Non-flammable Lower-GWP Refrigerant Blends to Replace R-134a for Military Applications

(Conf. Paper # 0943)

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Project Team

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U.S. DEPARTMENT OF COMMERCE

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  T. Fortin: measurement of blend properties ("comprehensive data")
  M. Huber: modeling of transport properties (viscosity and thermal conductivity)
  E. Lemmon: modeling of blend properties
  M. McLinden (Co-PI): measurement blend properties ("comprehensive data")
  S. Outcalt: measurement of blend properties (VLE, i.e., "limited data")
  R. Perkins: measurement of transport properties

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  V. Babushok, M. Hegetschweiler, D. Kim, and **G. Linteris**: flammability testing and modeling
  P. Domanski (PI): thermodynamic cycle analysis, system modeling
  M. Kedzierski: blend two-phase heat-transfer testing and modeling
  V. Payne: evaluation of blend performance in ECU in environmental chambers
  H. Skye: testing of blends in mini-breadboard heat pump apparatus

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Certain commercial entities, equipment, or materials may be identified in this document in order to describe an experimental procedure or concept adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the entities, materials, or equipment are necessarily the best available for the purpose.

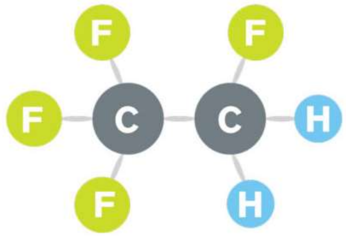
Overview and Objectives

Background

Statement of Need:

The U.S. military needs a non-flammable lower-GWP replacement for refrigerant R-134a (HFC-134a)

"R-134a" (CF_3CH_2F)



- Application focus: environmental control units (**ECU**)
- Replacement refrigerant requirements:
  - Nonflammable and low-toxicity → paramount importance
  - Low GWP ($GWP_{HFC\text{-}134a}$ = 1300)
  - Maintain performance (COP and volumetric capacity)
  - Commercially available (at least components)

ECU

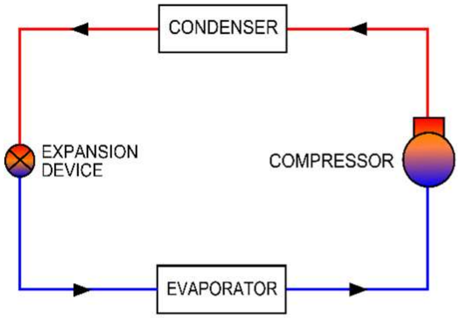
- Rugged, transportable units provide cooling in the field
- (10 to 20) kW cooling capacity

COP: coefficient of performance (efficiency) ECU: environmental control unit GWP: global warming potential

Technical Objective

- Identify three best non-flammable, lower-GWP blends to replace HFC-134a
- Test HFC-134a environmental control unit (ECU) charged with three blends

  (tests in environmental chambers)



Technical Objective

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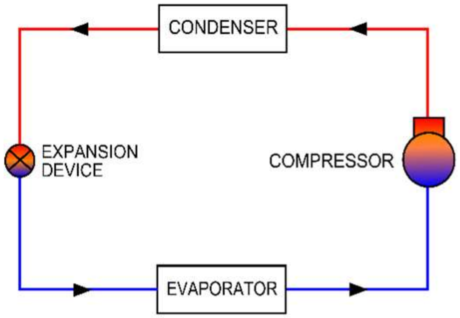
  (tests in environmental chambers)
- Evaluate replacements in an ECU optimized for each refrigerant
  (detailed simulations w/ machine-learning optimization)



Technical Objective

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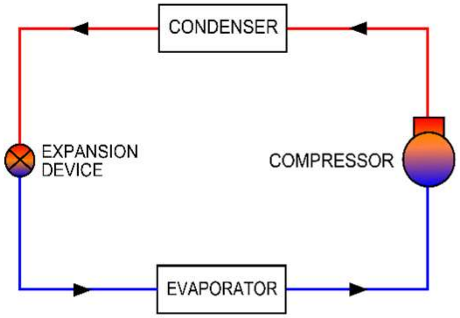
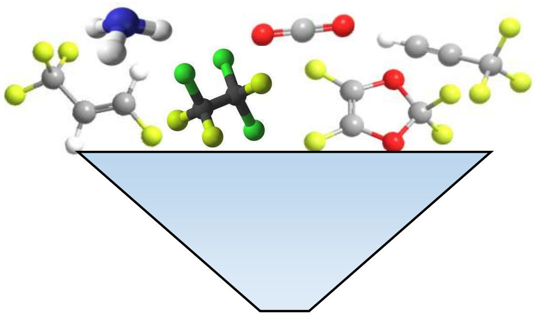
- Test HFC-134a environmental control unit (ECU) charged with three blends
  (tests in environmental chambers)
- Evaluate replacements in an ECU optimized for each refrigerant
  (detailed simulations w/ machine-learning optimization)
- Simulate ECU operating with carbon dioxide (not discussed here)



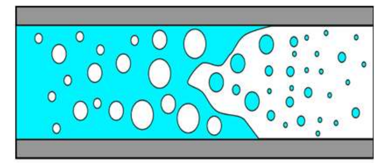
Technical Approach



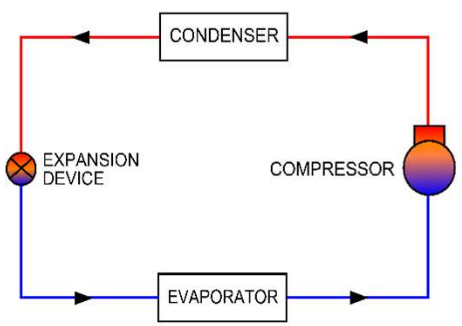
1 refrigerant screening (single components, blends)

2 thermophysical property measurements

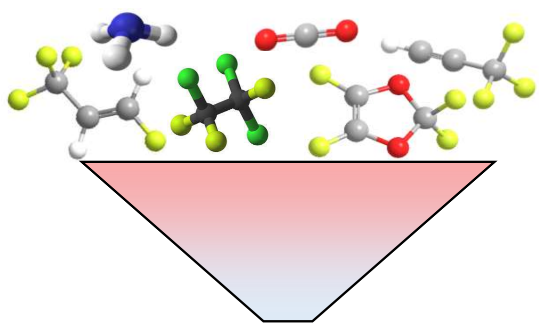
3 flammability testing



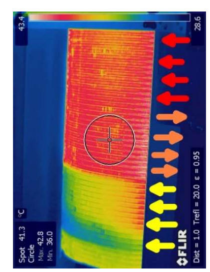
4 two-phase heat transfer measurements



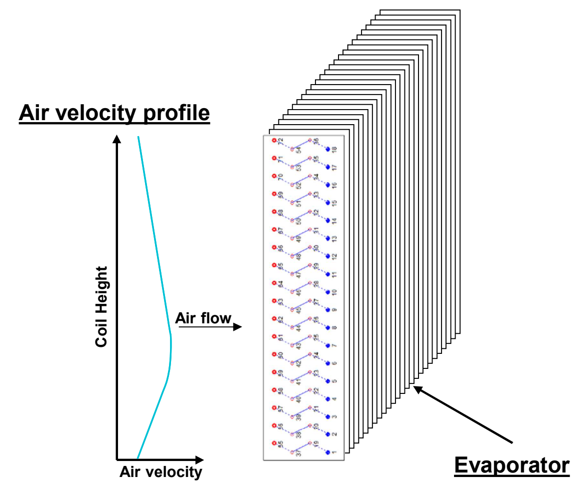
5 cycle performance in mini breadboard heat pump



6 final blend selection

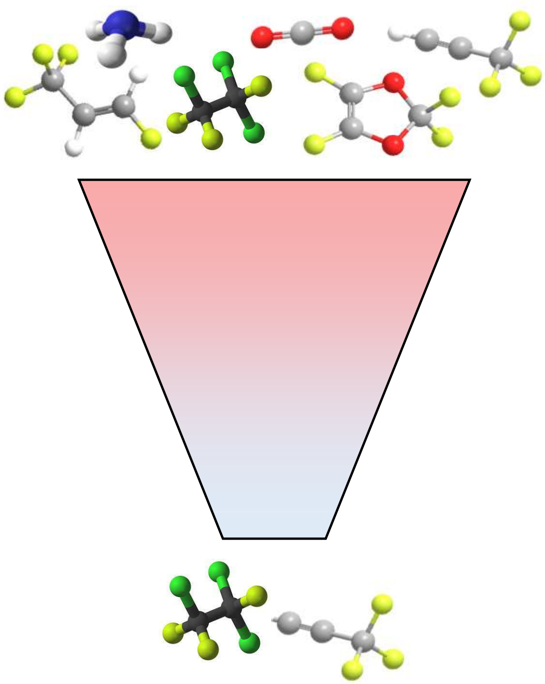


7 full-scale ECU tests



8 refrigerants in optimized ECU (simulations)

Refrigerant screening



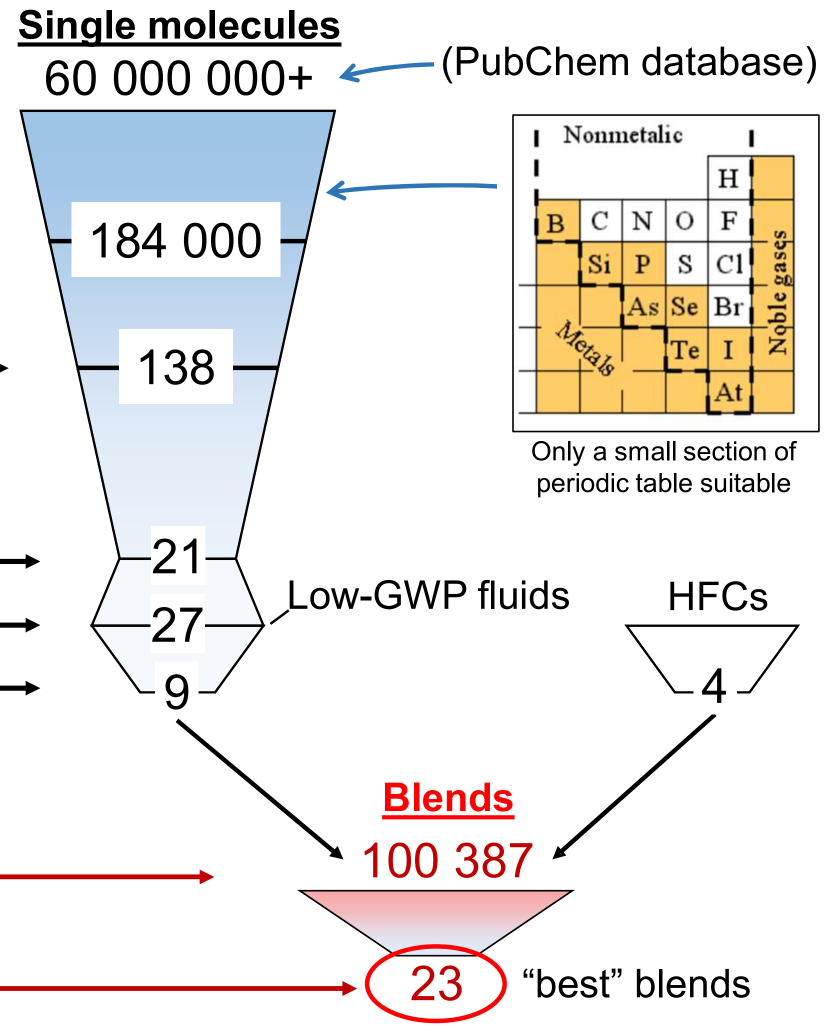
Preliminary refrigerant screening

[1]

Low-GWP single component filtering	
Component atoms:	C, H, N, O, S, F, Cl, Br
Maximum # atoms:	18
GWP_{100}:	< 1000
Critical temperature:	46 °C < Tcrit < 146 °C
Toxicity:	(MSDS, REL, TLV, =CF2)
Stability:	(e.g., drop –O–O–)
Volumetric capacity:	> 0.33 $Q_{vol,R\text{-}410A}$
+3 (commercial interest), + 3 (low Tcrit, e.g. CO_2)	
For HFC-134a applications	Pressure, flammability, GWP

[2,3]

Blend formation & filtering	
Binary + ternary blends:	Composition increment 4 %.
COP, Q_{vol}, GWP, Flammability index ($\overline{\Pi}$) [4]	Pareto optimized



23 "best" blends from preliminary screening [2,3]

Refrigerant screening

blends studied in detail here: 1. R-513A (row 2); 2. Tern-1 (row 4)

R-450A "like" (row 9)

	Components	Composition (mole fraction)	GWP_{100}	$\overline{\Pi}$	COP/ $COP_{R\text{-}134a}$	Q_{vol}/ $Q_{vol,\ R\text{-}134a}$
Class 1* non flame propagating (predicted)						
1	R-134a/1234yf	0.44/0.56	537	-0.1	0.987	1.025
2	R-134a/1234yf (R-513A)	0.468/0.532	573	-0.4	0.988	1.027
3	R-134a/1234yf/134	0.48/0.48/0.04	633	-1.1	0.987	0.975
4	R-134a/1234yf/1234ze(E)	0.52/0.32/0.16	640	-1.2	0.987	0.989
5	R-134a/1234yf	0.52/0.48	640	-1.2	0.989	1.029
6	R-134a/1234yf/134	0.4/0.44/0.16	665	-1.3	0.986	0.958
7	R-134a/125/1234yf	0.44/0.04/0.52	676	-1.5	0.985	1.049
8	R-134a/227ea/1234yf	0.40/0.04/0.56	681	-1.5	0.984	1.007
9	R-134a/1234ze(E)	0.60/0.40	745	-2.4	0.988	0.908
10	R-134a/1234yf	0.60/0.40	745	-2.4	0.990	1.031
11	R-134a/1234ze(E)/1243zf	0.60/0.36/0.04	750	-1.5	0.990	0.966
12	R-134a/1234yf/1234ze(E)	0.64/0.20/0.16	799	-3.0	0.990	0.986
13	R-134a/152a/1234yf	0.64/0.04/0.32	817	-1.8	0.993	1.023
14	R-134a/1234yf/134	0.52/0.32/0.16	824	-3.2	0.990	0.966
15	R-134a/1234ze(E)	0.68/0.32	852	-3.7	0.991	0.929
16	R-134a/1234yf/1243zf	0.68/0.2/0.12	870	-1.1	0.994	1.020
Class 2L* flammable (predicted)						
17	R-152a/1234yf	0.08/0.92	8	7.7	0.980	0.957
18	R-134a/1234yf	0.20/0.80	238	2.8	0.980	0.996
19	R-134a/152a/1234yf	0.20/0.16/0.64	270	8.7	0.987	0.984
20	R-152a/1234yf/134	0.16/0.48/0.36	417	7.5	0.984	0.900
21	R-134a/1234yf	0.36/0.64	436	1.0	0.985	1.018
22	R-134a/1234yf/1243zf	0.36/0.44/0.20	451	5.2	0.988	1.004
23	R-134a/152a/1234yf	0.36/0.20/0.44	496	8.3	0.994	0.994
3. R-450A	R-134a/1234ze(E)	0.42/0.58	547	-0.2	0.983	0.867
4. R-515B	R-1234ze(E)/227ea	0.938/0.062	344	2.0	0.972	0.738

blends studied in detail here: 3. R-450A; 4. R-515B

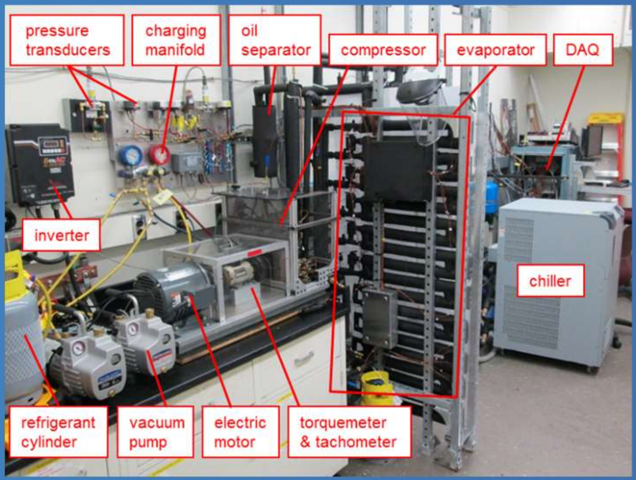
$$GWP \propto \frac{1}{flammability}$$

Flammability index ($\overline{\Pi}$) [4]

-100 to -10	nonflammable
-10 to 0	nonflammable (borderline)
0 to 10	flammable (borderline)
10 to 45	flammable

*ASHRAE 34 / ASTM E681 flammability classification

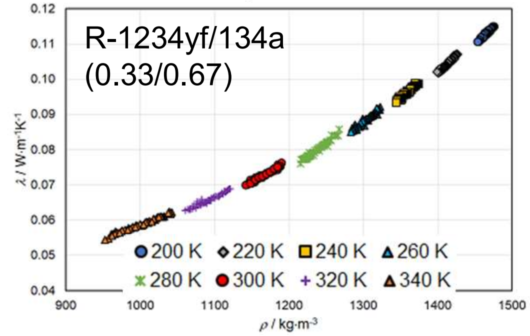
Laboratory testing



Results: property measurements

- Accurate properties needed for simulation & exp. meas.
- Comprehensive data on blends:
  (R-134a/1234ze(E); R-1234yf/1234ze(E); R-1234yf/134a)
  - vapor-liquid equilibrium (VLE)
  - (p, ρ, T, x) in liquid-phase and supercritical states
  - liquid-phase speed of sound, thermal conductivity, viscosity
- VLE-only on additional blends:
  R-125/1234yf; R-227ea/1234ze(E); R-152a/1234yf
- Property Reference Database – REFPROP [5]
  - These data, along with literature data, used to develop mixture model optimized for blends of low-GWP fluids.
  - Measurements show v10.0 used for screening study was sufficiently accurate.
  - Used in the detailed simulations of the ECU.

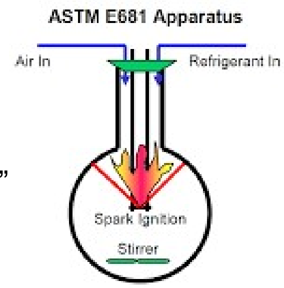
Measured thermal conductivity data versus density



2-Sinker densimeter for p-ρ-T measurements

Results: flammability

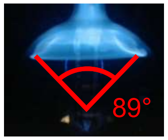
- ASTM E681 (ASHRAE Standard 34) test
  - Refrigeration industry standard. "Go/no-go".
  - R-513A, R-450A, R-515B, Tern-1 were "non-flame propagating"
  - Maybe insufficient for military applications



12 L vessel

ASTM E681 test

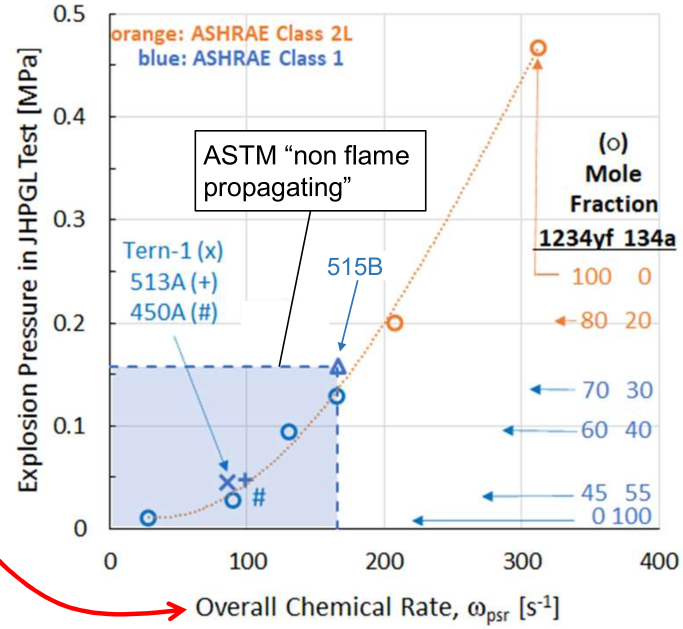
"Non-flame propagating"



"Flame propagating"

- Modified Japanese High-Press. Gas Law (JHPGL)
  - More intense ignition: molten droplets from fused Pt wire, turbulence. Can be a more stringent flammability test.
  - Measures maximum explosion pressure (p_{max})
  - Tested R-1234yf/134a blends with varied ratios
  - Low explosion pressure for Tern-1, R-513A, and R-450A, somewhat higher value for R-515B
  - Recommend live-fire tests to establish acceptance criteria

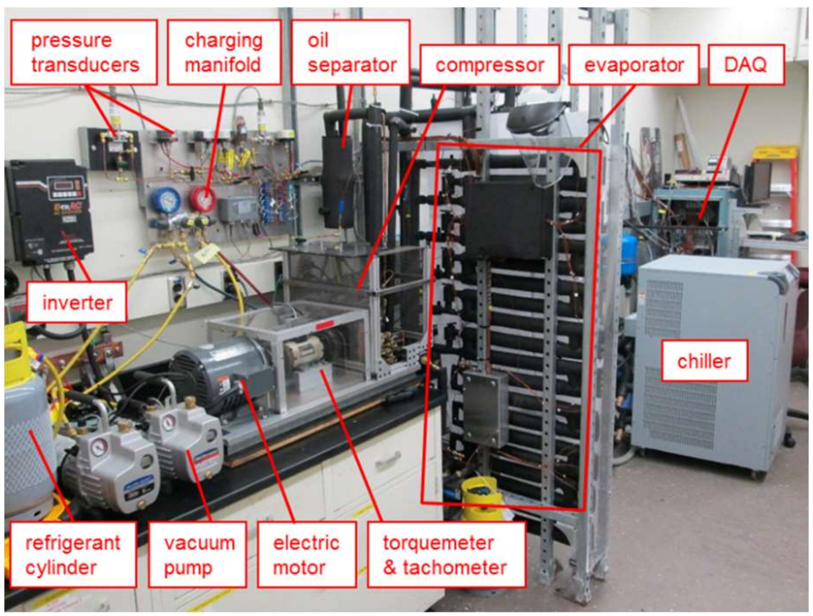
JHGPL test



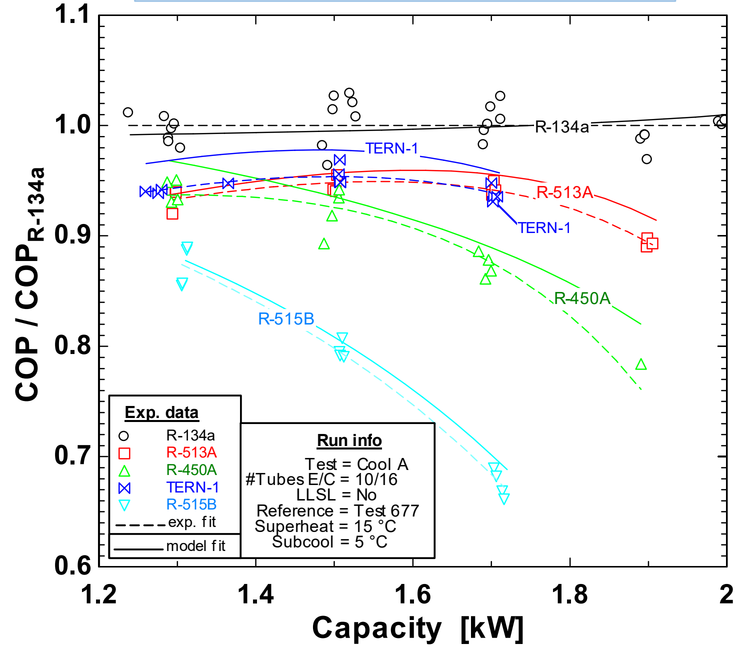
- Chemical kinetic prediction of blend reactivity
  - Predicts experimental flammability behavior
  - After correlation w/ live-fire test, can predict full-scale behavior
  - Predicts influence of other parameters (humidity, temp, etc.)
  - Useful for future refrigerant screening

Results: testing best blends in laboratory heat pump

- Measured cycle performance in miniature breadboard heat pump (MBHP)
- Qualified blends for ECU tests
- Validated CYCLE_D-HX [6] → used in preliminary blend screening [2,3]
  - Simulations predicted COP within ±(1.5 to 3) %
  - Correctly predicted 'ranking'



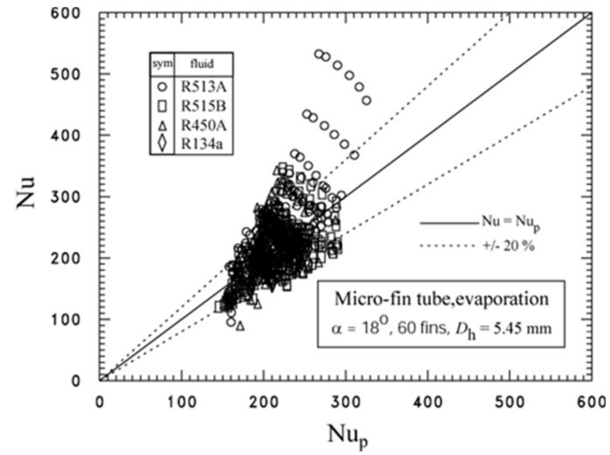
MBHP measurements & simulations



Results: flow boiling measurements

- 432 local convective-boiling measurements were taken and correlated

Predicted and measured Nusselt number



Nusselt number $= \frac{h_{2\phi} D_h}{k_l}$

thermodynamic quality

Bond number $= \frac{(\rho_l - \rho_v) g e D_h}{\sigma N}$

$$Nu_p = 242.5 Re^{0.26(1-x_q)} Bo^{0.28} B_{nd}^{-0.61 x_q}$$

Reynolds number $= \frac{G_r D_h}{\mu_l}$

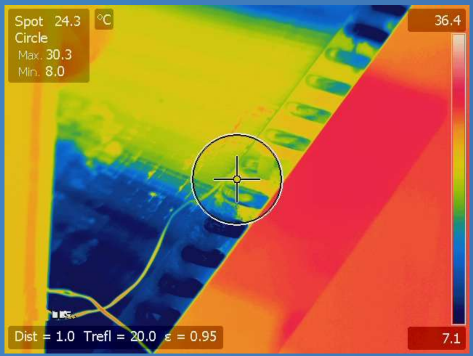
Boiling number $= \frac{q''}{G_r i_{fg}}$

Correlation used in ECU optimization simulations

43 % for old correlation

The new correlation predicts 71 % of the measured convective-boiling Nusselt numbers for R-515B, R-450A, R-513A, and HFC-134a to within approximately ± 20 %

Full-scale ECU testing

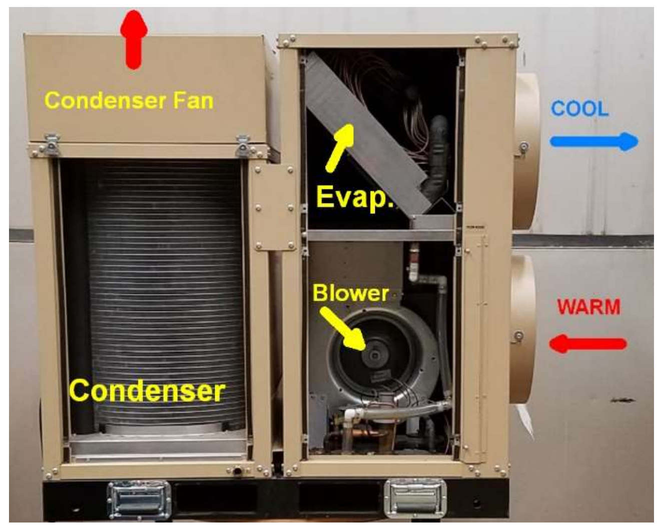


ECU test methods

- Tested refrigerants: HFC-134a, R-513A, Tern-1, R-515B
- Environmental conditions controlled by psychometric chamber
- "Drop-in" tests
- Soft-optimized cycle for each refrigerant:
  - Adjusted refrigerant charge to get target subcooling
  - Adjusted (or replaced) TXV to get target superheat

environmental conditions

Indoor T	Outdoor T
26.7 °C	27.8 °C
	35.0 °C
	46.1 °C
	51.7 °C

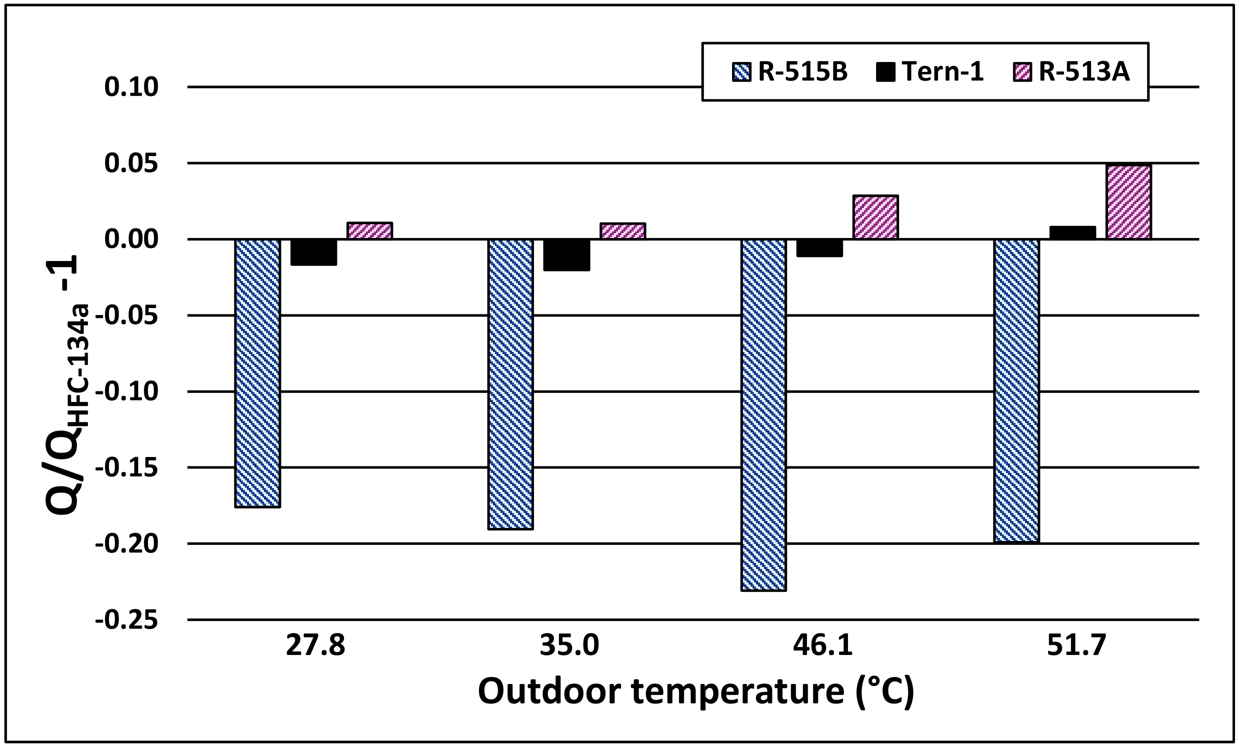


TXV: thermostatic expansion valve
EPR: evaporator-pressure regulator

ECU test results

- Total Capacity*
  - R-515B: (17 to 22) % lower capacity
  - Tern-1: 2 % lower to 1 % higher
  - R-513A: (1 to 5) % higher

Capacity (Q) – relative to HFC-134a

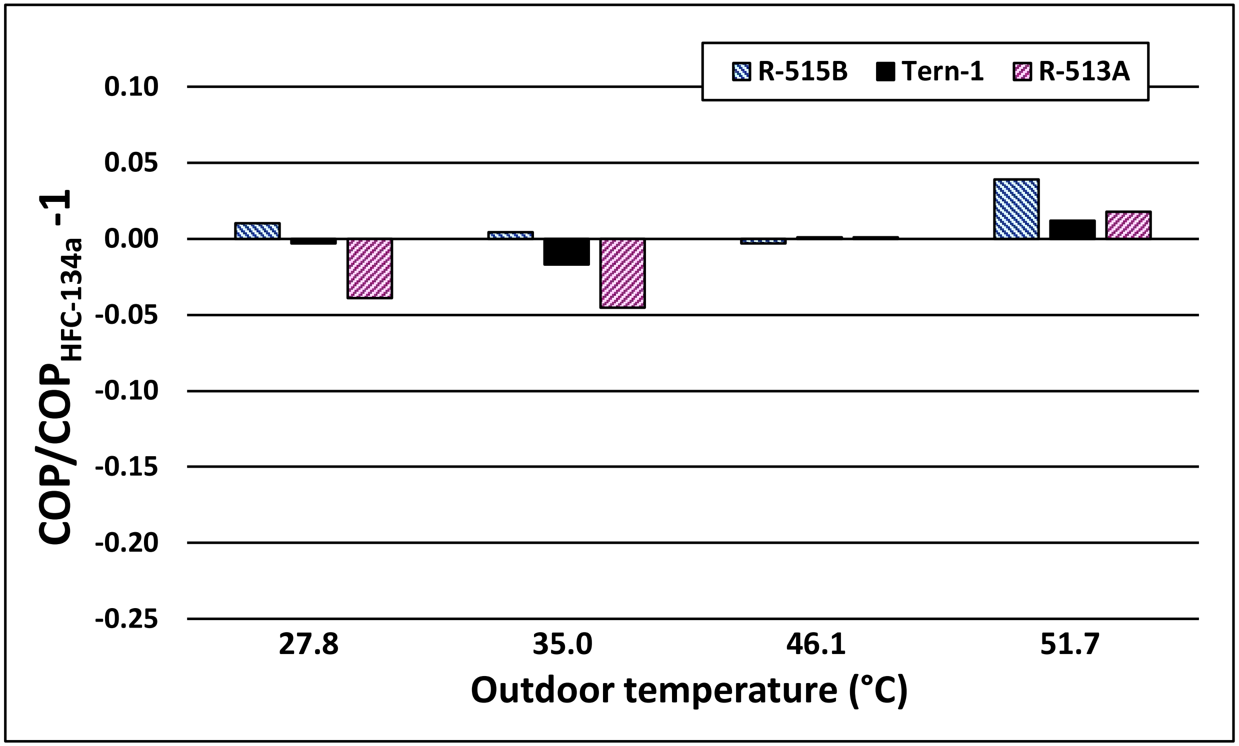


*measured on refrigerant side

ECU test results

- Coefficient of Performance (COP) = Capacity* / Power Input
  - R-515B: (0 to 4) % higher
  - Tern-1: 2 % lower to 2 % higher
  - R-513A: 5 % lower to 2 % higher

COP – relative to HFC-134a



*measured on refrigerant side

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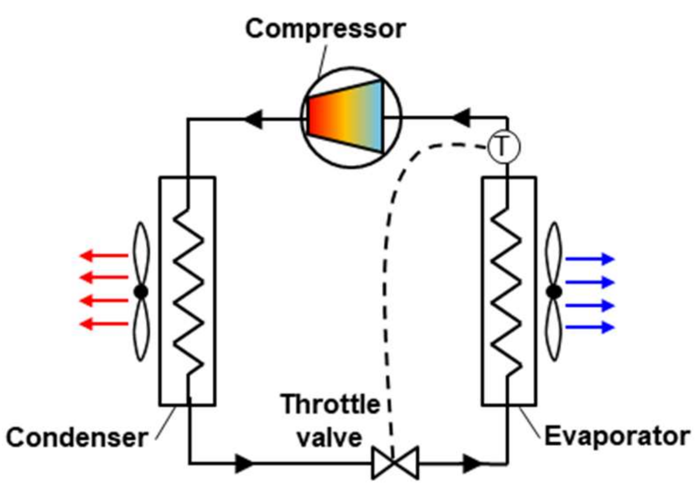
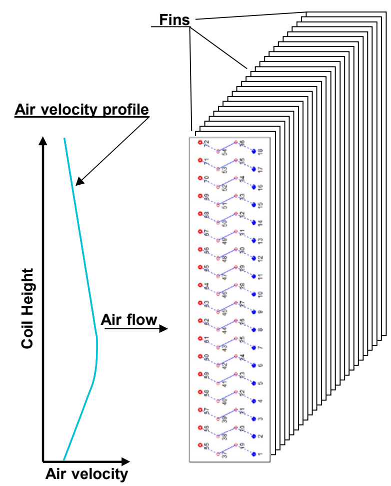
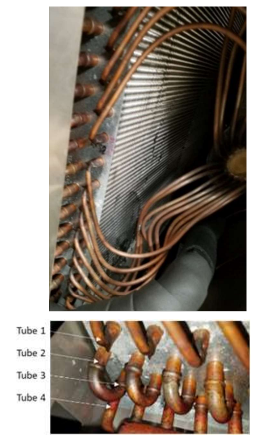
26TH INTERNATIONAL CONGRESS OF REFRIGERATION

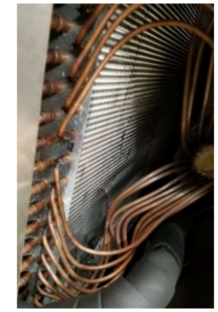
Refrigerant Optimized Performance in ECU (Simulation)



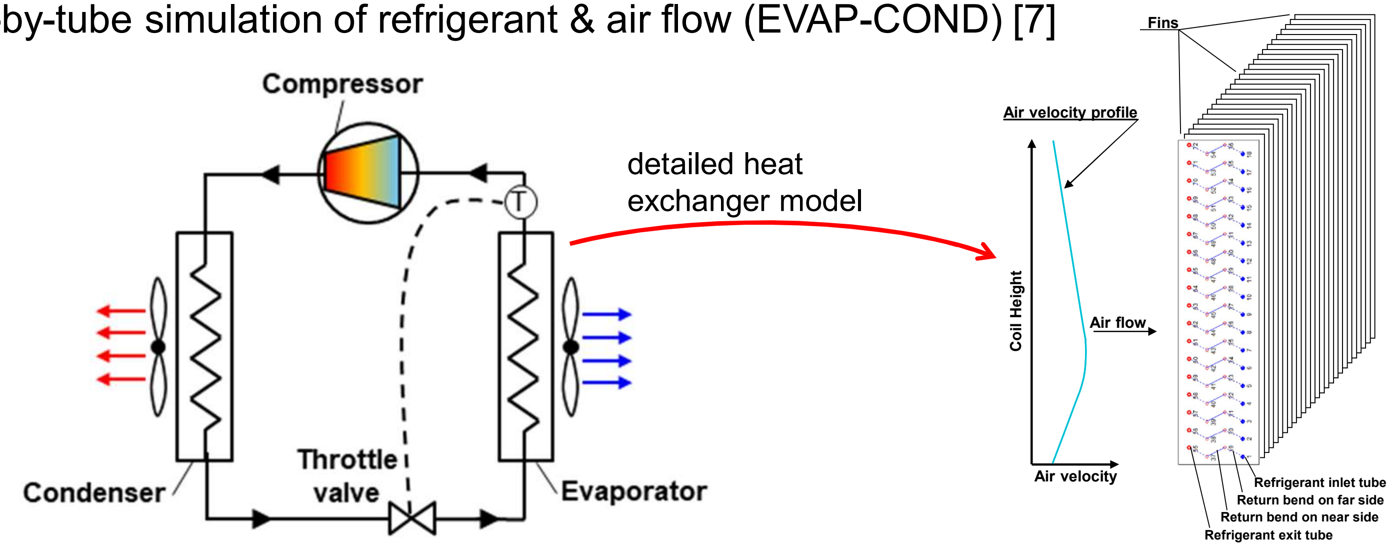




Simulation methods:



- Evaluate HFC-134a alternatives in ECU tailored to each refrigerant
  - Fairer comparison than ‘drop-in’ tests with fixed hardware
- Experimentally-tuned simulations using ACSIM
- Compressor: performance map w/ correction for high-ambient. Equal efficiency.
  - Adjusted displacement to imposed equal capacity @ 35 °C
- Heat exchanger: tube-by-tube simulation of refrigerant & air flow (EVAP-COND) [7]



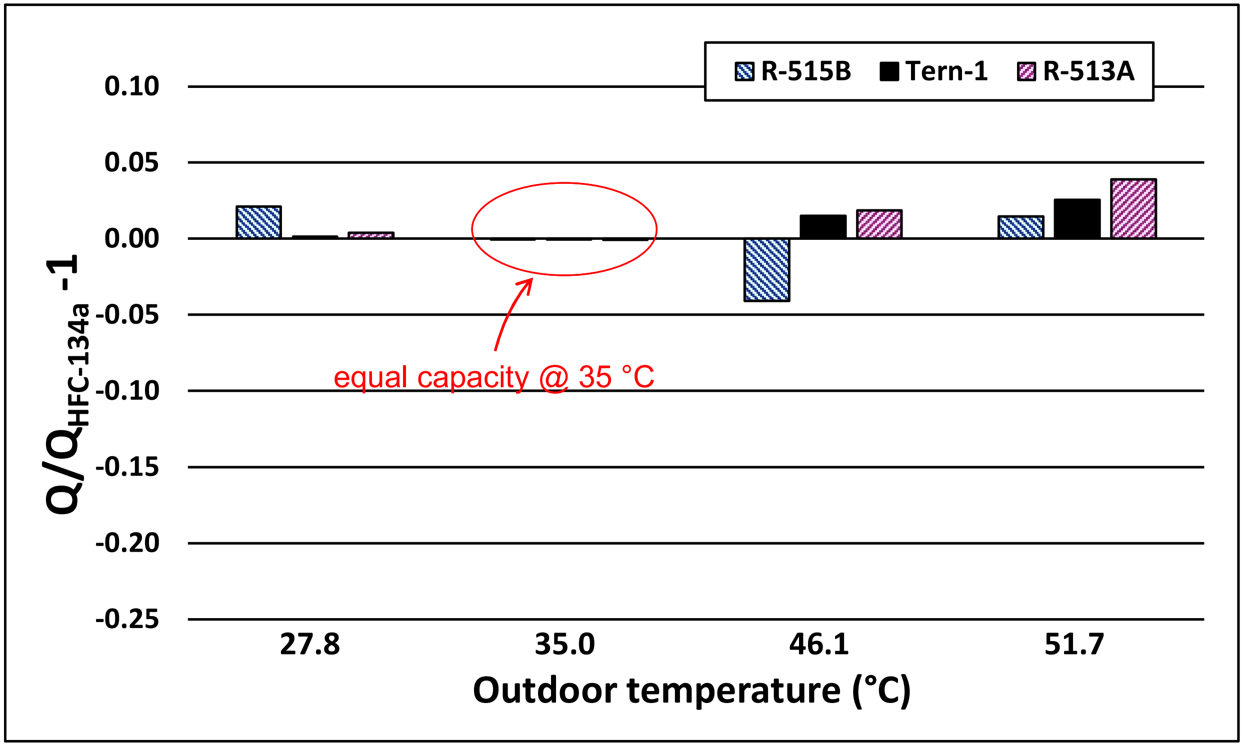
ACSIM - Cycle simulation

EVAP-COND - Evaporator & condenser simulation

Optimized ECU Results

- Capacity
  - Adjusted compressor size to match HFC-134a capacity at 35 °C
  - R-515B: 4 % lower to 2 % higher
  - Tern-1: (0 to 3) % higher
  - R-513A: (0 to 4) % higher

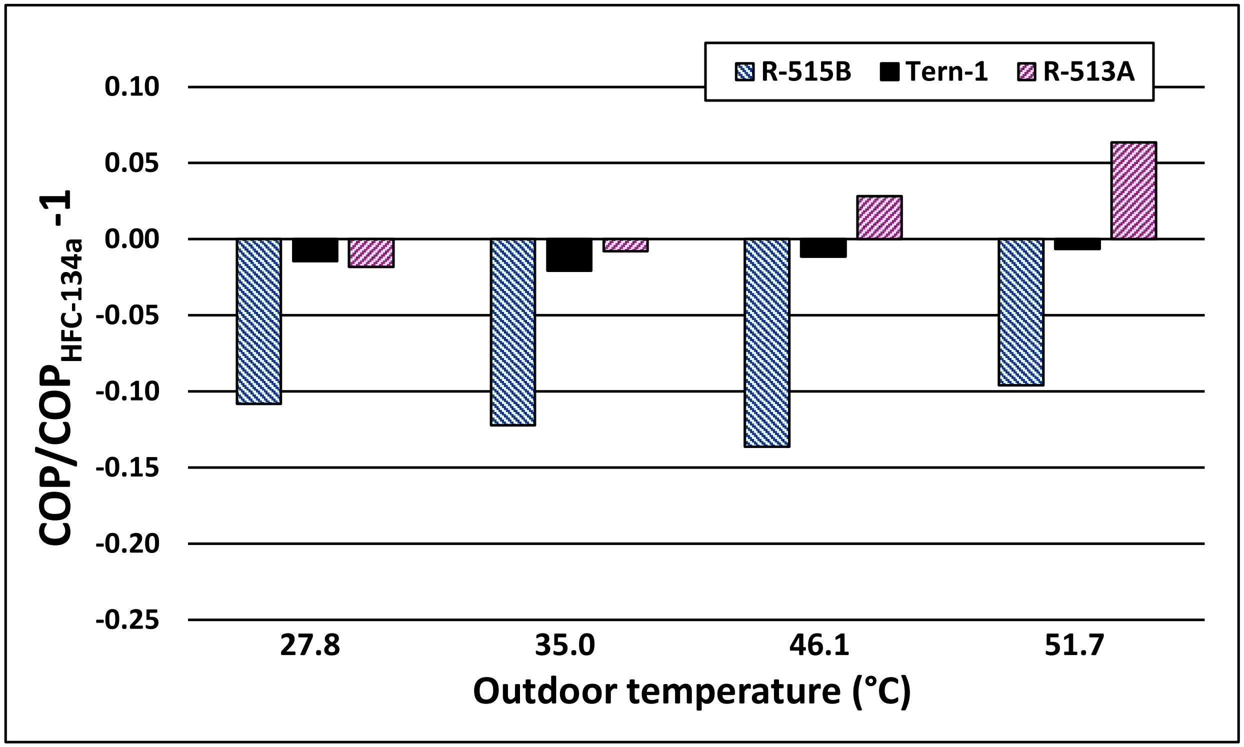
Capacity (Q) – relative to HFC-134a



Optimized ECU Results

- Results: COP (efficiency)
  - Adjusted compressor size to match HFC-134a capacity at 35 °C
  - R-515B: (10 to 14) % lower
  - Tern-1: (1 to 2) % lower
  - R-513A: 2 % lower to 7 % higher

COP – relative to HFC-134a



Conclusion

Conclusions *from the search for non-flammable, lower-GWP refrigerant blends to replace HFC-134a*

Refrigerant	GWP
HFC-134a	**1300**
Tern-1	640
R-513A	573
R-450A	457
R-515B	344
CO_2	1

Tern-1 and R-513A:

- Capacity and COP comparable to HFC-134a
- Reduce GWP > 50 %
- Might pass more-stringent military flammability criteria

R-450A:

- Performance between R-513A and R-515B

R-515B:

- Greater reduction in GWP, needs R&D to increase COP
- Likely fail flammability criteria if more stringent than ASTM E681

CO_2:

- Requires further R&D to increase capacity & COP
- Would pass any flammability test

- Recommend live-fire tests to establish flammability criteria for military
- If needed, use simulation tools to identify less-flammable (but higher-GWP) blends

Concluding report for this work

- Domanski, P. A., McLinden, M., Babushok, V., Bell, I., Fortin, T., Hegetschweiler, M., Kedzierski, M., Kim, D., Lin, L., Linteris, G., Outcalt, S., Payne, V., Perkins, R., Rowane, A., & Skye, H. (2023). *Low-GWP Non-Flammable Alternative Refrigerant Blends for HFC-134a: Final Report (NISTIR 8455)*. https://doi.org/10.6028/NIST.IR.8455

Conference paper

- Skye, H., Domanski, P. A., McLinden, M., Babushok, V., Bell, I., Fortin, T., Hegetschweiler, M., Kedzierski, M., Kim, D., Lin, L., Linteris, G., Outcalt, S., Payne, V., Perkins, R., Rowane, A.(2023). *Lower-GWP Non-Flammable Refrigerant Blends to Replace HFC-134a (#0943)*. Proceedings of the 2023 International Congress of Refrigeration, Paris, France, DOI: 10.18462/iir.icr.2023.0943

Additional References

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Abbreviations and Symbols

ACSIM – NIST first-principles-based simulation model of air-conditioning system

ASHRAE – international professional organization known as American Society of Heating Refrigerating and Air-Conditioning Engineers

ASTM – ASTM International, international standards organization known as American Society for Testing Materials

CF_3I – trifluoroiodomethane

CO_2 – carbon dioxide

COP – coefficient of performance

ECU – environmental control unit

EOS – equation of state

EVAP-COND – NIST first-principles-based simulation model of finned-tube heat exchangers

CYCLE_D-HX – NIST vapor-compression cycle simulation model

GWP – global warming potential

HFC – hydrofluorocarbon

HFO – hydrofluoroolefin

IIR – International Institute of Refrigeration

JPHGL – Japanese High-Pressure Gas-Law Test

Q_{vol} – volumetric capacity

REFPROP – NIST standard reference database for thermophysical properties

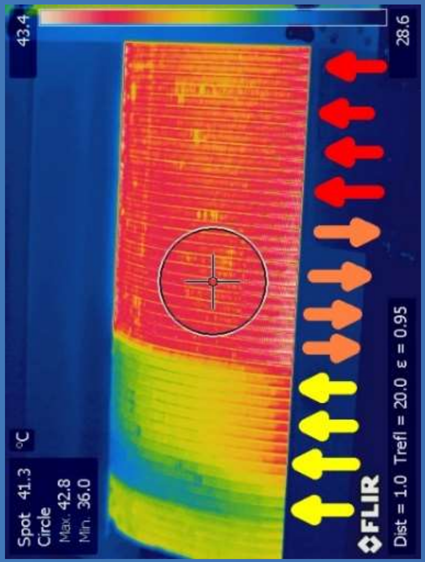
VLE – vapor-liquid equilibrium

$\overline{\Pi}$ - Flammability index

Acknowledgements

This work was partially supported by the Strategic Environmental Research and Development Program (SERDP); Project WP19-1385: “Low-GWP Alternative Refrigerant Blends for HFC-134a”, which was a follow-on project to WP-2740.

End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°C
Spot 41.3
Circle
Max 42.8
Min 36.0
FLIR
Dist = 1.0 Trefl = 20.0 ε = 0.95

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