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LOW-GWP REFRIGERANTS: PERFORMANCE ASSESSMENT AND SELECTION TRADEOFFS

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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' 27 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 probability of finding 'ideal', better-performing low-GWP fluids is minimal.

Keywords: Air Conditioning, COP, Global Warming Potential, Refrigerants, Volumetric Capacity

1. INTRODUCTION

As anticipated for some time, an addendum 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 developing countries.

Our search for low-GWP replacement fluids relied on the screening of a comprehensive database of chemical substances. To this database we applied filters representing different refrigerant selection criteria to reject unsuitable molecules and reduce the pool of candidates to only plausible fluids. This reduced pool of fluids underwent two rounds of thermodynamic cycle simulations, which revealed the group of the 'best' 27 low-GWP refrigerants.

In the course of this comprehensive project we published several papers to communicate intermediate results. Among them, Domanski et al. (2014) discussed the performance limits of the vapor compression cycle, McLinden et al. (2014) reported results of the first database screening and described refrigerant selection

tradeoffs, and McLinden et al. (2015) presented the results of the improved second database screening and provided cycle performance information based on simplified simulations for AC applications. The most complete description of the project is given in McLinden et al. (2017), which provides the final list of the 'best' 27 fluids with the cooling mode performance from cycle simulations with optimized heat exchangers, and includes a complete description of the screening methodology with an extensive list of references.

The current paper summarizes the second (final) screening of the database, discusses the importance of refrigerant thermophysical properties and heat exchanger optimization in cycle simulations, and provides a combined presentation of the performance of the 'best' 27 fluids in air conditioning [originally reported in McLinden et al. (2017)], heating, and refrigeration applications.

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 screens for a second screening. For this second (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. 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 comprising 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 screens 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 of the study. 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} estimate 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 screens of $GWP_{100} < 1000$ and $320\ K < T_{crit} < 420\ K$ 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 screens 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 –O–O– group), ketenes (compounds with the –C=C=O group), and allenes (compounds

with the –C=C=C– group). Compounds with a carbon-carbon triple bond were generally dropped as less stable than those with a double bond; for example, fluoroethyne (FC≡CH) is described as "treacherously explosive in the liquid state." (Middleton et al., 1959). There were exceptions, however, and trifluoropropyne was retained.

For the toxicity screen, in addition to considering functional groups, e.g., $=CF_2$ and -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 following a review of results of the first screening (McLinden et al., 2014) in which a flammability filter rejected a large number of flammable fluids, some of which perhaps could be used in several applications after implementing appropriate hazard mitigation measures.

3. PERFORMANCE EVALUATION

Performance merits of refrigerants are defined by COP and Q_{vol} obtained at specified operating conditions. 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 screen 320 K < T_{crit} < 420 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, cycle with a liquid-line/suction line heat exchanger (LL/SL-HX), and two-stage economizer cycle (Figure 1).

3.1 First round 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. 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).

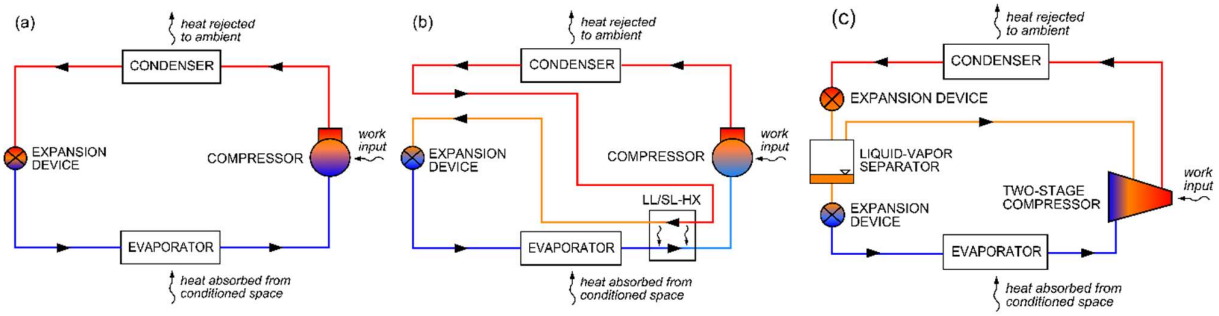

Figure 1: Schematic of (a) basic cycle, (b) cycle with liquid-line/suction line heat exchanger (LL/SL-HX), and (c) two-stage economizer cycle

Figure 2 presents COPs and volumetric capacities obtained from the first round 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 or a COP < 5. (For R-410A in the ideal cycle Q_{vol} = 6.62 MJ·m^{-3} and COP = 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.) This yielded a set of less than 30 low-GWP fluids for simulations in greater detail in the second simulation round.

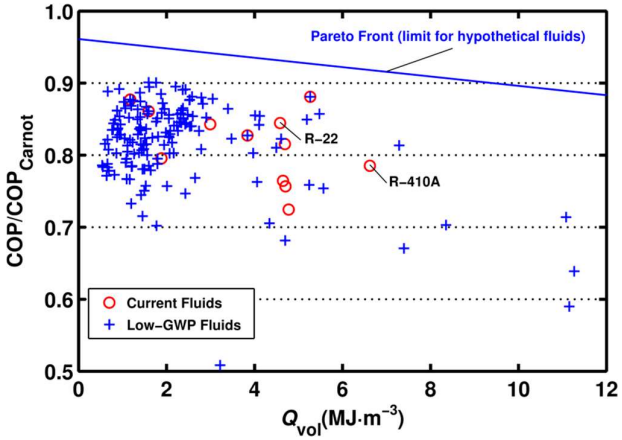

Figure 2: Ratio of COP to the Carnot COP in the ideal basic cycle for air-conditioning (McLinden et al., 2015)

3.2 Second round 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 (ΔT_{hx}) in the evaporator and condenser (Domanski and McLinden, 1992). This modeling approach facilitates accounting for refrigerant thermophysical properties, pressure drop, and heat-transfer coefficient on the cycle performance on a relative basis (Brown at 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 saturation temperature drop and results in increased mean effective temperature differences ΔT_{hx} in the heat exchangers. The refrigerant heat-transfer coefficient h also affects ΔT_{hx}; a higher h yields a lower ΔT_{hx}. A decrease in condenser and evaporator ΔT_{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 Δp are both a function of the refrigerant mass flux G, where h approximately increases proportionally to $G^{0.8}$, while Δp increases proportionally to G^2 (Collier and Thome, 1994). There is an optimum value of G that provides a best compromise between the opposite effects that h and Δp have on the system COP.

Figure 3 shows the dependency of h and Δp on the mass flux in evaporation at T_{sat} = 0 °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 Δp, respectively. The results shown are normalized by nominal h and Δp values for R-32 at G_{nom} = 100 kg·m^{-2}·s^{-1}, h_{nom} = 3.16 kW·m^{-2}·K^{-1} and Δp_{nom} = 1.26 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 Δp, x_{Start} is the quality corresponding to the isenthalpic expansion from a condenser saturation temperature of 45 °C and 3 K subcooling to evaporator conditions of T_{sat} = 0 °C, and x_{End} = 1.

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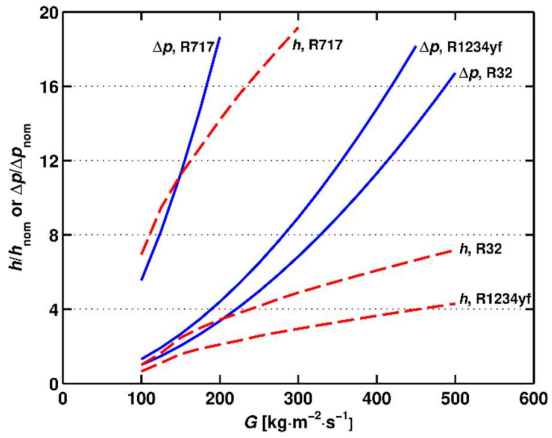

Figure 3: Effect of refrigerant mass flux on forced-convention evaporation and pressure drop

Figure 3 shows that an increase in refrigerant mass flux causes exponential increases in the pressure drop but only asymptotically increases the heat-transfer coefficient. First, comparing R-32 (a high-pressure fluid) and R-1234yf (a medium-pressure fluid), 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 $T_{sat} = 0$ °C, $dT/dp = 0.0934$ K·kPa^{-1} for R-1234yf and $dT/dp = 0.0384$ K·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.

The optimum refrigerant mass flux G is different for each refrigerant and depends on refrigerant thermodynamic and transport properties. 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 penalization 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 (Figure 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 less irreversibilities due to 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 and saturation temperature drops 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.

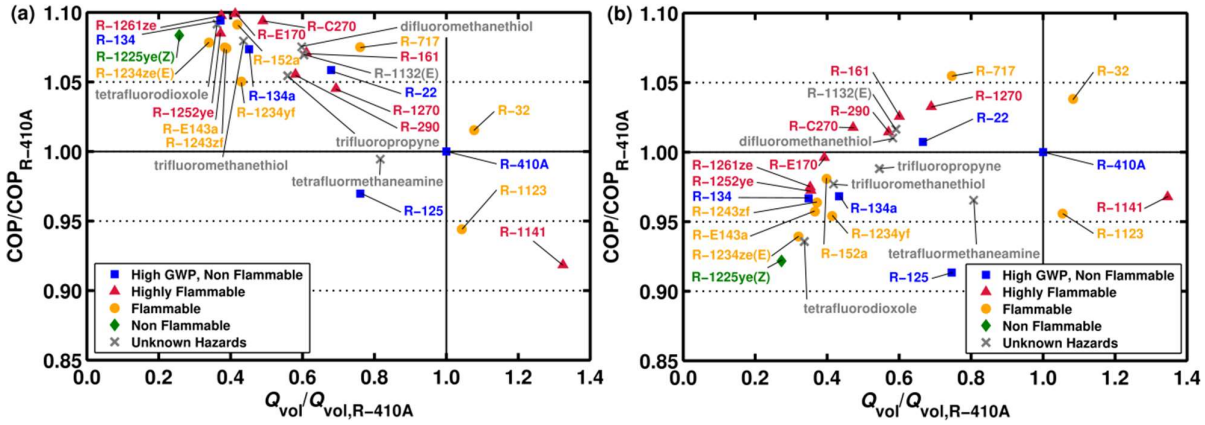

Figure 4: COP and Q_{vol} of selected fluids referenced to R-410A values; (a) 'ideal' CYCLE_D simulations and (b) CYCLE_D-HX simulations; air-conditioning application using the basic cycle, Figure 1(a)

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 simulation methodology used by CYCLE_D-HX is preferable for screening refrigerants for systems with forced-convection heat exchangers over CYCLE_D-type simulation models using imposed saturation temperatures in the evaporator and condenser.

4. SCREENING RESULTS

We completed the screening process based on CYCLE_D-HX simulation results for an air conditioner and generated a list of 27 fluids we deem to be the best single-component low-GWP replacements for small AC systems [see Table 1 in McLinden et al. (2017); Table 1 in the present paper lists the same fluids with COP and Q_{vol} for heating and refrigeration]. This list is a subset of the 138 fluids (i.e., those with 320 K < T_{crit} < 420 K) after unstable or toxic fluids were removed along with those having low Q_{vol} or COP. In this list of 27 we included R-1225ye(Z) and R-1123 based on evidence of some commercialization interest, and R-134 (GWP_{100} = 1120) since it may be considered as a blend component. Not simulated in our study (because of low T_{crit}) but included in the list of 27 are three high-pressure fluids: carbon dioxide (R-744), ethane (R-170) and fluoromethane (R-41). R-744 is the only low-toxicity, nonflammable, high-pressure fluid that was identified, but it would operate in a transcritical cycle. R-170 and R-41 would also operate near the critical point; being highly flammable, they do not seem to be attractive as single-component refrigerants, but may be considered as a blend component. These additional fluids were included with the intent to produce a 'complete' list of refrigerant options for small AC applications. 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.

The figures 4, 5, 6, and 7 present COP and Q_{vol} for the above-discussed fluids (except R-744, R-170 and R-41) for cooling, 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 majorities of fluids have been known and have ASHRAE designations (ASHRAE, 2013). Some of them are considered by industry for application as single-component refrigerants or a blend component. 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 non-flammable to highly flammable based on the lower flammability limit and heat of combustion, with one optional subclass (2L) based on the burning velocity (ASHRAE, 2013). Figures 4, 5, 6 and 7 show fluids in class 2 (including

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subclass 2L) using the color yellow, and denote class 3 fluids with red. Current air-conditioning systems predominantly use class 1 (non-flammable) 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 non-flammable 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 µL/L – 1000 µL/L (500 ppm – 1000 ppm by volume in air) (Schuster, 2009).

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. GWP_{100} are estimated by the method of Kazakov et al., (2010) 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			
				$\frac{COP}{COP_{R\text{-}410A}^*}$		$\frac{Q_{vol}}{Q_{vol,R\text{-}410A}^*}$		$\frac{COP}{COP_{R\text{-}404A}^*}$		$\frac{Q_{vol}}{Q_{vol,R\text{-}404A}^*}$	
				Basic	Econ.	Basic	Econ.	Basic	Econ.	Basic	Econ.
Hydrocarbons and dimethylether											
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
Fluorinated alkanes (HFCs)											
Fluoromethane	CH_3F	R-41	116†	§		§		§		§	
Difluoromethane	CH_2F_2	R-32	677†	1.025	1. 042	1.077	1.193	1.096	1.162	1.601	1.892
Fluoroethane	CH_2F-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
Fluorinated alkenes (HFOs) and alkynes											
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
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-tetrafluormethaneamine	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	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_2F	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:
$COP_{R\text{-}410A}$ = 4.68 and $Q_{vol,R\text{-}410A}$ = 4.85 MJ·m^{-3}; $COP_{R\text{-}404A}$ = 2.68 and $Q_{vol,R\text{-}404A}$ = 1.85 MJ·m^{-3}
†Literature value from Myhre et al., (2013) or E.U. regulation (EU, 2014)
‡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.

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' 27 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 that 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 GWP_{100} of 677. R-134 and R-E143a have GWP_{100} 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 27 fluids includes six novel molecules: tetrafluorodioxole, trifluoromethanethiol, trifluoropropyne, difluoromethanethiol, (E)-1,2-difluoroethene (R-1132(E)), and tetrafluoromethaneamine. Little data are available on these fluids so their risks are unknown, but 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 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 best performers and improved the worst 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 performance of all fluids, with the fluids performing worse in the basic cycle achieving a greater improvement than the best 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 the that of R-410A in the same economizer cycle.

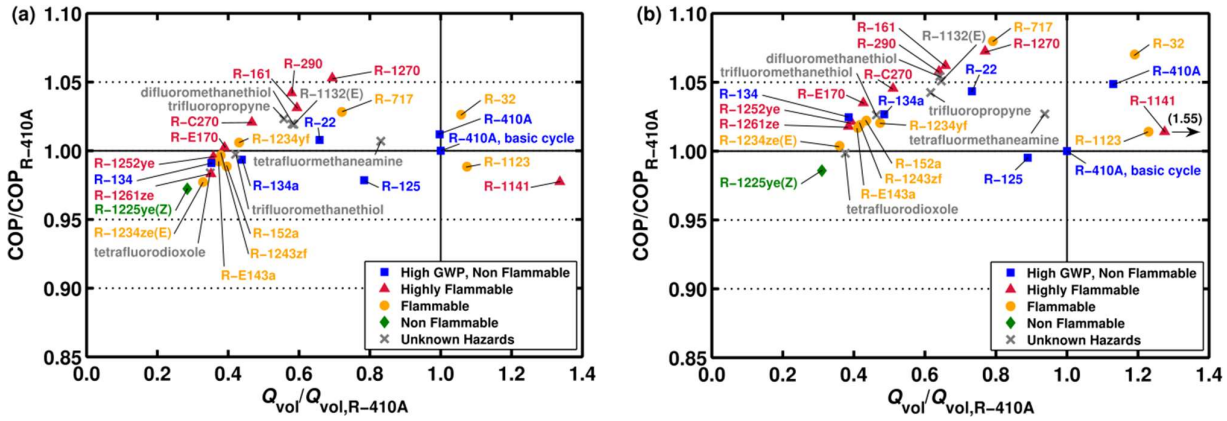

Figure 5: COP and Q_{vol} of selected fluids referenced to R-410A values; (a) cycle with LL/SL-HX, and (b) two-stage economizer cycle; CYCLE_D-HX simulations for an air-conditioning application

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 °C and a condensing temperature of 30 °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 that 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 °C for heating vs. 10 °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 °C for heating vs. 40 °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)).

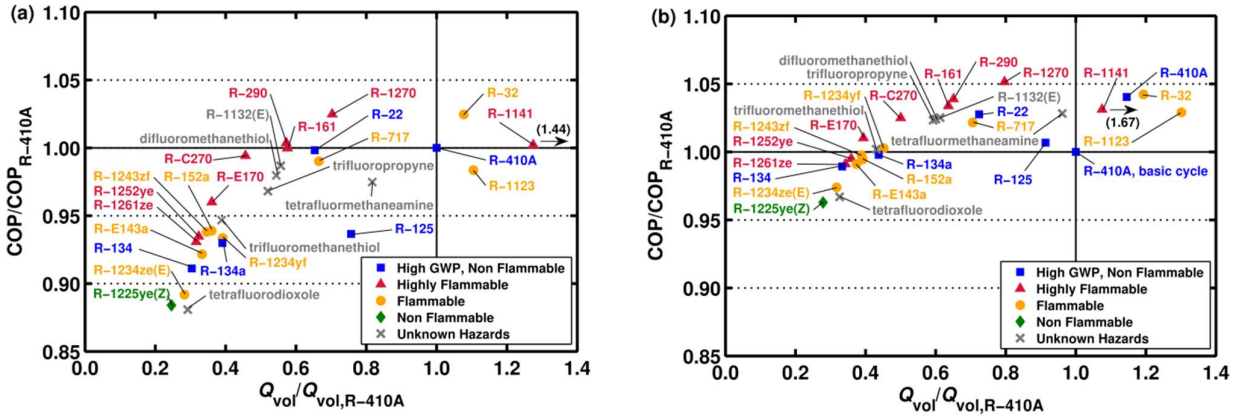

Figure 6: COP and Q_{vol} of selected fluids referenced to R-410A values from CYCLE_D-HX simulations for a heating application; (a) basic cycle, and (b) two-stage economizer cycle

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 °C and a condensing temperature of 30 °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.

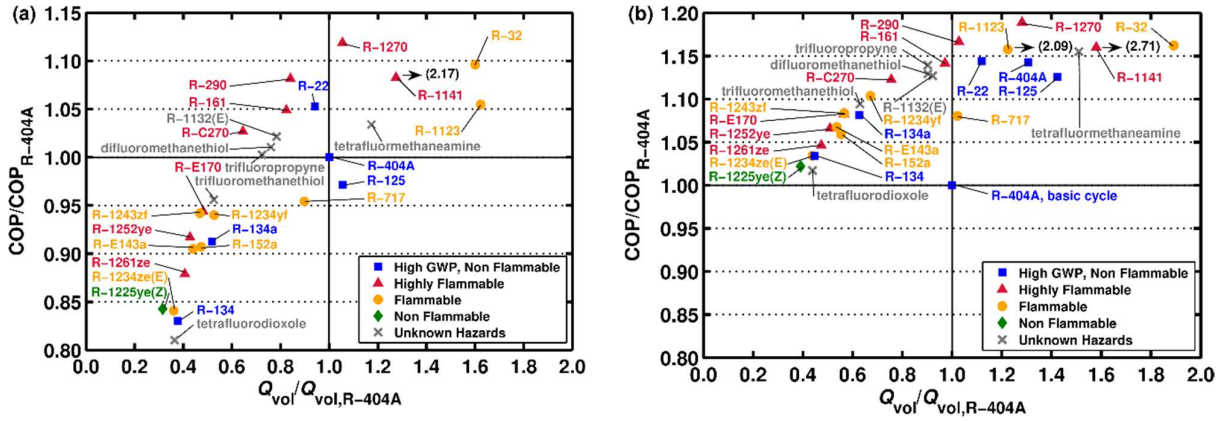

Figure 7: COP and Q_{vol} of selected fluids referenced to R-404A values from CYCLE_D-HX simulations for a refrigeration application; (a) basic cycle and (b) two-stage economizer cycle

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 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 a tradeoff between COP and volumetric capacity observed for an ideal cycle analysis based on thermodynamic properties alone. Refrigerant screening for such systems needs to include transport properties and heat exchanger optimization.

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NOMENCLATURE

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

Subscripts and symbols

crit	critical	sat	saturation
hx	heat exchanger	Δ	difference
nom	nominal		

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