NIST Technical Note 2014

Low-GWP Alternative Refrigerant Blends for HFC-134a

Strategic Environmental Research and Development Program Project: WP-2740; Final Report

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https://doi.org/10.6028/NIST.TN.2014

National Institute of
Standards and Technology
U.S. Department of Commerce

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September 2018

U.S. Department of Commerce
Wilbur L. Ross, Jr., Secretary

National Institute of Standards and Technology
Walter Copan, NIST Director and Undersecretary of Commerce for Standards and Technology

National Institute of Standards and Technology Technical Note 2014
Natl. Inst. Stand. Technol. Tech. Note 2014, 40 pages (September 2018)
CODEN: NTNOEF

This publication is available free of charge from:
https://doi.org/10.6028/NIST.TN.2014

Abstract

Objective

This study addresses the objectives of the Statement of Need number WPSON-17-20 “No/Low Global Warming Potential Alternatives to Ozone Depleting Refrigerant” of the Strategic Environmental Research and Development Program; the U.S. Department of Defense science and technology program executed in partnership with the U.S. Department of Energy and the U.S. Environmental Protection Agency.

The goal of this study was to identify nonflammable, nontoxic, low global-warming-potential (GWP) replacements for HFC-134a in an air-conditioning system that would maintain the energy efficiency and capacity. A prior exhaustive work demonstrated that all single-component refrigerants that could serve—from the performance stand-point—as a replacement for HFC-134a are at least mildly flammable. For this reason, this study undertook an evaluation of binary and ternary refrigerant blends to explore the possibility of formulating a nonflammable blend that would satisfy the requirements of military systems.

Technical Approach

The quest for suitable HFC-134a replacements undertaken in this study relied on an exhaustive search and evaluation of two- and three-component blends among a slate of 13 single-component refrigerants. All possible combinations of the 13 fluids were considered. A 0.04 mole fraction composition interval was applied resulting in 100,387 blends.

The selection of the “best” blends was a multi-parameter optimization process with four main objectives:

- Minimize/eliminate flammability:
  Military specifications require a flammability class designation of 1 (“no flame propagation”). For the estimation of flammability classification, we developed a novel method combining two flammability metrics: the adiabatic flame temperature and the ratio of the number fluorine atoms to (fluorine + hydrogen) atoms in the molecule.
- Minimize GWP:
  The GWP of a blend is defined as the mass-fraction-weighted GWP of the blend’s components. It is easily calculated once GWP values of the components and their composition in the blend are known.
- Maximize the coefficient of performance (COP):
  The COP characterizes the efficiency of the system. The larger the COP, the better the system efficiency. To estimate the COP, we used two cycle simulation models of different simulation detail. A simple model was used in the initial screening, and a more detailed model was used for the final assessment of the selected “best” blends.
- Match the volumetric capacity (Q_{vol}) of the baseline HFC-134a system:
  Q_{vol} of an air-conditioning system is a figure of merit that captures the size of the compressor. The larger Q_{vol}, the smaller the compressor needs to be for a given cooling capacity. As with COP, the Q_{vol} were obtained from the two cycle simulation models of different sophistication.

Results

The study identified 22 refrigerant blends, 14 of which have GWP ranging from 633 to 870 and were estimated to be “nonflammable”; the remaining eight have GWP ranging from 8 to 573 and were estimated to be “borderline flammable. The COP of these blends were from 0.6 % to 2.0 % below that for HFC-134a. The Q_{vol} varied in a larger range from -10 % to + 3.1 %. In general, the data showed a trend of COP increasing as the GWP increased.

The study yielded a novel method for estimating flammability of single-component refrigerants and refrigerant blends. This method was applied in the study in the blend selection process.

It can be concluded that it is possible to implement a nonflammable HFC-134a replacement blend with about 50 % lower GWP than that of HFC-134a. Selection of the optimal blend requires experimental validation of representative equipment under controlled conditions.

Benefits

The study explored available options for replacing HFC-134a using state-of-the-art prediction methods for refrigerant thermophysical properties, flammability classification, and vapor-compression cycle performance.

For selection of the optimal low-GWP blend to be applied in the field, the present results require experimental verification.

Table of Contents

List of Tables

List of Figures

List of Acronyms

AC	air conditioning
AHRI	Air-Conditioning, Heating and Refrigeration Institute
ANSI	American National Standards Institute
AREP	Alternative Refrigerant Evaluation Program
ASHRAE	American Society of Heating Refrigerating and Air-Conditioning Engineers
ASTM	American Society for Testing and Materials
CFC	chlorofluorocarbon
COP	coefficient of performance
CRP	cooperative research program
GWP	global warming potential
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFO	hydroflouroolefin
HTF	heat-transfer fluid
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
SAE	Society of Automobile Engineers

Key Words

Air conditioning; Coefficient of performance; Cycle simulation; Flammability; Refrigerants; Vapor compression; Volumetric capacity.

Acknowledgements

This work was supported by the Strategic Environmental Research and Development Program; project WP-2740. Dr. Robin Nissan was the Program Manager.

1. Objective

This study addressed the objectives of the Statement of Need number WPSON-17-20 "No/Low Global Warming Potential Alternatives to Ozone Depleting Refrigerant" of the Strategic Environmental Research and Development Program; the U.S. Department of Defense science and technology program executed in partnership with the U.S. Department of Energy and the U.S. Environmental Protection Agency.

The goal of this study was to identify nonflammable, nontoxic, low global-warming-potential (GWP) replacements for HFC-134a in an air-conditioning system that would maintain the energy efficiency and capacity. Additional refrigerant requirements are concerned with energy efficiency, materials compatibility, flammability and toxicity, with the last two having a decisive weight on refrigerant acceptance because of the unique operating environments of military systems.

The goal of this study was to identify nonflammable, nontoxic, low global-warming-potential (GWP) replacements for HFC-134a in an air-conditioning system that would maintain the energy efficiency and capacity. A prior exhaustive work demonstrated that all single-component refrigerants that could serve—from the performance stand-point—as a replacement for HFC-134a are at least mildly flammable [1, 2, 3]. For this reason, this study undertook an evaluation of binary and ternary refrigerant blends to explore the possibility of formulating a nonflammable blend that would satisfy the requirements of military systems.

2. Background

Concerns about climate change have provided a stimulus for limiting emissions of greenhouse gases resulting from human activities. Hydrofluorocarbons (HFCs), currently used as refrigerants in air-conditioning systems, are potent greenhouse gases, and their contribution to climate change will increase unless their emissions are curtailed. An Amendment to the Montreal Protocol [4] adopted in October 2016 calls for a significant reduction of the GWP-weighted production and use of the working fluids in air-conditioning and refrigeration equipment. Also, various national and regional regulations have been already put in place. In some applications, new generation, low-GWP refrigerants have already been introduced, *e.g.*, automotive AC systems.

The current transition to low-GWP fluids is more difficult to implement than the previous (1990s) transition to fluids with a zero ozone-depletion potential due to the increased number of refrigerant selection criteria. Over the past several years, industry and academia have made significant efforts searching for alternative refrigerants to replace R-410A (a blend of HFC-32 and HFC-125) and HFC-134a. For example, R-410A replacement options have been extensively researched within the AHRI Low-GWP Alternative Refrigerant Evaluation Program (AREP), and several new mixtures have been proposed. HFC-134a alternatives were also extensively researched within the SAE cooperative research programs (CRPs). For the automotive AC application, the majority of participants selected the mildly-flammable, single-component refrigerant HFO-1234yf while R-744 (carbon dioxide) was endorsed by a few companies in Europe.

Our 2011–2015 extensive screening study searching for low-GWP refrigerants showed limited options for single-component alternatives for R-410A and HFC-134a [1, 2, 3]. We screened an extensive database containing over 60 million molecules using filters (GWP, COP, etc.) that corresponded to the fluid selection criteria. The study yielded a group of 21 low-GWP fluids, which we considered to be of the primary interest. All of these fluids satisfied the thermodynamic criteria. Fifteen of them passed the toxicity and stability filters, but they are at least mildly flammable. The remaining six fluids are little known, and their risks have not been identified. We included these fluids in the list without screening for toxicity and stability, solely based on no evidence of their unfavorable effects.

The final list was expanded by seven additional entries to 28 fluids with the goal to provide a comprehensive list of fluids that could be used as single-component refrigerants or blend components [3]. The seven added fluids did not pass our screens, but they could be used in a transcritical cycle (*e.g.*, CO_2), which we did not model in our study, or as a blend component in a subcritical cycle.

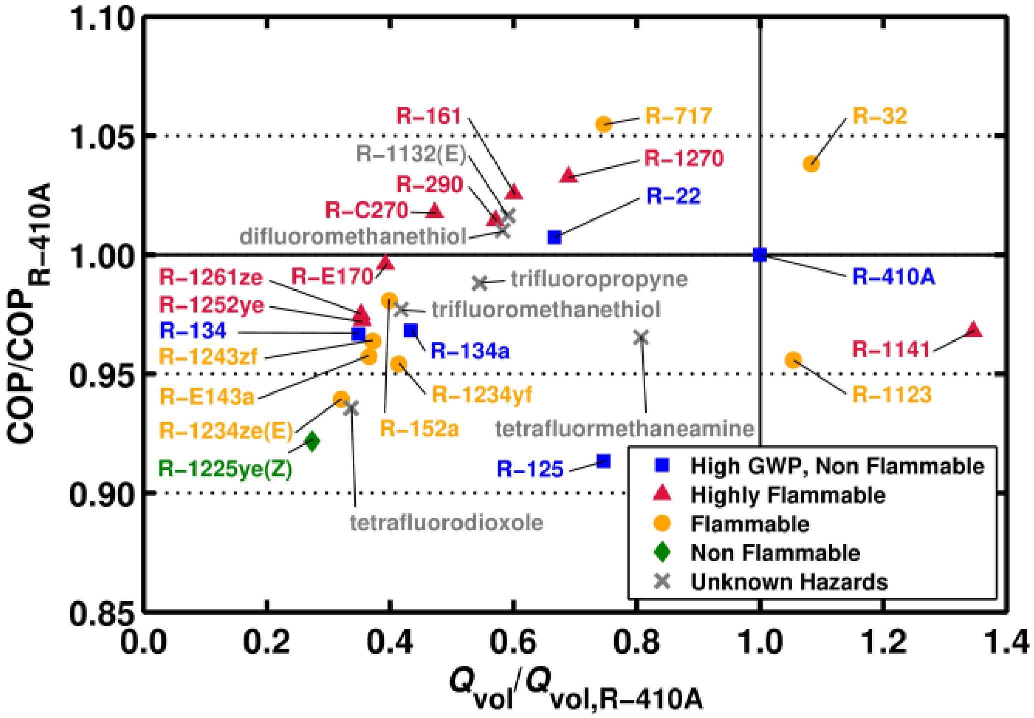

Figure 1. COP and Q_{vol} of selected fluids referenced to R-410A values [2], air-conditioning application

Figure 1 graphically presents cycle simulation results for the identified low-GWP fluids obtained from an advanced cycle simulation model. For comparison, the figure also includes the current high-GWP refrigerants. The hazards associated with the six fluids denoted by a grey symbol '×' are unknown. All other fluids (besides the high-GWP fluids and HFO-1225ye(Z) (labeled as R-1225ye(Z) in the figure), which has toxicity concerns, are at least mildly flammable. The fluids denoted with a yellow dot are of lower flammability (ASHRAE flammability class 2 or 2L). Unless any of the new fluids denoted by the gray symbol '×' are further examined and found to be non-flammable, stable, and of low toxicity, our prior study did not identify a nonflammable, single-component replacement for HFC-134a. For this reason, the present project focused on refrigerant blends.

3. Materials and Methods

3.1 Search Methodology for HFC-134a Replacement Blends

The quest for suitable HFC-134a replacement undertaken in this study relied on an exhaustive search and evaluation of two- and three-component blends among a slate of 13 single-component refrigerants. Nine of the single-component refrigerants have an “A” toxicity classification per ANSI/ASHRAE Standard 34 [5] and International Standard ISO 817 [6], indicating them as having “low toxicity,” which is the lowest toxicity designation under these standards. An additional four single-component refrigerants have not been classified but are expected to have similarly low toxicity.

To predict the performance and suitability of possible blends, we used refrigerant property estimation techniques, thermodynamic analysis, vapor-compression cycle simulations, and flammability estimations. The result was a dataset of refrigerant blends with their component composition, GWP, coefficient of performance (COP), volumetric capacity (Q_{vol}), and flammability assessment.

The selection of a refrigerant blend to replace refrigerant HFC-134a is a multi-parameter optimization process. There are four main objectives:

- Minimize/eliminate flammability:
  Military applications require refrigerants to be nonflammable. In this study we adopt the refrigerant flammability classification established by ANSI/ASHRAE Standard 34 [5] and International Standard ISO 817 [6]. For the estimation of flammability classification of the studied blends, we developed a novel method combining two flammability metrics: the adiabatic flame temperature and the ratio of the number fluorine atoms to hydrogen atoms in the molecule. We demonstrate that they yield a reliable prediction of the flammability class (1, 2L, 2, 3) according to applicable standards [5,6].

- Minimize GWP:
  The GWP of a blend is defined as the mass-fraction-weighted GWP of the blend’s components. It is easily calculated once GWP values of the components and their composition in the blend are known. Several time horizons are possible for the calculation GWP, but it is most common to consider a 100-year time horizon (sometimes denoted as GWP_{100}), and we used this metric here.

- Maximize the COP:
  The COP characterizes the efficiency of the system. The larger the COP, the better the system efficiency. To estimate the COP, we used two cycle simulation models of different simulation detail. A simple model was used in the initial screening, and a more detailed model was used for the final assessment of the selected “best” blends.

- Match the Q_{vol} of the baseline system:
  Q_{vol} of an air conditioning system is a figure of merit that captures the size of the compressor. The larger Q_{vol}, the smaller the compressor needs to be for a given cooling capacity. As with COP, the Q_{vol} were obtained from the two cycle simulation models of different sophistication.

Our search for optimal HFC-134a replacement blends involved the above four figures of merit (attributes) and consisted of the following stages:

- Selection of blend constituents; *i.e.*, 13 single-component refrigerants of low toxicity that could possibly form a replacement blend.
- Determination of figures of merits of the blends (COP, Q_{vol}, flammability classification, GWP) for an exhaustive matrix of possible binary and ternary mixtures. In this step, we evaluated COP and Q_{vol} using a simplified cycle model.
- Selection of "best" blends based on the determined attributes.
- Determination of COP and Q_{vol} of the "best" blends using an advanced cycle model.

The exhaustive approach of the study, *i.e.*, evaluation of the entire set of possible blends, allows for a quick re-examination of optimal blend choices for a change in the objective function (for example, emphasizing low GWP over a high COP). Such re-examination would involve a simple scan of the dataset, rather than a complete rerunning of the optimization.

3.2 Selection of Blend Constituents for Screening

For blending, we selected 13 fluids within a range of pressure, flammability, and GWP values that might produce a blend with desired characteristics of HFC-134a replacement fluid (Table 1). With the exception of HFC-143a, these fluids came from the list of 28 fluids discussed in Section 2. Looking at Fig. 1, the immediate neighbors of HFC-134a were selected (except for trifluoromethanethiol and R-E143a for which we would not be able to assess flammability if used in mixtures) and the highly flammable fluids (denoted by a red triangle). The selected fluids include hydrofluoroolefins (HFOs), which have very low GWP values but are mildly flammable; hydrofluorocarbons (HFCs) with moderate-to-high GWP values that are nonflammable and, thus, might serve to suppress the flammability of a blend; additional mildly flammable HFCs; and carbon dioxide (CO_2), which is nonflammable with GWP = 1, but would raise the working pressure of a blend. We did not include the highly flammable fluids because only a small percentage of a hydrocarbon in a blend would result in a flammable blend.

Additional considerations were the commercial availability of the fluid and the availability of property data (in the form of an accurate equation of state). To ensure reasonable uncertainties of our cycle simulations, we only selected fluids that are included in REFPROP, the NIST fluid thermodynamic and transport properties database [7]. REFPROP calculates the thermodynamic and transport properties of industrially important fluids and their mixtures. It is based on the most accurate pure fluid and mixture models currently available, and it is used worldwide by academia and industry alike in research and development efforts.

The global warming potential values are tabulated in several sources, and here we used the values based on a 100-year horizon [8]. Four fluids do not have assigned ASHRAE safety classification; the remaining nine fluids are of low toxicity, *i.e.*, they have an "A" classification under the relevant standards [5, 6].

Table 1. Single-component fluids selected in this study and selected characteristics.

ASHRAE designation	Chemical class	IUPAC name	Formula	T_c/K	GWP100	ASHRAE class	$\bar{\Pi}^*$
R-134a	**HFC**	**1,1,1,2-tetrafluoroethane**	$\mathbf{CF_3CH_2F}$	**374.2**	**1300**	**A1**	**–9.7**
R-744	Inorganic	carbon dioxide	CO_2	304.1	1	A1	n.a.
R-125	HFC	pentafluoroethane	CHF_2CF_3	339.2	3170	A1	–36.9
R-227ea	HFC	1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3	374.9	3350	A1	–37.6
R-134	HFC	1,1,2,2-tetrafluoroethane	CHF_2CHF_2	391.8	1120	**	–5.5
R-1234ze(E)	HFO	trans-1,3,3,3-tetrafluoroprop-1-ene	$CHF{=}CHCF_3$	382.5	1	A2L	5.9
R-1234yf	HFO	2,3,3,3-tetrafluoroprop-1-ene	$CF_3CF{=}CH_2$	367.9	1	A2L	5.9
R-32	HFC	difluoromethane	CH_2F_2	351.3	677	A2L	34.0
R-143a	HFC	1,1,1-trifluoroethane	CF_3CH_3	345.9	4800	A2L	26.2
R-1243zf	HFO	3,3,3-trifluoroprop-1-ene	$CH_2{=}CHCF_3$	376.9	1	§	43.1
R-1234ze(Z)	HFO	cis-1,3,3,3-tetrafluoropropene	$CHF{=}CHCF_3$	423.3	1	†	5.9
R-152a	HFC	1,1-difluoroethane	CHF_2CH_3	386.4	138	A2	54.6
R-41	HFC	fluoromethane	CH_3F	317.3	116	‡	67.5

* Normalized flammability index (see Section 3.4)
**Classification not assigned by ASHRAE Standard 34, but is estimated to be A1
†Classification not assigned by ASHRAE Standard 34, but is estimated to be A2L
§Classification not assigned by ASHRAE Standard 34, but is estimated to be A2
‡Classification not assigned by ASHRAE Standard 34, but is estimated to be A3

An initial assessment included only ten fluids that were commercially available. This list was augmented by the addition of HFC-134, HFC-41, and HFO-1243zf. While these three fluids are not widely available, they were included in order to carry out the most exhaustive search practical. Additional fluids are of interest (*i.e.*, those of “unknown hazards” shown in Fig. 1), but the lack of property data did not allow their inclusion in the study.

The screening involved an exhaustive evaluation of all possible combinations of the 13 fluids listed in Table 1, taken two or three at a time (*i.e.*, all possible binary and ternary blends). A composition interval of 0.04 mole fraction was applied, which yielded 100,387 blends. In addition, we considered the R-134a/1234yf binary blend with composition of (0.468/0.532) mole fraction designated by ASHRAE Standard 34 [5] as R-513A with an A1 safety classification *i.e.*, “nonflammable”. GWP values, flammability classifications, COP, and Q_{vol} were determined for the complete set of these blends, with cycle simulations carried out using a simplified cycle model. Twenty-two “best” blends were then evaluated using an advanced cycle model for more accurate predictions of COP and Q_{vol}.

3.3 Determination of COP and Q_{vol} by a Simplified Cycle Model

The cycle model is based upon a simplified analysis of a four-component air-conditioning system with lumped pressure drops. Figure 2 shows a schematic of the system, and Fig. 3 shows the thermodynamic diagrams.

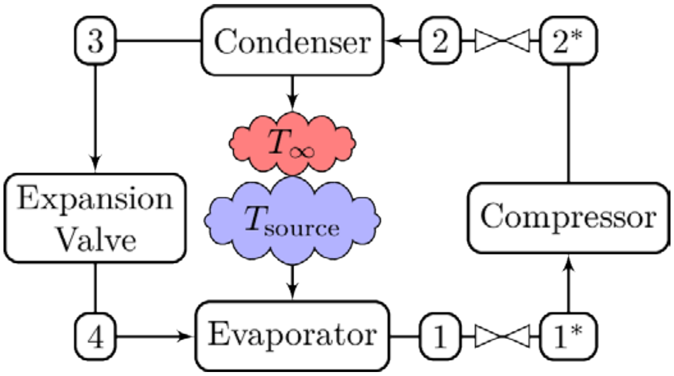

Figure 2. System schematic. (The "valves" between points 1 & 1^* and 2 & 2^* represent pressure drop in the evaporator and condenser, which the simplified cycle model lumped at the compressor inlet and outlet, respectively.)

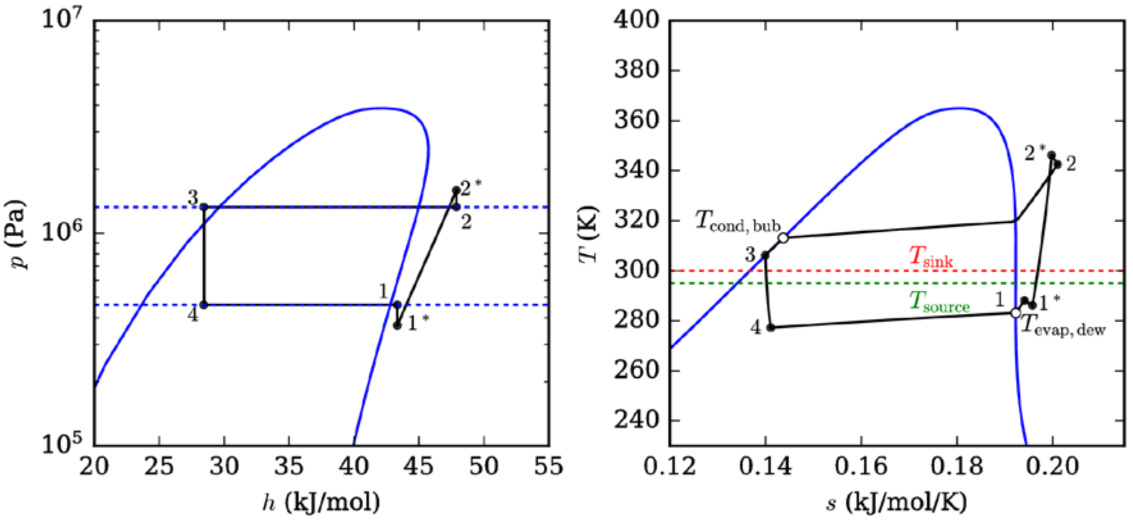

Figure 3. Pressure-enthalpy (*p*-*h*) and temperature-entropy (*T*-*s*) diagrams for an equimolar mixture of HFC-125 + HFO-1234ze(E) showing the vapor-compression cycle. Calculations were carried out with NIST REFPROP [7].

Due to the subtle complexities of modeling blends in thermodynamic cycles, we describe the cycle model in some depth. The specification of the model parameters was as follows:

- Evaporator dew-point temperature $T_{\mathrm{evap,dew}}$: 10 °C
- Condenser bubble-point temperature $T_{\mathrm{cond,bub}}$: 40 °C
- Evaporator outlet superheat ΔT_{sh}: 5 K
- Condenser exit subcooling ΔT_{sc}: 7 K
- Compressor adiabatic efficiency η_{a}: 0.7
- Evaporator pressure drop: for the baseline system, a reduction of dew-point temperature of 2 K
- Condenser pressure drop: for the baseline system, a reduction of bubble-point temperature of 2 K

The key difference between this cycle model and other simplified cycle models is the inclusion of a simplified pressure drop model. It is assumed that the pressure drop from the high-side components and the low-side components can be lumped into pressure drops at the inlet and outlet of the compressor, respectively. Therefore, the compressor sees a larger pressure lift than that corresponding to the pressures in the evaporator and condenser. The drop in saturation temperature for high- and low-sides of the system are specified for the baseline HFC-134a system, and the pressure drop scaling (described below) is used to calculate the pressure drop for the refrigerant blends.

In the simplified cycle analysis, the pressures in the evaporator and condenser are assumed to be constant, given by vapor-liquid equilibrium calculations at the respective saturation pressure:

$$p_{\mathrm{evap}} = p_{\mathrm{dew}}(T_{\mathrm{evap,dew}}) \tag{1}$$

$$p_{\mathrm{cond}} = p_{\mathrm{bub}}(T_{\mathrm{cond,bub}}). \tag{2}$$

The selection of the saturation states used to define the low- and high-side pressures is based on a rudimentary pinch analysis. This pinch analysis assumes that the source and sink temperatures are fixed, that the condenser outlet pinch is fixed, and that the evaporator outlet pinch is fixed. Therefore, stacking up the temperature differences (plus the respective superheat or subcooling), we can arrive at the relevant saturation temperature. This method is the worst-case simplified cycle analysis option for mixtures with temperature glide because the heat-transfer irreversibilities are maximized [9]. This represents a conservative approach in the sense that it favors drop-in replacements that would require little or no modifications of existing systems. For blends having significant temperature glide, and systems with counterflow or cross-counterflow heat exchange, the temperature profiles of the source and sink fluids and that of the working mixture may be better aligned, resulting in lower heat transfer irreversibilities and higher efficiencies.

Condenser. The outlet enthalpy of the condenser is given by

$$h_3 = h\,(T_3, p_{\mathrm{cond}}), \tag{3}$$

where the outlet temperature of the condenser T_3 is given by

$$T_3 = T_{\mathrm{cond,bub}} - \Delta T_{\mathrm{sc}}, \tag{4}$$

and where the bubble-point temperature of the condenser is given by

$$T_{\mathrm{cond,bub}} = T_{\mathrm{bub}}\,(p_{\mathrm{cond}}). \tag{5}$$

The pressure drop in the condenser Δp_{high} is given by Eq. (15), in which ρ'' and μ'' are evaluated at the dew point at the condensing pressure p_{cond}.

Evaporator. The dew-point temperature is imposed for the evaporator, as is its inlet enthalpy (because the outlet state of the condenser is fully specified) and the throttling process is assumed to be adiabatic. Therefore, the states 3, 4, and 1 can be fully specified and the enthalpies calculated from

$$h_4 = h_3 \tag{6}$$

$$h_1 = h\,(T_{\mathrm{evap}} + \Delta T_{\mathrm{sh}}, p_{\mathrm{evap}}) \tag{7}$$

The pressure drop in the evaporator Δp_{low} is given by Eq. (15), in which ρ'' and μ'' are evaluated at the dew point at the evaporator pressure p_{evap}.

Compressor. The pressure drops in the cycle are lumped at the compressor. Therefore, the inlet state of the compressor 1 is given by the pressure drop relative to the state point 1:

$$h_{1*} = h_1 \tag{8}$$

$$T_1 = T\,(h_{1*}, p_{\mathrm{evap}} - \Delta p_{\mathrm{low}})$$

Similarly, the outlet pressure of the compressor p_2 is given by $p_{2*} = p_{\mathrm{cond}} + \Delta p_{\mathrm{high}}$. The classical adiabatic efficiency formulation is used for the compressor, assuming that there is no heat transfer from the compressor to the environment. Therefore, the adiabatic efficiency is defined by

$$\eta_{\mathrm{a}} = \frac{h_{2\mathrm{s}} - h_{1*}}{h_{2*} - h_1} \tag{10}$$

where the isentropic enthalpy h2s is obtained from

$$h_{2\mathrm{s}} = h\,(s_{1*}, p_{2*}). \tag{11}$$

Cycle metrics. The coefficient of performance (COP) of the heat pump is given by

$$\mathrm{COP} = \frac{h_1 - h_4}{h_{2*} - h_{1*}} \tag{12}$$

and the volumetric capacity of the heat pump is given by

$$Q_{\mathrm{vol}} = (h_4 - h_1) \cdot \rho\,(T_1*, p_1*) \tag{13}$$

Pressure drop modeling. The inclusion of pressure drop in the model (even if approximate), is crucial to yield a fair screening of refrigerants [2]. The simplified pressure drop in our analysis is based upon scaling the system for the refrigerant blends to have the same capacity as the baseline HFC-134a system.

The pressure drop in each of the heat exchangers is assumed to be based upon a frictional pipe flow analysis of a homogeneous fluid (making use of the Fanning friction factor f_{F}) given by

$$\Delta p = \frac{2 f_{\mathrm{F}} G^2 L}{\rho D} = \frac{2L}{D} \frac{m^2}{A^2} \frac{1}{\rho} f_{\mathrm{F}}. \tag{14}$$

For a specified pressure drop Δp and equality of system cooling capacity $Q = m / (h_1 - h_4)$, after canceling all non-thermophysical properties and lumping them into a constant, the system term $C_{\Delta p}$ is given by

$$C_{\Delta \mathrm{p}} = \frac{\Delta p p'' \, (h_1 - h_4)^{1.8}}{\mu''^{0.2}} \tag{15}$$

which is obtained for the baseline system (all units are base SI), for an imposed pressure drop given as a change in saturation temperature for HFC-134a. The obtained pressure drop coefficient is then used for each of the blends, where the thermophysical properties (density ρ" and viscosity μ") are evaluated at the dew-point state at the specified heat exchange pressure.

3.4 Estimation of Flammability

In ANSI/ASHRAE Standard 34 [5] and ISO Standard 817 [6], flame propagation and the lower flammability limit are determined by the test method specified in ASTM E681 [10], with slight modifications. The flammability of a refrigerant is classified based on its heat of combustion, lower flammability limit, and laminar burning velocity. The classes range from "1" (fluids exhibiting "no flame propagation") to "3" ("higher flammability"). Class 3 fluids exhibit flame propagation (at 60 °C) and have a heat of combustion greater than 19 MJ/kg *or* a lower flammability limit less than 0.10 kg/m^3. Class 2 fluids ("lower flammability") exhibit flame propagation (at 60 °C) and have a heat of combustion less than 19 MJ/kg *and* a lower flammability limit greater than 0.10 kg/m^3. Class 2L fluids (a sub-category of class 2 fluids) meet the additional condition of a maximum burning velocity less than 10 cm/s. Class 1 fluids do not exhibit "flame propagation" (at 60 °C), as defined in ANSI/ASHRAE Standard 34 and ISO Standard 817; *i.e.*, a maximum flame angle in the test apparatus of less than 90°.

For the refrigerant blend flammability assessment, we developed a new method [11] based on two parameters that can be readily evaluated for a given mixture: the adiabatic flame temperature T_{ad}, and the F-substitution ratio $F/(F + H)$. The adiabatic flame temperature is the temperature reached by a reacting mixture of fuel (*e.g.*, refrigerant) and oxidizer (*e.g.*, humid air) that undergoes an exothermic (heat-releasing) reaction to its most stable equilibrium products, under adiabatic conditions. The F-substitution ratio $F/(F + H)$ is the ratio of the number of fluorine atoms to the sum of fluorine and hydrogen atoms in the reacting mixture of air with refrigerant. This approach is based on historical work showing the influence of the adiabatic flame temperature on hydrocarbon flammability limits, and the influence of fluorine-containing species on the combustion chemistry of hydrocarbon flames [11].

The adiabatic flame temperature was calculated using the open-source thermodynamics, transport, and kinetics solver Cantera [12] together with thermodynamic databases for hydrofluorocarbons developed at NIST [13]. The calculation requires the molar composition of the refrigerant blend, the molar composition of the oxidizer (*i.e.*, air and water vapor), and an estimate of the molar stoichiometric oxidizer requirement for peak temperature. The F-substitution ratio $F/(F + H)$ is calculated from this initial reaction mixture based on the molar composition and number of H and F atoms in each constituent.

Using the ASHRAE Standard 34 refrigerant database, we benchmarked our approach by comparing the flammability class with the calculated values of T_{ad} and $F/(F + H)$, for each of the HFC- and HFO-containing refrigerants and refrigerant blends in the database [5]. A plot of T_{ad} vs. $F/(F + H)$ (Fig. 4) shows how these parameters are related to the ASHRAE Standard 34 flammability designations: flammable (classes 2 and 3), mildly flammable (class 2L), and non-flammable (class 1). In Fig. 4, dotted lines have been drawn to demarcate the flammability regions. These lines originate at $F/(F + H) = 0$ and $T_{\mathrm{ad}} = 1600$ K based on the observation that hydrocarbons (for which $F/(F + H) = 0$) do not burn when diluted with an inert gas such that their adiabatic flame temperature falls below 1600 K.

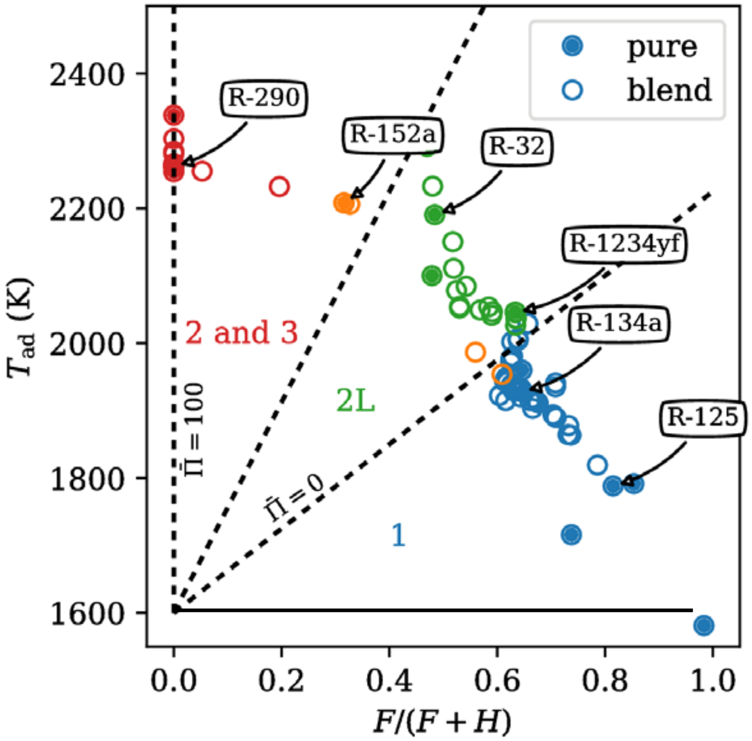

Figure 4. ASHRAE Standard 34 flammability classification indicated by color (1: blue, 2L: green, 2: orange, 3: red) and plotted as a function of the adiabatic flame temperature T_{ad} and $F/(F + H)$ for blends (open circles) and pure compounds (closed circles).

Based on Fig. 4, we defined a "flammability index" Π as the angle the line connecting a given point ($F/(F + H)$, T_{ad}) and the origin point (0, 1600) makes with a horizontal line crossing $T_{\mathrm{ad}} = 1600$. To calculate the flammability index, the temperature difference ($T_{\mathrm{ad}} - 1600$) is normalized by a reasonable upper-limit T_{ad}, which we select to be 2500 K:

$$\Pi = \operatorname{arctan2}\left(\frac{T_{\mathrm{ad}} - 1600}{2500 - 1600}, \frac{F}{F + H}\right) \cdot \left(\frac{180}{\pi}\right) \tag{16}$$

where arctan2(y, x) gives the four-quadrant arctangent angle in the domain [– π, π], and the angle is then shifted to the domain [–180°, 180°]. Further, we defined a "normalized flammability index" $\overline{\Pi}$ as

$$\overline{\Pi} = \frac{\Pi - \Pi_{1,2\mathrm{L}}}{90 - \Pi_{1,2\mathrm{L}}} \cdot 100 \tag{17}$$

where $\Pi_{1,2\mathrm{L}}$is equal to 34.78, (*i.e.*, $\Pi_{1,2\mathrm{L}}$ corresponds to the dotted line marking the class 1 to class 2L boundary). This results in a normalized flammability index, which is zero at the 1/2L boundary and 100 for the highly-flammable hydrocarbons. Hence, positive values for $\overline{\Pi}$ indicate fluids with a certain degree of flammability, while values less than zero indicate that the fluid is probably non-flammable according to the ASHRAE Standard 34 criteria. We placed the 1/2L boundary in a conservative way; that is, some refrigerants or blends with $\overline{\Pi}$ less than about 3.0 (which the method would predict to be marginally flammable) may, in fact, be nonflammable when tested according to the ASTM E681 protocol.

The developed method provides a reasonable estimate of the flammability for the HFC and HFO compounds evaluated via the ASHRAE criteria. Moreover, the angle between the horizontal line crossing T_{ad} = 1600 K and the line connecting the origin ($F/(F + H) = 0$, T_{ad} = 1600 K) and a fluid data point ($F/(F + H)$, T_{ad}), *i.e.*, the flammability index defined above, can provide a relative measure of the flammability of a refrigerant. For an arbitrary blend, this approach provides a first estimate of the flammability of a new blend.

Note that the flammability estimates presented here assumed moist air (water content corresponding to 50 % relative humidity at T = 23 °C) as the oxidizer, consistent with ASHRAE Standard 34. Adding moisture to the air adds hydrogen atoms to the chemical system, increasing the overall rate of reaction. Increased moisture in the air generally increases the flammability of fluids for which $F/(F + H) > 0.5$ (*i.e.*, flames for which there are more fluorine atoms than hydrogen).

3.5 Determination of COP and Q_{vol} by an Advanced Cycle Model

We performed detailed cycle simulations for the 22 blends selected as the "best" fluids from the complete set of evaluated blends. The goal of these simulations was to establish more accurate predictions of COP and Q_{vol} over those obtained from the simplified cycle model, which was used for simulations on the entire set of the blends. This step was not included in the original project proposal; it was added to this effort once the advanced model, referred to as CYCLE_D-HX, had been fully developed and documented [14, 15].

CYCLE_D-HX simulates the performance of single-component refrigerants and refrigerant blends in subcritical vapor-compression refrigeration cycles. The basic system simulated by CYCLE_D-HX consists of a compressor, discharge line, condenser, expansion device, evaporator, compressor suction line, and an optional liquid-line/suction-line heat exchanger. The other cycles may contain a second compressor, one or two economizers, or an intercooler. In contrast to simplified vapor compression cycle models, such as CYCLE_D [16], which require refrigerant saturation temperatures in the evaporator and condenser as input, CYCLE_D-HX establishes saturation temperatures in the heat exchangers using the temperatures profiles of heat source and heat sink and the mean effective temperature differences (ΔT_{hx}) in the evaporator and condenser, respectively, which are specified as input to the program. This representation of heat exchangers facilitates the inclusion of both thermodynamic and transport properties in cycle simulations and makes CYCLE_D-HX suitable for comparative evaluations of different refrigerants, particularly when applied in systems relying on forced-convection heat transfer of refrigerant in the heat exchangers.

The evaporator and condenser can be counterflow, crossflow, or parallel flow. (They are modeled as crossflow here.) During the iteration procedure, CYCLE_D-HX calculates heat the exchanger ΔT_{hx} using equation 18 [17]:

$$\frac{1}{\Delta T_{\mathrm{hx}}} = \frac{Q_1}{Q_{\mathrm{hx}}\Delta T_1} + \frac{Q_2}{Q_{\mathrm{hx}}\Delta T_2} + \ldots = \frac{1}{Q_{\mathrm{hx}}}\sum \frac{Q_{\mathrm{i}}}{\Delta T_{\mathrm{i}}} \tag{18}$$

In this equation, ΔT_{hx} is a harmonic mean weighted with the fraction of heat transferred in individual sections of the heat exchanger, based on the assumption of a constant overall heat-transfer coefficient throughout the heat exchanger. Each term represents the contribution of a heat exchanger section. At the outset, the model calculates ΔT_{hx} based on sections corresponding to the subcooled liquid, two-phase, and superheated regions. Then, the model bisects each section and uses equation 18 to calculate a new value of ΔT_{hx}. The model repeatedly bisects each subsection until the ΔT_{hx} obtained from two consecutive evaluations agree within a convergence parameter.

As an alternative to specifying ΔT_{hx}, the heat exchangers can be characterized by the overall heat conductance $UA_{\mathrm{hx}} = 1/R_{\mathrm{hx}}$, where R_{hx} is the total resistance to heat transfer in the heat exchanger. In this case, the model calculates the corresponding ΔT_{hx} from the basic heat-transfer relation, $\Delta T_{\mathrm{hx}} = Q_{\mathrm{hx}}/UA_{\mathrm{hx}}$, where Q_{hx} is the product of refrigerant mass flow rate and enthalpy change in the evaporator or condenser, as appropriate. The representation of heat exchangers by their UA_{hx} allows for inclusion of refrigerant heat transfer and pressure drop characteristics in comparable evaluations of different refrigerants. For this purpose, CYCLE_D-HX considers R_{hx} to consists of the resistance on the refrigerant side (R_{r}), and combined resistances of the heat exchanger material and heat-transfer-fluid (HTF) side, ($R_{\mathrm{tube}} + R_{\mathrm{HTF}}$):

$$R_{\mathrm{hx}} = R_{\mathrm{r}} + (R_{\mathrm{tube}} + R_{\mathrm{HTF}}) \tag{19}$$

$$R_{\mathrm{r}} = 1/(\alpha_{\mathrm{r}} \cdot A_{\mathrm{r}}) \tag{20}$$

where α_{r} is the refrigerant heat-transfer coefficient. and A_{r} is the refrigerant-side surface area.

The refrigerant heat-transfer resistance varies with operating conditions and refrigerant, but the resistances ($R_{\mathrm{tube}} + R_{\mathrm{HTF}}$) are assumed to stay constant. Their combined value can be calculated from UA_{hx}, α_{r}, and A_{r} during a simulation run for the "reference" refrigerant, for which the ΔT_{hx} values are known from laboratory measurements and provided as input. CYCLE_D-HX calculates ($R_{\mathrm{tube}} + R_{\mathrm{HTF}}$) for the evaporator and condenser within this "reference run" and stores their values for use in subsequent simulation runs for calculation of UA_{hx} characterizing the heat exchangers with a new refrigerant or operating conditions.

CYCLE_D-HX requires the following operational input data for the "reference run": HTF inlet and outlet temperatures for the evaporator and condenser; ΔT_{hx} for the evaporator and condenser (to achieve the measured evaporator and condenser saturation temperatures); evaporator superheat and pressure drop; and condenser subcooling and pressure drop. Additional "reference run" inputs include compressor isentropic and volumetric efficiencies, and electric motor efficiency. Heat exchanger geometry inputs include the tube inner diameter and length, the number of refrigerant circuits, and the number of tubes per circuit.

In the CYCLE_D-HX simulations, we used the option to optimize the number of parallel circuits in the evaporator and condenser for each refrigerant to maximize the system's COP. This optimization capability represents a design environment where the HTF and number of refrigerant tubes are constant, but tube connections can be changed to implement a different number of parallel circuits with a changed refrigerant mass flux. The use of optimized refrigerant circuits is important for determining the relative performance merits of refrigerants operating in systems with serpentine air-to-refrigerant heat exchangers.

The series of CYCLE_D-HX simulations of the "best" 22 blends started with HFC-134a simulations, which served as the "reference" refrigerant. For this purpose, we established an HFC-134a system, in which operating parameters approximated those used in the simplified cycle simulations: the same evaporator outlet superheat (5 K), condenser exit subcooling (7 K), compressor isentropic efficiency (0.7), compressor volumetric efficiency (1.0), and electric motor efficiency (1.0) were used. However, refrigerant pressure drop (corresponding to 2 K drop in saturation temperature) was imposed in the heat exchangers (as opposed to the compressor suction and discharge sides in the simplified simulations), and average two-phase temperatures in the heat exchangers were considered as opposed to the dew-point temperature (evaporator) and bubble-point temperature (condenser). The circuitry in the HFC-134a system was optimized to attain the maximum COP, and the performance on this HFC-134a optimized system became the reference for normalization of COP and Q_{vol} of the "best" 22 blends.

3.6 Uncertainties and Limitations of the Method

The uncertainty in the simulated cycle performance arises from several sources. The first source stems from the assumptions and idealizations made in the two cycle models. Here, all fluids were simulated with the same assumptions, and we were concerned with relative difference between fluids. We estimated the uncertainty arising from this source based on the difference between the COP or Q_{vol} calculated by the simplified cycle model and the advanced cycle model for the 22 blends calculated with both models. The average difference in COP was –1.5 % and the average difference in Q_{vol} was – 0.5 %. These reflect the degree to which the approximations made in the simplified model differed from the advanced model, but again these approximations were the same for all blends. The standard deviations of 0.8 % in the COP difference and 2.2 % in the Q_{vol} difference indicate the uncertainty associated with the screening of tens of thousands of blends (with the simplified model) compared to the more advanced cycle model. In other words, the screening study must, by necessity, use the simplified model, and it was these results that were used to select the "best" blends for further consideration with the advanced cycle model, which would give a more accurate representation of the true performance of a blend in actual equipment. Any consistent difference between the two models for the different blends would not affect the relative ranking or choice of "best" blends. Any scatter in the COP or Q_{vol} differences (as characterized by the standard deviations) could affect the choice and must be considered as an uncertainty associated with the modeling.

The second source of uncertainty in the simulation results stemmed from refrigerant blend thermodynamic and transport properties. The thermodynamic properties are expressed in terms of an "equation of state" (EOS). For the 13 pure fluids considered here, high-accuracy EOS explicit in the Helmholtz energy were available and implemented in NIST REFPROP [7]. Thus, we consider the uncertainties in the thermodynamic properties of the pure fluids to be negligible for the purpose of this study.

The properties of a refrigerant blend are given by a combination of the equations of state for the constituent pure fluids in the blend plus additional EOS terms representing the mixture. The representation of a mixture is based on “mixing coefficients” for all binary pairs of the single-component fluids in the mixture. For many of the blends simulated here these mixing coefficients were based on the estimation method of Lemmon and McLinden [18]. The uncertainty in this method is indicated in Fig. 5, which shows the predicted versus experimentally-based values of the mixing coefficient. This figure indicates an uncertainty in the mixing coefficient of 0.05. The method was developed largely with CFC, HCFC, and HFC blends, plus a few hydrocarbon-containing blends. Blends with HFOs show somewhat higher errors, and we take 0.10 as a conservative estimate for the uncertainty in a predicted value of the mixing parameter. Even for HFO-containing blends that have been fitted to experimental measurements, the data are generally limited, and an uncertainty of 0.02 is appropriate. We thus take 0.05 as an average value for the uncertainty in the mixing parameter. The propagation of this uncertainty to the calculated COP is shown in Fig. 6 for the case of the R-134a/1234yf blend. Here we calculated the COP with the simplified cycle model over a range of values for the mixing parameter corresponding to its uncertainty. The result is an uncertainty of 1.9 % in the COP. The corresponding uncertainty in Q_{vol} is larger, about 18 %, as shown in Fig. 6.

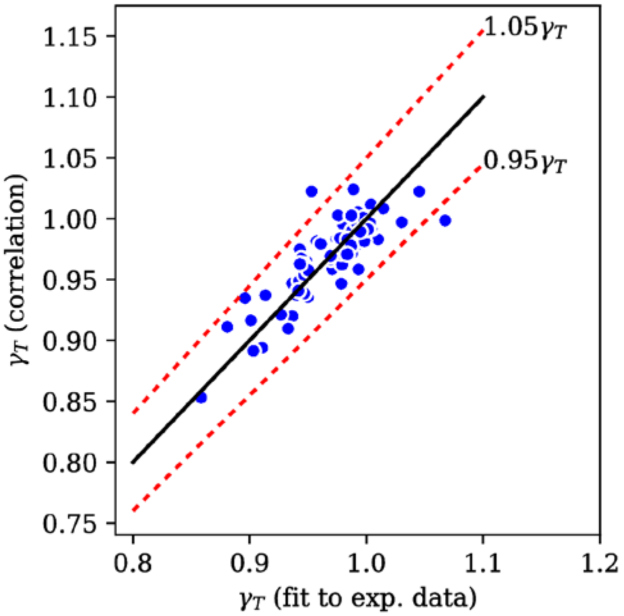

Figure 5. Comparison of estimated versus experimentally fit values of the mixing parameter from the estimation method of Lemmon and McLinden [18]; an uncertainty of 0.05 in the mixing parameter is indicated.

The final source of uncertainty in COP arises from the uncertainties associated with the prediction of two-phase heat transfer. The uncertainty in the two-phase heat transfer coefficient is related to a significant degree to the uncertainly in the value of liquid thermal conductivity. Assuming that the uncertainty of predicted liquid thermal conductivity of a blend is 20 %, which includes the uncertainty of values for blend components, the standard uncertainty in COP is

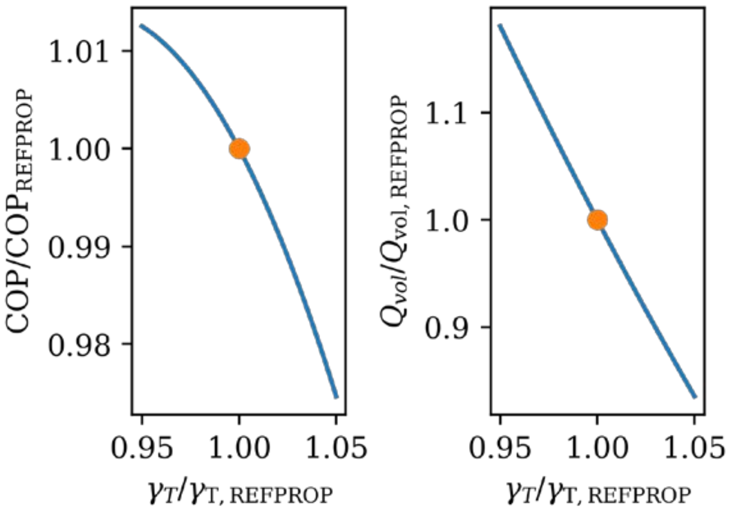

Figure 6. Propagation of the uncertainty in the mixing parameter to uncertainty in the COP and volumetric capacity. An uncertainty of +1.2 % to –2.6 % in COP is indicated; we approximate this range as ±1.9 %.

about ±1%. This estimation is based on a parametric simulation study that estimated the impact of refrigerant property uncertainties on performance prediction of a vapor compression cycle [19]. For multi-component refrigerants, the uncertainty in the prediction of the heat transfer coefficient has an additional contribution from the uncertainty in the prediction of the heat-transfer mixture effect, which increases for increasing temperature glides. An average uncertainly due to prediction of the heat transfer mixture effect is estimated to be 20 %. When the uncertainties for the thermal conductivity and the mixtures effect are linearly combined, the standard uncertainty in the COP due to the prediction of mixture two-phase heat transfer is conservatively estimated to be 1.4 %.

According to the ISO Standard for expressing uncertainty [20] an overall, combined uncertainty is given by a square root of the sum of squares of the individual uncertainty contributions. Thus, the combined uncertainty in the COP is 2.8 %; the uncertainty in Q_{vol} is dominated by the blend property uncertainty of 18 %.

The above discussion does not consider “systems effects” that may influence the performance a refrigerant may achieve when tested in a laboratory. Interaction of a refrigerant with a compressor lubricant is an example, in particular when blends are used. Refrigerant/lubricant miscibility may significantly affect the heat-transfer performance in the heat exchangers and may alter the outline of the thermodynamic cycle. Hence, the system effects result in an additional uncertainty contribution to that estimated above for simulation results.

The uncertainties in the flammability predictions in the present model are primarily from those in test data in the ASHRAE Standard 34 database used to form the model. Those uncertainties result from variability in how the test is conducted. As described in [21], various parameters in the ASTM E681 test (stopper weight, vessel tubing penetrations, electrodes, etc.) are typically not controlled at different (or perhaps even at a given) laboratories, and so the flammability behavior in the E681 test will have unquantified variability. Uncertainties in the parameters of the present model are very small: the F substitution ratio is calculated exactly for a given mixture, and the T_{ad} is calculated within 1 %.

Finally, flammability limits are generally device-dependent [22]. So while the current estimation method can predict the behavior of a mixture in the ASTM E681 test protocol (for constituents which are chemically similar to those used to develop the model; *i.e.*, hydrocarbons, HFCs, HFOs, etc.), the behavior of the mixtures in other flammability tests or actual full-scale configurations having more powerful ignition sources, clutter, turbulence, etc., may not be predicted as well. Thus, for the present study, whether the ASTM E681 flammability test method is applicable to military applications is perhaps more relevant than the uncertainties in the method itself. For example, for an explosive projectile going into an air-conditioning coil, a more conservative flammability metric may be required than that used in the E681 test. Thus, we present blends with a range of normalized flammability index and note that the appropriate value of $\overline{\Pi}$ at the flammable/nonflammable boundary may be different for more severe experimental configurations.

4. Results and Discussion

4.1 Overview of Screening Results

The screening resulted in a large dataset of binary and ternary blends formed of the 13 components (Table 1) with an assessment of the figures of merit for each blend: GWP, normalized flammability index, and COP and Q_{vol} from simplified cycle simulations. Figure 7 presents an overview of the simulation results (COP versus GWP) sorted into four flammability ranges based on the normalized flammability index defined in section 3.4: $10 < \overline{\Pi} < 45$ corresponds to class 2L fluids); $0 < \overline{\Pi} < 10$ is near, but on the flammable side of the flammability boundary (ASHRAE class 2L); $–10 < \overline{\Pi} < 0$ is near the flammability boundary, but is likely nonflammable (ASHRAE class 1), and $–100 < \overline{\Pi} < –10$ corresponds to “nonflammable.” Note that we plot only those blends with GWP < 1300, *i.e.*, less than that of HFC-134a, but otherwise Fig. 7 shows all of the blends simulated.

Several general trends and conclusions can be observed in Fig. 7. First, all the clearly non-flammable blends ($–100 < \overline{\Pi} < –10$) have very low COPs compared to HFC-134a. Many of these blends contain a significant fraction of CO_2. Among the blends with $–10 < \overline{\Pi} < 0$ (*i.e.*, the blends that are likely class 1), there is a clear lower limit of GWP ~ 640; this corresponds to a HFC-134a composition of about 50 mole %. This is the minimum fraction of HFC-134a necessary to suppress the flammability of HFO-1234yf or HFO-1234ze(E). (Other nonflammable fluids, such as HFC-125 or HFC-227ea, could serve to suppress flammability, but these have higher GWP values.)

There is a general trend of the upper limit of COP increasing with GWP and with flammability. This is not a fundamental trade-off but is a consequence of the nature of the very-low-GWP HFO refrigerants: the HFOs are more complex molecules compared to the corresponding HFCs that they are intended to replace, and this molecular complexity carries a performance penalty in the vapor-compression cycle.

Figure 8 zooms into the regions of most interest in Fig. 7, namely the blends with COP > 5 in the middle two flammability ranges. This figure plots COP versus GWP and also indicates the composition and normalized flammability index—see figure caption. The left panel ($0 < \overline{\Pi} < 10$) is plotted only up to GWP = 600; while there are many blends in this flammability range with higher values of GWP they would be of limited interest.

There are patterns observed in Fig. 8 corresponding to “families” of blends with similar components and compositions that vary in even increments. The upper limit of COP in the right panel corresponds, in most cases, to the R-134a/1234yf binary blend (indicated by the heavy black symbols), and this binary continues into the left panel. An example is indicated by the shaded area in the left panel of Fig. 8. Starting with the R-134a/1234yf binary with composition (0.24/0.76), replacing HFO-1234yf with HFC-152a (shown with circles) increases the COP, but also increases the flammability (as indicated by color increasingly shifting towards yellow) until a normalized flammability index $\overline{\Pi} = 9.1$ is reached at a HFC-152a content of 0.16 mole fraction at a constant HFC-134a content. The GWP also increases as HFO-1234yf (GWP = 1) is replaced with HFC-152a (GWP = 138). Returning to the R-134a/1234yf binary, replacing HFO-1234yf with HFO-1234ze(E) (shown with “+”) decreases the COP, but the GWP and flammability are little affected, since HFO-1234yf and HFO-1234ze(E) have identical molecular weights and similar GWP values and flammability characteristics. Again, returning

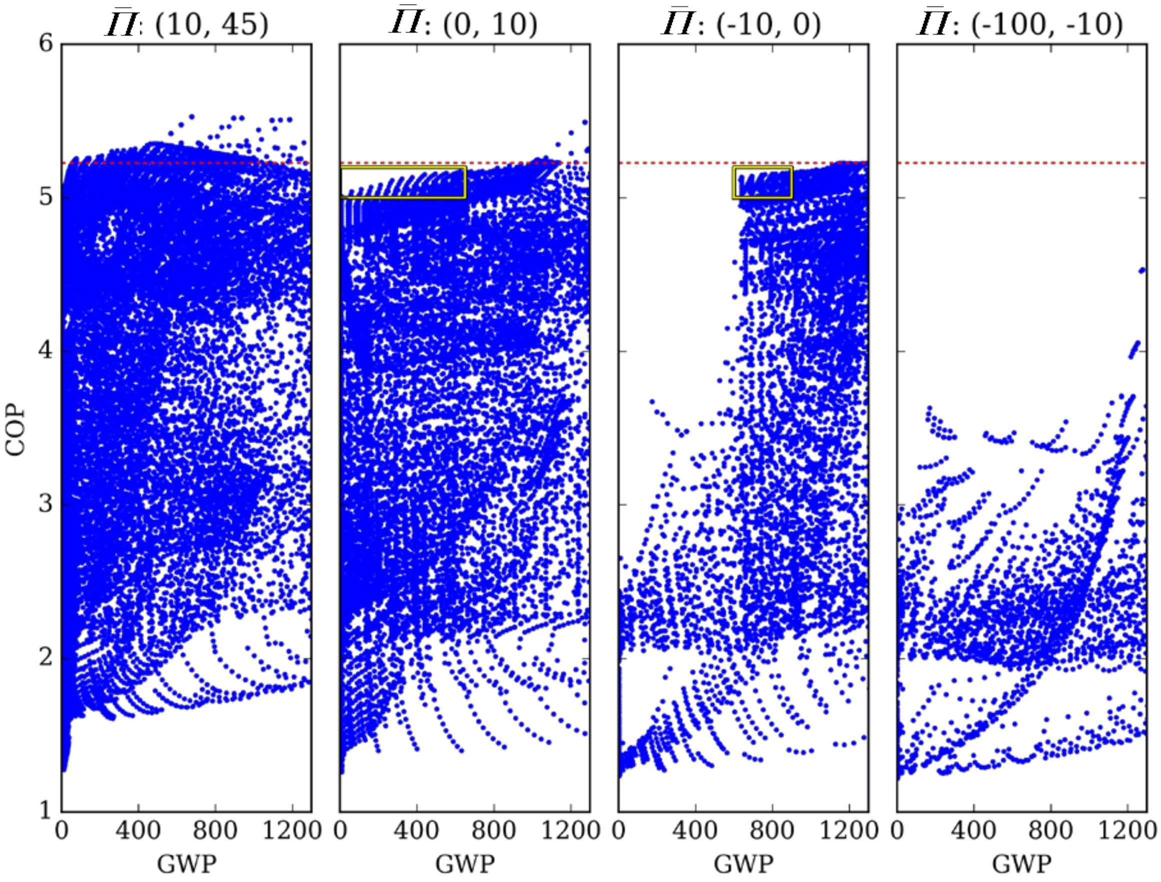

Figure 7. Overview of cycle simulation results sorted into bins of estimated flammability. The red dashed line indicates the COP of the HFC-134a baseline system, and the yellow boxes correspond to the zoomed-in views shown in Fig. 8.

to the R-134a/1234yf binary, replacing HFO-1234yf with HFO-1243zf (shown with pentagons) results first in an increase in COP and then a decrease as the HFO-1243zf content increases; the GWP values increase slightly because of the different molecular weights. Here the flammability increases significantly as the HFO-1243zf content increases.

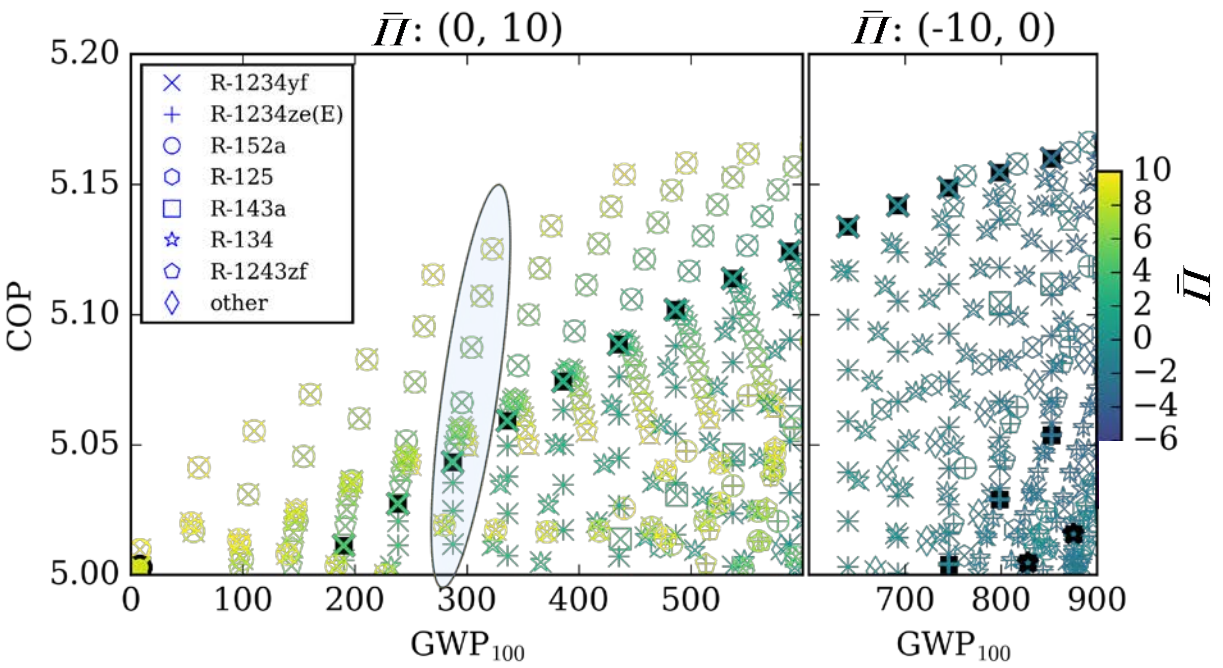

Figure 8. Zoomed in view of Fig. 7 showing the blends with COP > 5.0 for two "bins" of flammability; the left panel shows blends that are "borderline flammable" and the right panel shows blends that are estimated to be "nonflammable." The symbols plot the COP simulated with the simple vapor compression cycle model versus the GWP of the blend. The different symbols indicate the components of the blend; the majority of the blends shown have HFC-134a as a component, and the shapes indicate the other component(s). For example, the superposition of an "×" and a "○" indicates a R-134a/1234yf/152a ternary blend. The heavy black symbols denote the R-134a/1234yf, R-1234a/1234ze(E), and R134a/134 binaries. The colors of the symbols indicate the normalized flammability index estimated by the method described in Section 3.4; the color key is at the right side of the plot. The points inside the shaded oval are discussed in the text.

Figure 9 provides a somewhat different overview of the results; here scatter plots of the COP versus Q_{vol} values are sorted into nine "bins" of GWP and flammability. The flammability indices of the bins are ($-100 < \overline{\Pi} < 0$) for the "nonflammable" bin, ($0 < \overline{\Pi} < 45$) for the "mildly flammable" bin and ($\overline{\Pi} > 45$) for the "flammable" bin; thus, this is a coarser sorting compared to Figures 7 and 8. In the upper left-hand corner of the figure are mixtures that are probably nonflammable according to our flammability assessment and have a GWP < 150, *i.e.*, less than 12 % that of HFC-134a. Although the mixtures in the nonflammable/low GWP bin meet two of the desired objectives, they suffer from a much lower efficiency than the baseline HFC-134a system.

The bin for 150 < GWP < 650 in the nonflammable (left-hand-side) column contains some fluids with the COP very closely approaching the COP of HFC-134a. Moving down to the lower left-hand corner for 650 < GWP < 1300, the number of blends with the COP similar to that of HFC-134a is increased. For the column with mildly flammable blends (middle column), the number of well-performing fluids is increased with some having a COP greater than that of

HFC-134a. Also of note here is a second maximum in the COP values at Q_{vol} values about 2.5 times that of HFC-134a; these blends have HFC-32 as a major component, but the normalized flammability index is greater than 10, and so these blends do not appear in Figures 7 and 8.

Figure 10 shows a graphical representation of the prevalence of each component in the different bins. Each time a component occurs in a bin, its mole fraction in the mixture is added to the running sum for that bin. The mole-fraction-weighted prevalences are then normalized within the bin to yield the relative prevalence of each component. In many of the bins there are components (or a family of components, *e.g.*, the HFOs) that dominate nearly the entire bin.

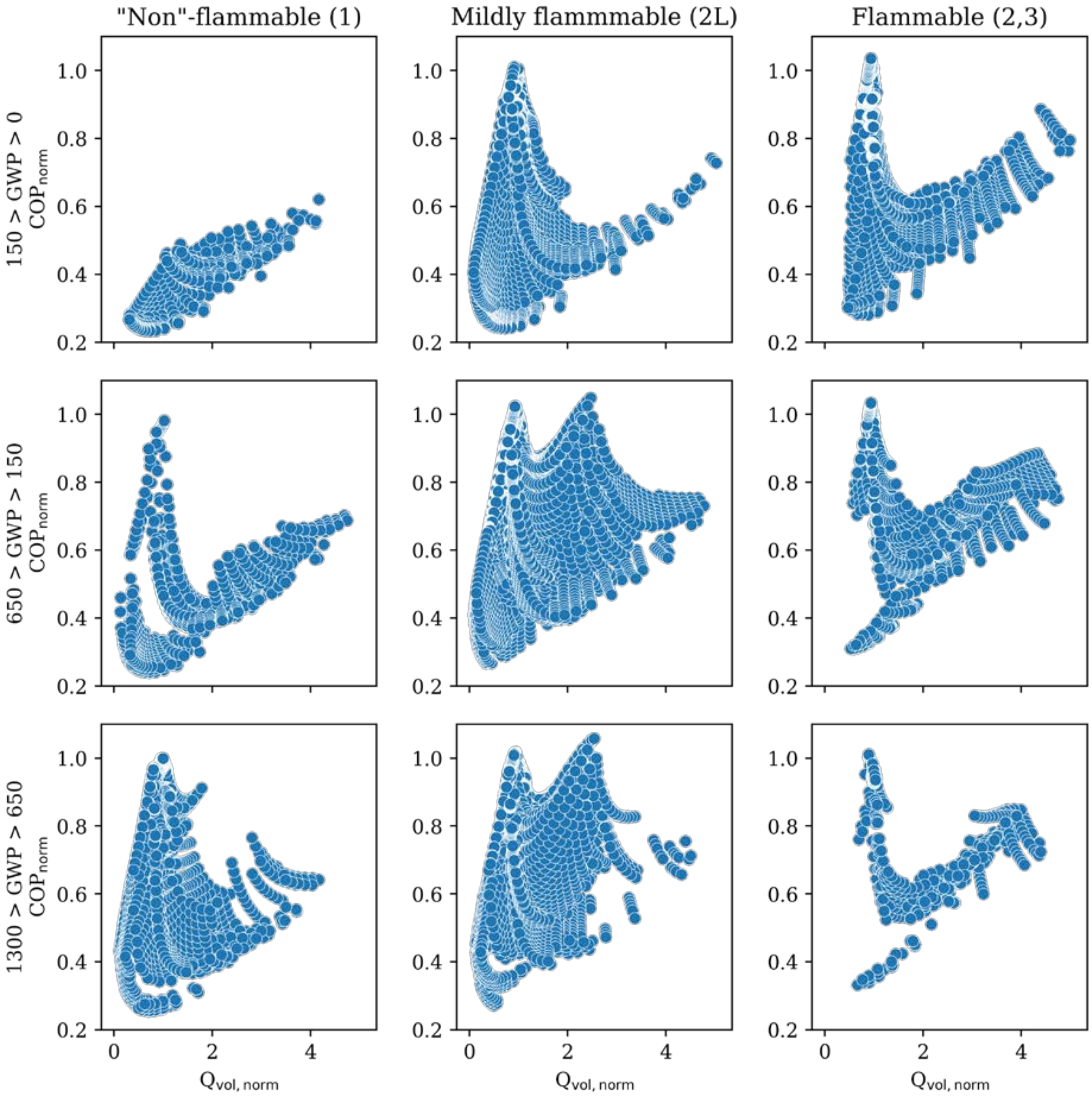

Figure 9. An overview of the cycle figures of merit for the ternary blends studied, divided into bins of GWP and estimated flammability. The “preferred” bin is at the upper left, and the bins moving towards the lower right are worse according to our objective functions.

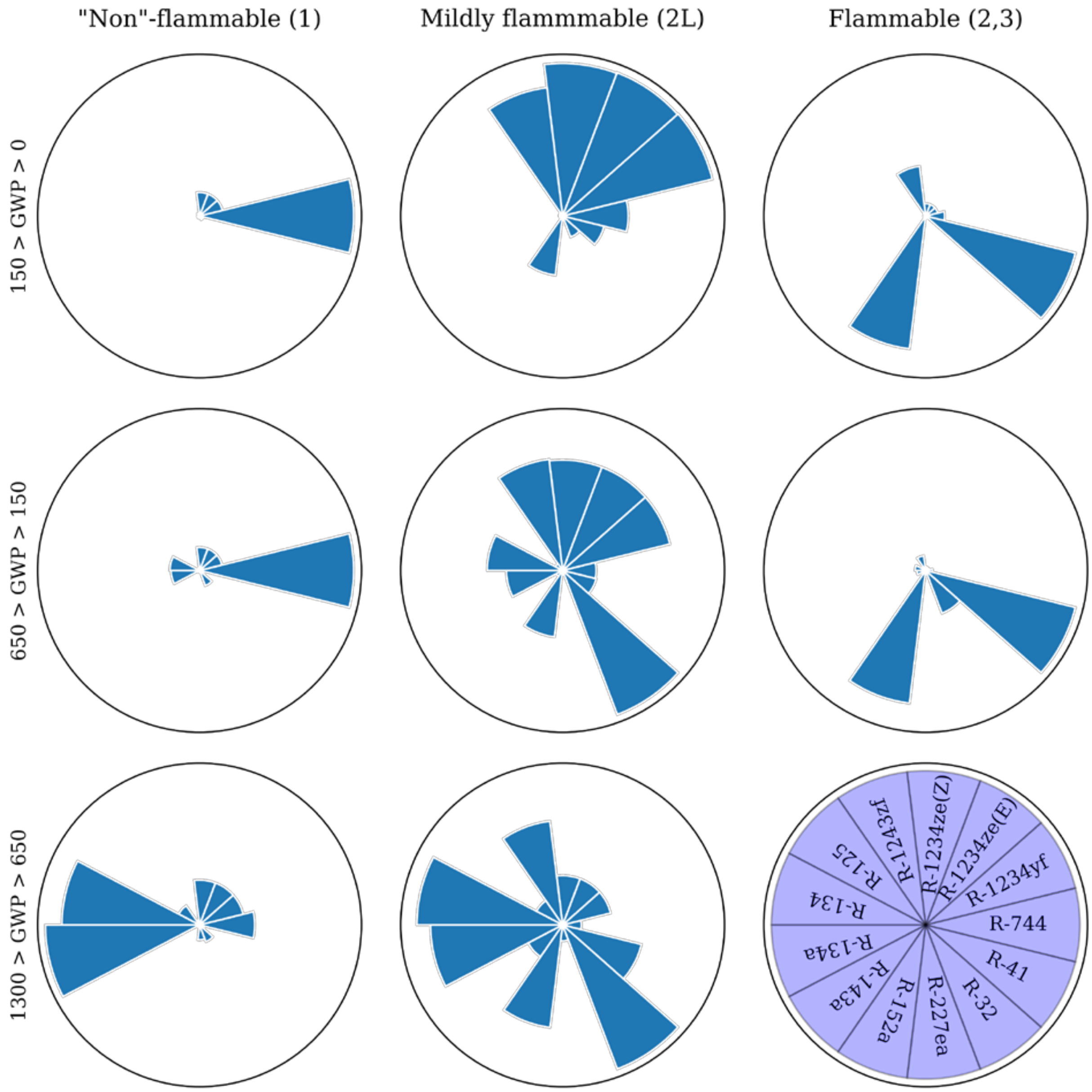

Figure 10. Radial histograms showing the prevalence of each component in each of the bins. The key in the lower right corner is aligned with the radial histograms in each bin. Note that these represent the distribution of all the blends studied.

4.2 Selection of the Best Blends

The production of the large dataset discussed above was, in some sense, the easy part of this study. Because it was not possible to simultaneously achieve a high COP, low GWP and nonflammability, the determination of the "best" refrigerant blends represents a difficult balancing of tradeoffs. In fact, the selection of the "best" blend depends largely on how the user weights the available figures of merit. The Q_{vol} of all of the blends with high values of COP was comparable to $Q_{\mathrm{vol,R\text{-}134a}}$, largely removing this factor. Note that we did not separately select blends having very similar compositions to the "best" blends unless they offered a distinct advantage in one of our metrics.

From the entire dataset, we selected 22 "best" blends. The selection of these blends represented different compromises between GWP, COP, and flammability. In addition, in view of the uncertainty in COP and flammability (as discussed in Section 3.6), we selected blends to give a diversity in the blend components and also selected blends that we predicted to be mildly flammable by the estimation method presented in Section 3.4. The list of best blends is presented in Table 2; 14 were estimated to be nonflammable (*i.e.*, $-10 < \overline{\Pi} < 0$) and eight were estimated to be mildly flammable ($0 < \overline{\Pi} < 10$). Even the "nonflammable" blends were all near the borderline of flammability. All of the blends with $\overline{\Pi} < -10$ (*i.e.*, those that would be clearly nonflammable) had low values of COP and none were chosen.

Among the "nonflammable" blends (see right panel in Fig. 8) many of the highest COPs obtained were for binary blends R-134a/1234yf, and three compositions of this binary were chosen, representing a range of COP versus GWP tradeoffs. The highest COPs were for the ternary R-134a/152a/1234yf, and we selected one such blend with GWP = 817. A majority of the "nonflammable" blends with COP > 5.0 contained some combination of HFC-134a, HFO-1234yf, and HFO-1234ze(E). We selected two blends of the R-134a/1234ze(E) binary and two blends of the R-134a/1234yf/1234ze(E) ternary to "sample" this composition space.

A significant number of "nonflammable" blends contained HFC-134, primarily ternary blends of R-134a/1234yf/134. As HFC-134a was replaced with HFC-134 the COP decreased, and the GWP also decreased, but more modestly. We selected two representative examples of these blends.

Given the uncertainty in the COP, which was due in large part to the uncertainty in the mixing parameters, all of the blends shown in Fig. 8 have COPs that are within the uncertainty bounds. Thus, we selected additional blends to include additional components, namely HFC-125, HFC-227ea, and HFO-1243zf. These blends serve to hedge our bets in the event that the mixture properties (as calculated based on the estimated mixing parameters) were significantly in error. (HFC-143a was a component in several "nonflammable" blends, but at very low concentrations and with flammability indices only slightly above zero and, thus, was not selected. That HFC-143a appeared at all among the "nonflammable" blends is somewhat counterintuitive: HFC-143a is flammable and has a high GWP. But its properties modify the overall thermodynamic characteristics of the blend in a favorable way. This illustrates the benefit of the exhaustive search of blend compositions.)

Given the uncertainty in the flammability estimation method and also the fact that the lowest GWP among the "nonflammable" blends was 633, we selected additional blends from the set of borderline flammable fluids (left panel of Fig. 8). One such blend, the R-134a/1234yf binary with composition of (0.468/0.532) mole fraction (or (44.0/56.0) mass percentage) is designated R-513A with an A1 safety classification, *i.e.*, "nonflammable," by ASHRAE Standard 34. The GWP of this blend is 573. It is worth noting, however, that in the application for this blend to the Standard 34 committee a flame angle of 55° was observed in the ASTM E681 test; fluids with flame angles less than 90° are considered "nonflammable" according to the ASTM test method. This again illustrates the point that flammability is a continuum. Two additional "flammable" compositions of the R-134a/1234yf blend were selected.

Table 2. Selected “best” blends and simulation results from CYCLE_D-HX, sorted by GWP.

Components	Composition (mole fraction)	GWP	$\overline{\Pi}$	COP/ $\mathrm{COP}_{\text{R-134a}}$	Q_{vol}/ $Q_{\mathrm{vol,\,R\text{-}134a}}$
Borderline flammable					
R-152a/1234yf	0.08/0.92	8	8.7	0.980	0.957
R-134a/1234yf	0.20/0.80	238	3.9	0.980	0.996
R-134a/152a/1234yf	0.20/0.16/0.64	270	9.6	0.987	0.984
R-152a/1234yf/134	0.16/0.48/0.36	418	8.4	0.984	0.900
R-134a/1234yf	0.36/0.64	436	2.0	0.985	1.018
R-134a/1234yf/1243zf	0.36/0.44/0.20	451	6.2	0.988	1.004
R-134a/152a/1234yf	0.36/0.20/0.44	496	9.1	0.994	0.994
R-134a/1234yf	0.468/0.532	573	0.6*	0.988	1.027
“Nonflammable”					
R-134a/1234yf/134	0.48/0.48/0.04	634	–0.0	0.987	0.975
R-134a/1234yf/1234ze(E)	0.52/0.32/0.16	640	–0.1	0.987	0.989
R-134a/1234yf	0.52/0.48	640	–0.1	0.989	1.029
R-134a/1234yf/134	0.40/0.44/0.16	665	–0.3	0.986	0.958
R-134a/125/1234yf	0.44/0.04/0.52	676	–0.4	0.985	1.049
R-134a/227ea/1234yf	0.40/0.04/0.56	681	–0.5	0.984	1.007
R-134a/1234ze(E)	0.60/0.40	745	–1.4	0.988	0.908
R-134a/1234yf	0.60/0.40	745	–1.4	0.990	1.031
R-134a/1234ze(E)/1243zf	0.60/0.36/0.04	750	–0.6	0.990	0.966
R-134a/R1234yf/1234ze(E)	0.64/0.2/0.16	799	–2.0	0.990	0.986
R-134a/152a/1234yf	0.64/0.04/0.32	817	–0.9	0.993	1.023
R-134a/1234yf/134	0.52/0.32/0.16	825	–2.2	0.990	0.966
R-134a/1234ze(E)	0.68/0.32	852	–2.7	0.991	0.929
R-134a/1234yf/1243zf	0.68/0.2/0.12	870	–0.2	0.994	1.020

*This blend is classified as “nonflammable” by ASHRAE Standard 34.

The left panel of Fig. 8 shows a Pareto front of COP versus GWP comprising blends of R-134a/1234yf/152a. (Note that the upper limit of this front terminates with $\overline{\Pi} \sim 10$ as the HFC-152a content increases.) We selected two compositions along this front. Starting with the R-134a/1234yf binary blends, the addition of HFC-1243zf results in first a modest increase in COP and then a decrease as the HFC-1243zf content is further increased, and we selected one such ternary blend at the peak value of COP. We selected the blend with the lowest GWP, namely the R-152a/1234yf binary with GWP = 8. HFC-134 appeared in four blends but was not the main component in any of them.

4.3 Performance Simulation of the Best Blends

We simulated performance of the 22 “best” blends with the detailed CYCLE_D-HX model to more accurately assess their performance (Table 2, Fig. 11). For this group, the GWP values vary from 8 to 870. The normalized values for COP range from 0.980 to 0.994, and for Q_{vol} are in a wider range from 0.900 to 1.031.

Figure 11 shows a general trend of COP increasing as the GWP increases, although the total range of COP is limited and within the uncertainty of the COP calculation. This is not a direct cause-effect relationship, but rather arises from the nature of the fluids involved. The low-GWP refrigerants are generally more complex molecules (*i.e.*, they typically have a backbone of three carbon atoms) compared to the nonflammable, high-GWP refrigerants with a two-carbon backbone. It is the greater molecular complexity that is associated with a lower COP rather than the lower GWP value, itself. The distribution of $Q_{\mathrm{vol}}/Q_{\mathrm{vol,R\text{-}134a}}$ in Fig. 12 shows no specific trend.

The refrigerant to be replaced, HFC-134a, is the most common blend component; it is listed in 20 out of 22 “best” blends, and it is a component in every blend categorized in Table 2 as “nonflammable”, with a mole composition of at least 40 %. The most common HFO components are HFC-1234yf followed by HFC-1234ze(E) and HFC-1243zf.

A blend R-134a/1234yf (0.468/0.532), which we estimated to be “borderline flammable”, is an azeotropic blend with the ASHRAE designation R-513A and an A1 safety classification (low toxicity, nonflammable). It has 1.2 % lower COP than HFC-134a but has the advantage of a higher Q_{vol} by 2.7 %. The study identified two additional R-134a/1234yf blends with a higher COP than R-513A but with a higher GWP (up to 745), which indicates a trade-off between a COP and GWP. Among blends estimated to be “nonflammable”, R-134a/1234yf/134 (0.48/0.48/0.04) has the lowest GWP of 633. It has a 1.3 % lower COP and 2.5 % lower Q_{vol} compared to that of HFC-134a.

The highest COP blends (0.6 % lower than HFC-134a) were R-134a/152a/1234yf (036/0.30/0.44) and R-1234a/1234yf/1234zf (0.68/0.20/0.12). The first blend is estimated to be “borderline flammable” and has GWP = 496; the second blend is estimated to be nonflammable but has GWP = 870. R-134a/1234ze(E) has the lowest value of flammability index among the 22 blends; its drawback is the second highest GWP of 852.

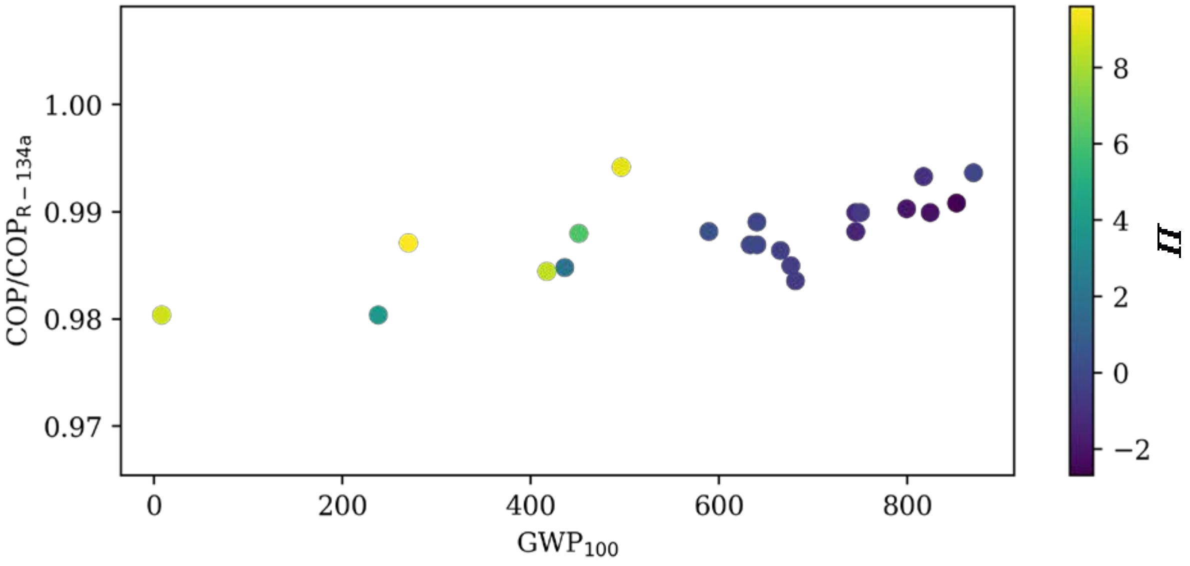

Figure 11. COP of the selected ”best” blends (Table 2) normalized by $COP_{R\text{-}134a}$, plotted as a function of the GWP values; the colors indicate the estimated normalized flammability index, with the color scale on the right side of the figure.

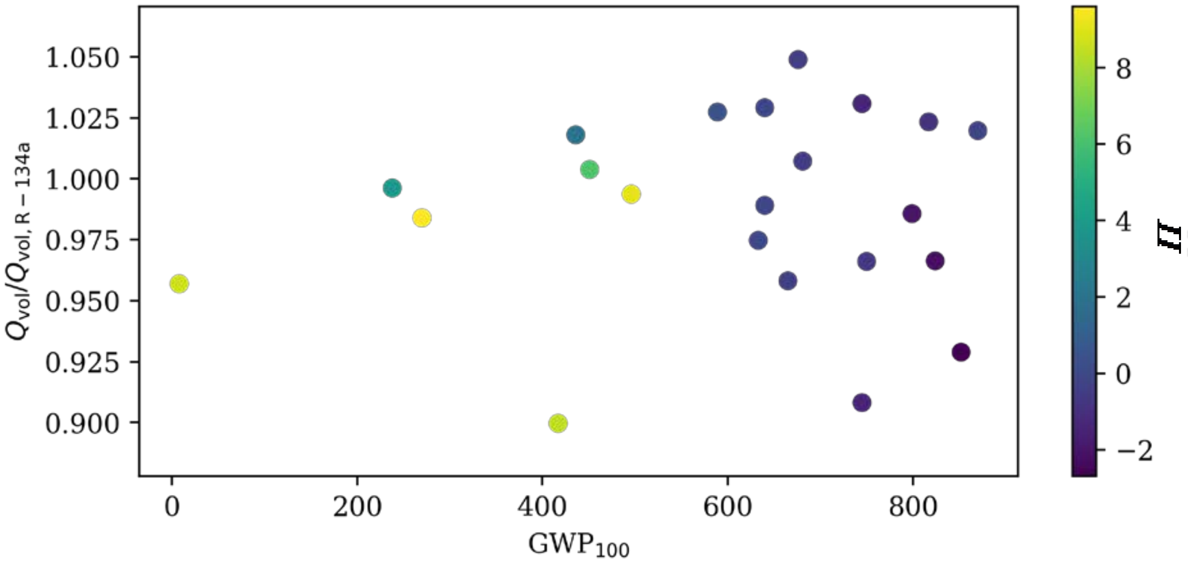

Figure 12. Q_{vol} of the selected ”best” blends (Table 2) normalized by $Q_{vol,R\text{-}134a}$, plotted as a function of the GWP values; the colors indicate the estimated normalized flammability index, with the color scale on the right side of the figure.

5. Conclusions and Implications for Future Research/Implementation

5.1 Conclusions

Considering the main goal of this study to find a nonflammable, low-GWP replacement blend for HFC-134a (GWP = 1300), the study identified 14 blends with GWP values ranging from 633 to 870, which were estimated to be nonflammable. Additionally, the study identified eight blends with GWP values ranging from 8 to 573, which were estimated to be “borderline flammable”. Our detailed cycle simulations predicted their COPs to be within 2.0 % below $\mathrm{COP}_{\text{R-134a}}$, and volumetric capacities being in a wider range from –10.0 % to +4.9 % as compared to $Q_{\text{vol,R-134a}}$. In general, blends having a higher GWP attained a higher COP.

The selection of single-compound fluids to be considered in this study was guided by results of our prior comprehensive study within which a chemical database with 60 million fluids was screened in search of low-GWP refrigerants [2]. That study, and subsequent work, identified 28 single-compound fluids of interest, which included low-GWP fluids and higher-GWP fluids that could be used in blends. The present study included about half of those fluids, but neglected the other half, for the following reasons. The hydrocarbons (four compounds) were eliminated because their addition to a blend even in small quantities would make it flammable. Dimethylether (R-E170) is also highly flammable; furthermore, our simple estimation method could not estimate its flammability, and thus, we did not include it here. Finally, the six novel fluids were not considered because we do not know their safety hazards. All of the included fluids from the list were mildly flammable, and these were blended with the nonflammable compounds HFC-125, HFC-134a, HFC-134, HFC-227ea, and R-744. If any of the six novel fluids are proven, upon further examination, to be stable, of low toxicity, and nonflammable (or, at least, no worse than marginally flammable) there may be further options; otherwise it is very likely that the options for low-GWP refrigerants replacing HFC-134a will remain those outlined here.

Based on this study, it can be concluded that it is possible to implement a nonflammable HFC-134a replacement blend with about 50 % lower GWP than that of HFC-134a. Selection of the optimal blend requires experimental validation of performance of selected fluids presented in Table 2.

5.2 Implications for Future Research

The objective of this limited-scope project was to explore low-GWP replacements for HFC-134a. Our study relied on the NIST refrigerant property modeling tools and vapor-compression cycle simulation models. We used state-of-the-art modeling approaches in these areas; however, limited availability of data on HFO refrigerants warrants the recognition of uncertainties of the developed results. These uncertainties are related to the uncertainties of predicting thermophysical properties of individual single-component refrigerants, predictive algorithms for mixing coefficient for involved pairs of pure fluids, refrigerant heat-transfer coefficient, and cycle modeling simplifications. The experimental verification of simulation results was not possible within the limited scope of the current project.

A follow-up experimental research effort is required before the optimal blend can be selected and implemented in the field. The ultimate validation of results of this study can be achieved from tests of a typical military environmental control unit (ECU), which currently uses HFC-

134a. Such tests should be performed in environmental chambers under controlled environmental conditions. At minimum, the tested unit should be “soft optimized” (optimization of the expansion device and refrigerant charge) for each blend, and results from these tests should be extrapolated by simulations of a validated ECU simulation model to estimate the effect of optimized heat exchangers on the unit performance. It is recommended for these tests to include HFC-134a and three “best” blends.

A few research tasks should precede the ECU tests to ensure the correctness of the blend selection process. These tasks should include:

1. Tests of the best performing blends in a small laboratory test apparatus to validate the relative performance ranking of the blends obtained from cycle simulations. The laboratory set-up should allow for quick refrigerant testing and identification of the four “best” blends.
2. Flammability testing in the ASTM E681 apparatus to validate the predictions of flammability class of the “best” blends, and further testing to determine the relevance of the ASTM method for military applications.
3. Experimental measurements of blend properties and development of mixture equation of state. The simulation of cycle performance, the analysis of laboratory measurements in equipment, and heat-transfer experiments in support of cycle simulation model require thermodynamic properties of the blends. The properties of a refrigerant blend are given by a combination of the constituent pure fluids in the blend plus additional terms representing the mixture. This task would carry out the measurements necessary to define these mixture terms. These terms are expressed in terms of binary pairs of components; three-component mixtures, for example, are expressed in terms of the binary pairs A-B, A-C, and B-C.
4. Refrigerant forced-convection heat-transfer testing to validate the heat-transfer correlation for HFO blends. The refrigerant two-phase heat transfer coefficient has significant effect of the thermodynamic cycle irreversibilities in the evaporator and condenser. Between these two heat exchangers, capturing the performance of candidate blends in the evaporator is more important because of a greater complexity of physical phenomena taking place in the forced-convection evaporator and the inherently greater impact of the evaporator performance on the COP. The improved refrigerant heat-transfer correction will facilitate the ECU performance simulations to assess the performance potential of the competing blends.

The key outputs of the described follow-up effort will be two-fold:

1. Performance of the three best low-GWP, nonflammable blends in a typical ECU after soft optimization to fluid properties, from laboratory tests.
2. Performance of these competing blends in a system with optimized heat exchangers, from simulations using a first-principles-based model.

Based on the obtained results, additional tests with modified (optimized) heat exchanger circuitries could be performed.

In summary, this described follow-project would provide authoritative, experimentally verified information on low-GPW, nonflammable replacements for HFC-134a.

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7. Appendices

A. Supporting Data Publications

This limited-scope project did not result in data publications.

B. List of Scientific/Technical Publications

1. Bell, I., Domanski, P.A., Linteris, G., McLinden, M. (2018). Evaluation of binary and ternary blends as replacements for R-134a in an air-conditioning system. Presented at 17th International Refrigeration and Air Conditioning Conference at Purdue, July 9-12, 2018.

2. Linteris, G., Bell, I., McLinden, M. (2018). An Empirical Model for Refrigerant Flammability Based On Molecular Structure and Thermodynamics. Presented at 17th International Refrigeration and Air Conditioning Conference at Purdue, July 9-12, 2018.