Chlorine is more effective than fluorine in suppressing flammability, but it is a heavier atom and increases the critical temperature more than fluorine. Thus, chlorine-containing molecules with only a single carbon can have values of T_{crit} suitable for refrigerants (*e.g.*, R-22, CHClF_2 and R-12, CCl_2F_2), but they are also high-GWP and ozone-depleting fluids.

The GWP of an HFC can be lowered by adding an additional reactive group to the molecule, such as the double bond in the HFOs. But the double bond, which reacts with atmospheric hydroxyl, also contributes to the reaction with oxygen, *i.e.*, flammability. For example, R-134a ($\text{CF}_3\text{-CH}_2\text{F}$) and R-1234yf ($\text{CF}_3\text{-CF=CH}_2$) both have four fluorines and two hydrogens and have similar T_{crit} and Q_{vol} , but R-134a is nonflammable while R-1234yf is marginally flammable (ASHRAE classification A2L). R-1234yf is a more complex molecule than R-134a—three carbon atoms versus two. Adding an additional fluorine to R-1234yf results in either R-1225ye(E) or R-1225ye(Z), which are nonflammable, but which also have higher values of T_{crit} .

The mechanism behind the ability of fluorine to suppress flammability can be understood, in an approximate way, by examining the enthalpy of formation, H_f . Combustion is the reaction of a fuel (*e.g.*, a refrigerant) with an oxidizer (most often, oxygen) with the release of heat. A reaction is thermodynamically favorable if the change in Gibbs free energy (where $G = H - TS$) is negative, *i.e.*, when

$$\sum (H - TS)_{\text{products}} - \sum (H - TS)_{\text{reactants}} < 0. \quad (2)$$

The enthalpy term is (usually) dominant. The enthalpy of formation is defined as the change in enthalpy in creating a compound from its constituent elements, and the net change in enthalpy of any reaction is given by difference in the enthalpies of formation of the products and reactants:

$$\Delta H = \sum (\Delta H_f)_{\text{products}} - \sum (\Delta H_f)_{\text{reactants}} \quad (3)$$

The carbon-fluorine bond is the strongest (most stable) single bond in chemistry, and thus a molecule with more fluorines will have a more negative value of heat of formation, corresponding to a more stable molecule. This is illustrated in Figure 8, which shows the trend of H_f with the number of fluorines for the two-carbon HFCs.

Our analysis points to simple molecules as tending to have better performance. Why are the low-GWP fluids more complex than the HFCs? Basically, as the constraints imposed on a refrigerant have increased, the choices have decreased. When the CFC refrigerants were introduced in the 1930s there was no concept of ODP or GWP, and a molecule could be constructed by adding chlorine or fluorine or hydrogen to a carbon backbone. This freedom led to single-carbon refrigerants, such as R-12 and R-22. With the recognition of ozone depletion, chlorine was taken off the table, and now, the requirement of a low GWP has further restricted the possibilities.

CONCLUSIONS

Our search for single-component low-GWP fluids for use in small air-conditioning, heating, and refrigeration systems showed that the refrigerant options for these applications are very limited, particularly for fluids with volumetric capacities similar to R-410A or R-404A. The identified fluids with good COP and low toxicity are at least mildly flammable. Refrigerant blends can be used to increase flexibility in choosing tradeoffs between COP, volumetric capacity, flammability, and GWP.

Accepting the thermodynamic argument that viable refrigerants are restricted to small molecules, it is our contention that our screening process has yielded a list of the ‘best’ low-GWP fluids, i.e., the probability of finding any better-performing low-GWP single-component fluid subject to the criteria and constraints applied at this particular historical moment is minimal.

Most of the identified fluids are relatively large molecules with relatively large molar heat capacities. As such, these fluids experience greater throttling losses in the basic vapor-compression cycle than currently used HFC refrigerants and will benefit from implementation of the LL/SL-HX cycle or economizer cycle, which can minimize throttling irreversibilities.

Performance of different refrigerants in systems employing heat exchangers relying on forced-convection evaporation and condensation heat transfer do not exhibit the tradeoff between COP and volumetric capacity observed for an ideal cycle analysis based on thermodynamic properties alone. For such systems, higher-pressure refrigerants give higher COPs at relatively high volumetric capacity. Different type of equipment may still show a COP-versus-capacity tradeoff and favor moderate-pressure refrigerants.

The demonstrated limited refrigerant options and environmental concerns mandate judicious use of refrigerants, which shall include selection of refrigerant for each application recognizing environmental and safety risks, development of high-efficiency and leak-free equipment, and improved refrigerant handling practices during equipment commissioning, servicing, and decommissioning.

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NOMENCLATURE

AC	air conditioning
COP	coefficient of performance
<i>G</i>	mass flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
GWP	global warming potential
GWP₁₀₀	GWP for a time horizon of 100 years
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
<i>h</i>	heat transfer coefficient ($\text{kW}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$)
LL/SL-HX	liquid-line/suction-line heat exchangers
MSDS	material safety data sheet
ODP	ozone depletion potential
<i>p</i>	pressure (kPa)
<i>Q_{vol}</i>	volumetric capacity ($\text{kJ}\cdot\text{m}^{-3}$)
<i>T</i>	temperature (K or °C)
<i>x</i>	refrigerant quality (fraction)
<i>H_f</i>	enthalpy of formation ($\text{kJ}\cdot\text{mol}^{-1}$)

crit	critical
hx	heat exchanger
nom	nominal
sat	saturation
	difference

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Figure 1.
Schematic of (a) basic cycle, (b) cycle with liquid-line/suction line heat exchanger (LL/SL-HX), and (c) two-stage economizer cycle

Figure 2.
Ratio of COP to the Carnot COP in the ideal basic cycle for air conditioning (McLinden et al., 2015)

Figure 3.
Effect of refrigerant mass flux on forced-convection evaporation and pressure drop

Figure 4. COP and Q_{vol} of selected fluids referenced to R-410A values; (a) ‘ideal’ CYCLE_D simulations and (b) CYCLE_D-HX simulations; air-conditioning application using the basic cycle, Figure 1(a)

Figure 6. COP and Q_{vol} of selected fluids referenced to R-410A values from CYCLE_D-HX simulations for a heating application; (a) basic cycle, and (b) two-stage economizer cycle

Figure 7. COP and Q_{vol} of selected fluids referenced to R-404A values from CYCLE_D-HX simulations for a refrigeration application; (a) basic cycle and (b) two-stage economizer cycle

Figure 8.
Trend of heat of formation with number of fluorine atoms for the two-carbon HFCs

Table 1

COP and volumetric capacity of selected low-GWP fluids and current HFC and HCFC fluids in the basic and two-stage economizer (Econ.) cycles. Values are from CYCLE_D-HX simulations with optimized heat exchangers relative to the performance in the basic cycle of R-410A and R-404A for heating and refrigeration, respectively. GWP₁₀₀ are estimated by the method of Kazakov *et al.*, (2012) unless noted. The fluids are grouped by chemical class and, within classes, listed in order of increasing critical temperature.

IUPAC Name	Structure	ASHRAE Designation	GWP ₁₀₀	Heating				Refrigeration			
				COP		Q _{vol}		COP		Q _{vol}	
				COP _{R-410A} [*]		Q _{vol,R-410A} [*]		COP _{R-404A} [*]		Q _{vol,R-404A} [*]	
				Basic	Econ.	Basic	Econ.	Basic	Econ.	Basic	Econ.
<u>Hydrocarbons and dimethylether</u>											
Ethane	CH ₃ -CH ₃	R-170	6 [†]	§	§	§	§	§	§	§	§
Propene (propylene)	CH ₂ =CH-CH ₃	R-1270	2 [†]	1.025	1.051	0.703	0.797	1.119	1.189	1.055	1.281
Propane	CH ₃ -CH ₂ -CH ₃	R-290	3 [†]	1.004	1.039	0.572	0.651	1.082	1.167	0.841	1.028
Methoxymethane (dimethylether)	CH ₃ -O-CH ₃	R-E170	1 [†]	0.960	1.010	0.360	0.394	0.944	1.083	0.482	0.565
Cyclopropane	-CH ₂ -CH ₂ -CH ₂ -	R-C270	86	0.994	1.025	0.456	0.500	1.027	1.123	0.645	0.756
<u>Fluorinated alkanes (HFCs)</u>											
Fluoromethane	CH ₃ F	R-41	116 [†]	§	§	§	§	§	§	§	§
Difluoromethane	CH ₂ F ₂	R-32	677 [†]	1.025	1.042	1.077	1.193	1.096	1.162	1.601	1.892
Fluoroethane	CH ₂ F-CH ₃	R-161	4 [†]	1.000	1.034	0.576	0.636	1.049	1.142	0.824	0.972
1,1-Difluoroethane	CHF ₂ -CH ₃	R-152a	138 [†]	0.939	0.994	0.360	0.392	0.907	1.059	0.474	0.553
1,1,2,2-Tetrafluoroethane	CHF ₂ -CHF ₂	R-134	1120 [†]	0.911	0.989	0.304	0.333	0.830	1.034	0.378	0.447
<u>Fluorinated alkenes (HFOs) and alkynes</u>											
1-1-Difluoroethene	CF ₂ =CH ₂	R-1132a	<1 [†]	§	§	§	§	§	§	§	§
Fluoroethene	CHF=CH ₂	R-1141	<1 [†]	1.002	1.031	1.440	1.666	1.083	1.158	2.169	2.707
1,1,2-Trifluoroethene	CF ₂ =CHF	R-1123	3	0.984	1.029	1.105	1.302	1.055	1.160	1.623	2.087
3,3,3-Trifluoroprop-1-yne	CF ₃ -C≡CH	n.a.	1.4	0.968	1.023	0.520	0.593	1.003	1.139	0.724	0.902
2,3,3,3-Tetrafluoroprop-1-ene	CH ₂ =CF-CF ₃	R-1234yf	<1 [†]	0.934	1.003	0.391	0.452	0.940	1.104	0.527	0.672
(E)-1,2-Difluoroethene	CHF=CHF	R-1132(E)	1	0.987	1.025	0.557	0.613	1.022	1.127	0.784	0.922

IUPAC Name	Structure	ASHRAE Designation	GWP ₁₀₀	Heating				Refrigeration			
				COP		Q_{vol}		COP		Q_{vol}	
				COP _{R-410A} [*]	Econ.	COP _{R-410A} [*]	Econ.	COP _{R-404A} [*]	Econ.	COP _{R-404A} [*]	Econ.
3,3,3-Trifluoroprop-1-ene	CH ₂ =CH-CF ₃	R-1243zf	<1 [†]	0.938	0.997	0.346	0.388	0.942	1.084	0.468	0.566
1,2-Difluoroprop-1-ene [‡]	CHF=CF-CH ₃	R-1252ye [‡]	2	0.935	0.995	0.323	0.359	0.917	1.066	0.428	0.509
(E)-1,3,3,3-tetrafluoroprop-1-ene	CHF=CH-CF ₃	R-1234ze(E)	<1 [†]	0.892	0.974	0.283	0.317	0.841	1.034	0.360	0.439
(Z)-1,2,3,3,3-pentafluoro-1-propene	CHF=CF-CF ₃	R-1225ye(Z)	<1 [†]	0.884	0.963	0.246	0.279	0.843	1.022	0.315	0.391
1-Fluoroprop-1-ene [‡]	CHF=CH-CH ₃	R-1261ze [‡]	1	0.931	0.991	0.361	0.342	0.879	1.046	0.406	0.474
Fluorinated oxygenates											
Trifluoro(methoxy)methane	CF ₃ -O-CH ₃	R-E143a	523 [†]	0.922	0.991	0.333	0.374	0.905	1.067	0.440	0.536
2,2,4,5-Tetrafluoro-1,3-dioxole	-O-CF ₂ -O-CF=CF-	n.a.	1	0.881	0.967	0.292	0.326	0.810	1.017	0.365	0.439
Fluorinated nitrogen and sulfur compounds											
N,N,1,1-tetrafluoromethanamine	CHF ₂ -NF ₂	n.a.	20	0.975	1.028	0.817	0.962	1.034	1.155	1.174	1.510
Difluoromethanethiol	CHF ₂ -SH	n.a.	1	0.980	1.024	0.544	0.601	1.010	1.129	0.761	0.903
Trifluoromethanethiol	CF ₃ -SH	n.a.	1	0.947	1.002	0.388	0.431	0.956	1.094	0.526	0.630
Inorganic compounds											
Carbon dioxide	CO ₂	R-744	1.00 [†]	§	§	§	§	§	§	§	§
Ammonia	NH ₃	R-717	<1 [†]	0.990	1.022	0.665	0.706	0.954	1.081	0.898	1.022
Current HFCs and HCFC											
Pentafluoroethane	CF ₃ -CHF ₂	R-125	3170 [†]	0.937	1.007	0.757	0.914	0.971	1.126	1.056	1.423
R-32/125 (50.0/50.0)	blend	R-410A	1924	1.000	1.040	1.000	1.145				
R-125/143a/134a (44.0/52.0/4.0)	blend	R-404A	3943					1.000	1.143	1.000	1.306
Chlorodifluoromethane	CHClF ₂	R-22	1760 [†]	0.998	1.028	0.653	0.724	1.053	1.144	0.941	1.119
1,1,1,2-Tetrafluoroethane	CF ₃ -CH ₂ F	R-134a	1300 [†]	0.930	0.998	0.391	0.437	0.913	1.081	0.518	0.627

^{*} Values are relative to those for R-410A or R-404A in the basic cycle.

COP_{R-410A} = 4.68 and $Q_{vol,R-410A} = 4.85 \text{ MJ}\cdot\text{m}^{-3}$; COP_{R-404A} = 2.68 and $Q_{vol,R-404A} = 1.85 \text{ MJ}\cdot\text{m}^{-3}$

[†] Literature value from Myhre et al., (2013) or E.U. regulation (EU, 2014)

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[‡]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.