Low-GWP Alternative Refrigerant Blends for HFC-134a

WP19-1385

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14. ABSTRACT
The technical objectives of this project are listed below:
- Identify replacements for HFC-134a
  - o Identify three best non-flammable blends to replace HFC-134a
  - o Test HFC-134a environmental control unit (ECU) charged with three blends
  - o Extrapolate laboratory results to a 'fully optimized' ECU by detailed ECU simulations
  - o Simulate ECU operating with carbon dioxide (CO2)

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Project Team

- **NIST, Applied Chemicals and Materials Division, Boulder, CO**

  I. Bell: modeling of blend properties and thermodynamic cycle analysis
  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

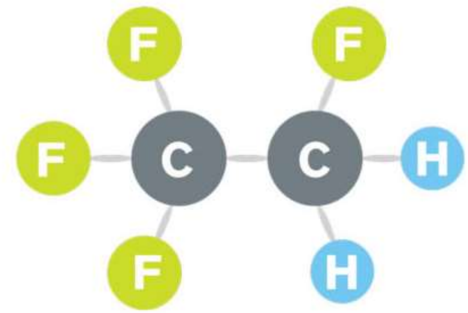
- **NIST, Building Energy and Environment Division, Gaithersburg, MD**

  V. Babushok, M. Hegetschweiler, D. Kim (postdoc) 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

Background

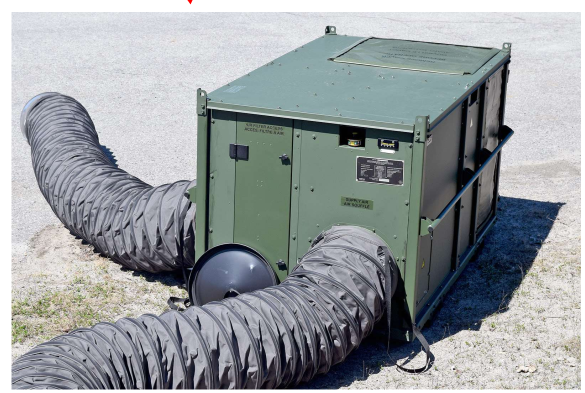
Statement of Need:

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



"HFC-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)
- Project initiated: Sept. 2019



- Transportable units provide cooling in the field
- (10 to 20) kW cooling capacity

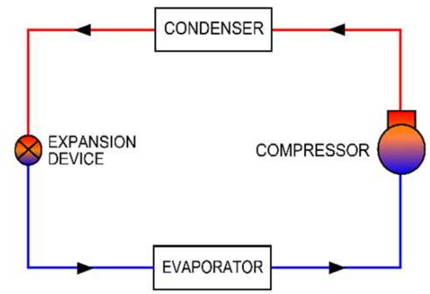
COP: coefficient of performance (efficiency) ECU: environmental control unit GWP: global warming potential

Technical Objective

Identify replacements for HFC-134a

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

  (tests in environmental chambers at wide range of operating conditions)



To authoritatively reach the project objective, this project includes:

- Fundamental measurements and modeling of **thermophysical properties**
- Fundamental measurements and modeling of **two-phase heat transfer**
- Fundamental measurements and analysis of **flammability behavior**
- Qualifying tests of selective blends in a laboratory **mini-breadboard heat pump** apparatus

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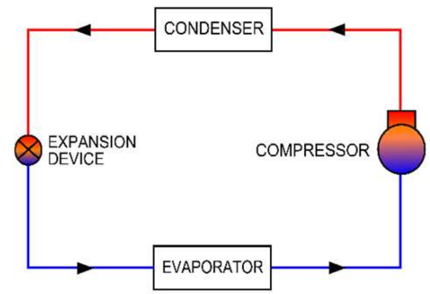
  (includes machine-learning-based optimization of heat exchangers)



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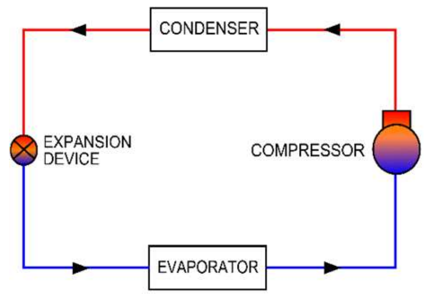
- Extrapolate laboratory results to a 'fully optimized' ECU by detailed ECU simulations
  (includes machine-learning-based optimization of heat exchangers)
- Simulate ECU operating with carbon dioxide (CO_2)
  (w/optimization)



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Technical Approach

Preliminary modeling — **Screening Study** WP-2740 [1]

Fundamental data and modeling — **Task 1** Property Measurements; **Task 4** Heat-Transfer Measurements; **Task 2** Flammability Assessment

Lab-scale testing — **Task 3** Mini-Breadboard Testing

Fluid selection & consideration of new fluids — **Task 5** Selection of Blends

CF_3I

WP19-1385 interim report [2]

Task 6 Interim Report

Reporting

Full-scale testing in environmental chambers and modeling — **Task 7** Evaluation of Blends in ECU

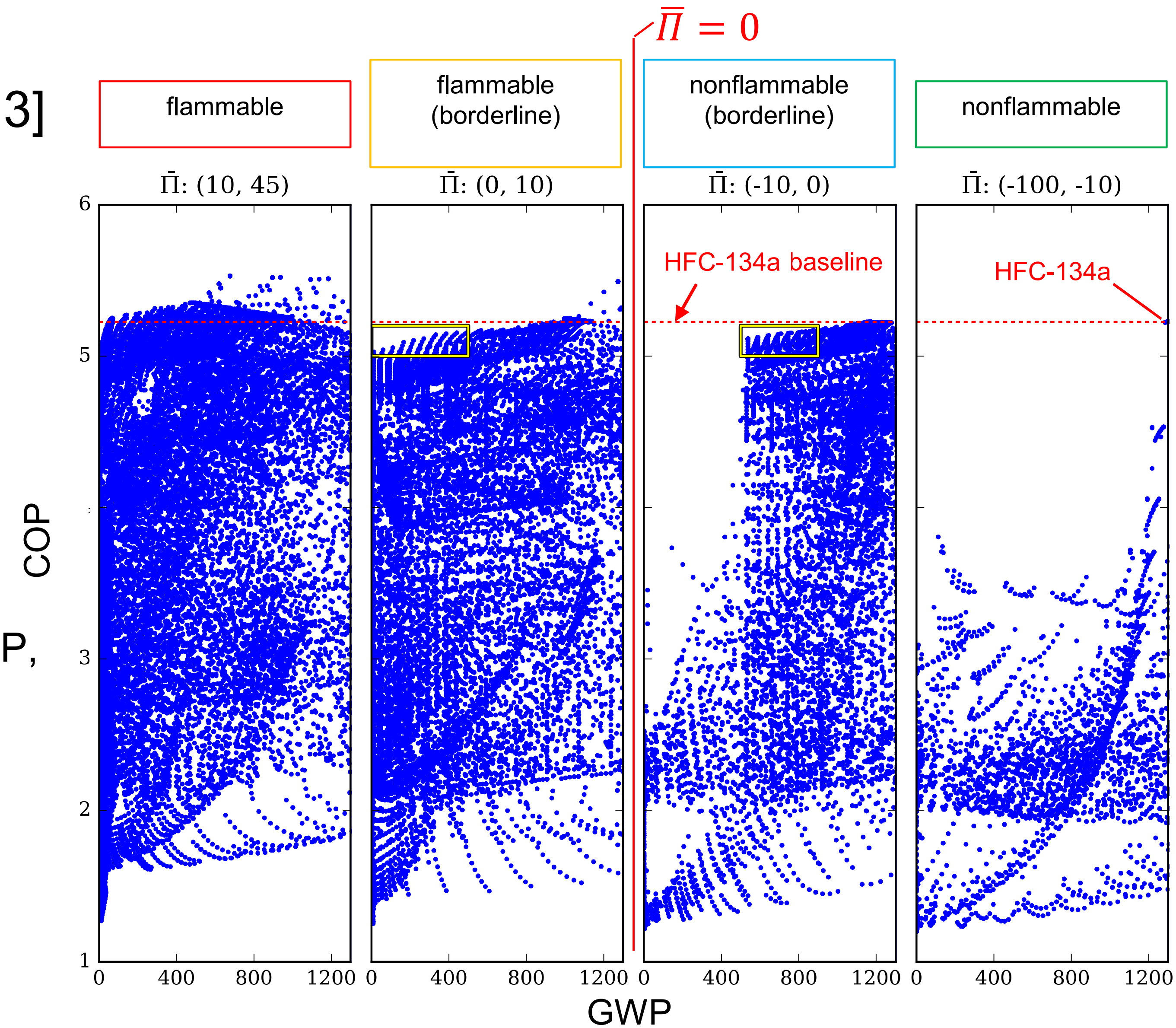
Task 8 Final Report

[1] Domanski et al., **2018**, *Low-GWP Alternative Refrigerant Blends for HFC-134a*, WP-2740 https://doi.org/10.6028/NIST.TN.2014
[2] Domanski et al., **2021**, *Low-GWP Alternative Refrigerant Blends for HFC-134a: Interim Report*, WP 19-1385 https://doi.org/10.6028/NIST.IR.8395

Results

Preliminary Study. Blend screening (WP-2740 [1])

- Component screening [1,3]
  - ♦ 60M+ in PubChem → 13
- Evaluated all binary and ternary combinations
  - ♦ 100,387 blends
  - ♦ Simplified cycle model
  - ♦ Figures of merit: COP (efficiency), capacity, GWP, flammability index ($\bar{\Pi}$) [8]
  - ♦ No nonflammable blends with GWP_{100} < 537



Results

Preliminary Study. Blend screening (WP-2740 [1])

23 "best" blends

	Components	Composition (mole fraction)	GWP_{100}	$\bar{\Pi}$	COP/ $COP_{R\text{-}134a}$	Q_{vol}/ $Q_{vol,\ R\text{-}134a}$
Class 1 nonflammable (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
	R-134a/1234ze(E)	0.42/0.58	547	-0.2	0.983	0.867
	R-1234ze(E)/227ea	0.938/0.062	344	2.0	0.972	0.738

blends studied in detail here:
1. R-513A (row 2)
2. Tern-1 (row 4)
3. R-450A (R-134a/1234ze(E))
4. R-515B (R-1234ze(E)/227ea)

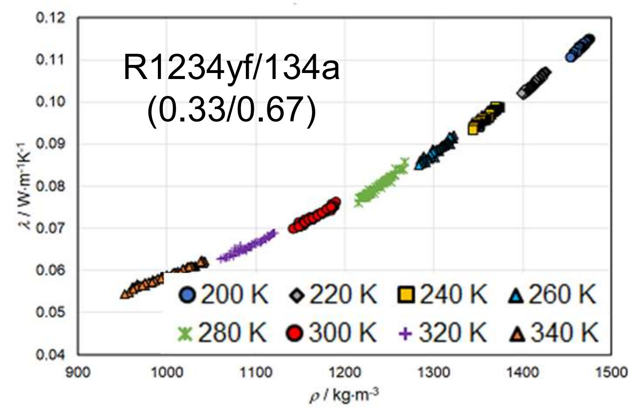
R-450A "like" (row 9)

Results

Task 1. 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 [4]
  - 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 Task 7.

Measured thermal conductivity data versus density



2-Sinker densimeter for p-ρ-T measurements

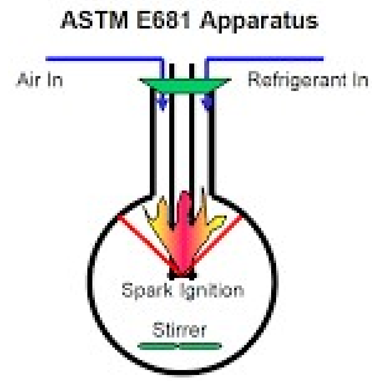
Results

Task 2. Flammability assessment

- ASTM E681 (ASHRAE Standard 34) test
  - Refrigeration industry standard. "Go/no-go".
  - All blends of interest passed as "non-flame propagating"
  - Maybe insufficient for military applications
- Modified Japanese High-Press. Gas Law (JHPGL)
  - Measures maximum explosion pressure (p_{max})
  - More intense ignition: molten droplets from fused Pt wire, turbulence. Can be a more stringent flammability test.
  - 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
  - Live-fire tests to establish acceptance criteria

recommendation

- Chemical kinetic prediction of blend reactivity
  - Predicts experimental flammability behavior
  - After correlation with live-fire test, can be used to predict full-scale behavior
  - Predicts influence of other parameters (humidity, temp, etc.)



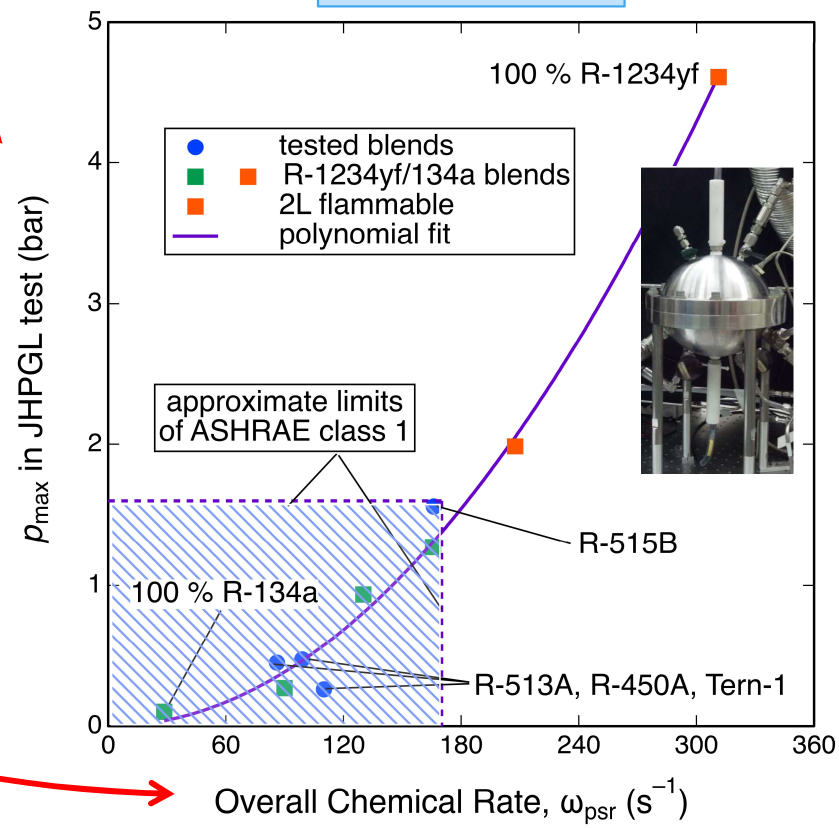
12 L vessel

ASTM E681 test

"Non-flame propagating"

"Flame propagating"

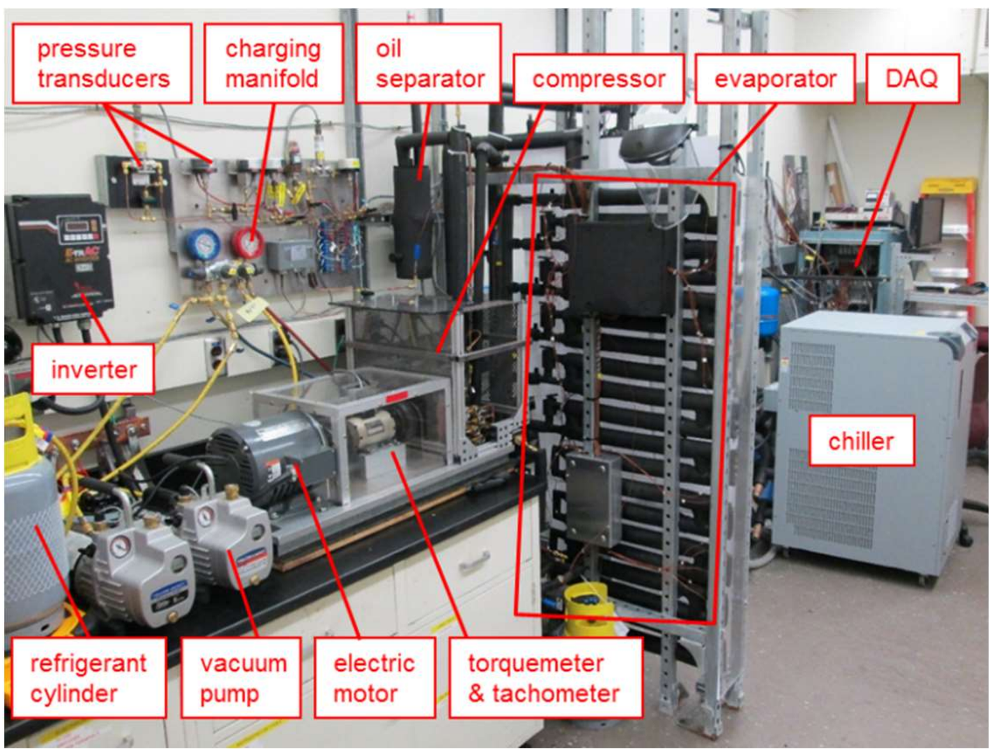
JHGPL test



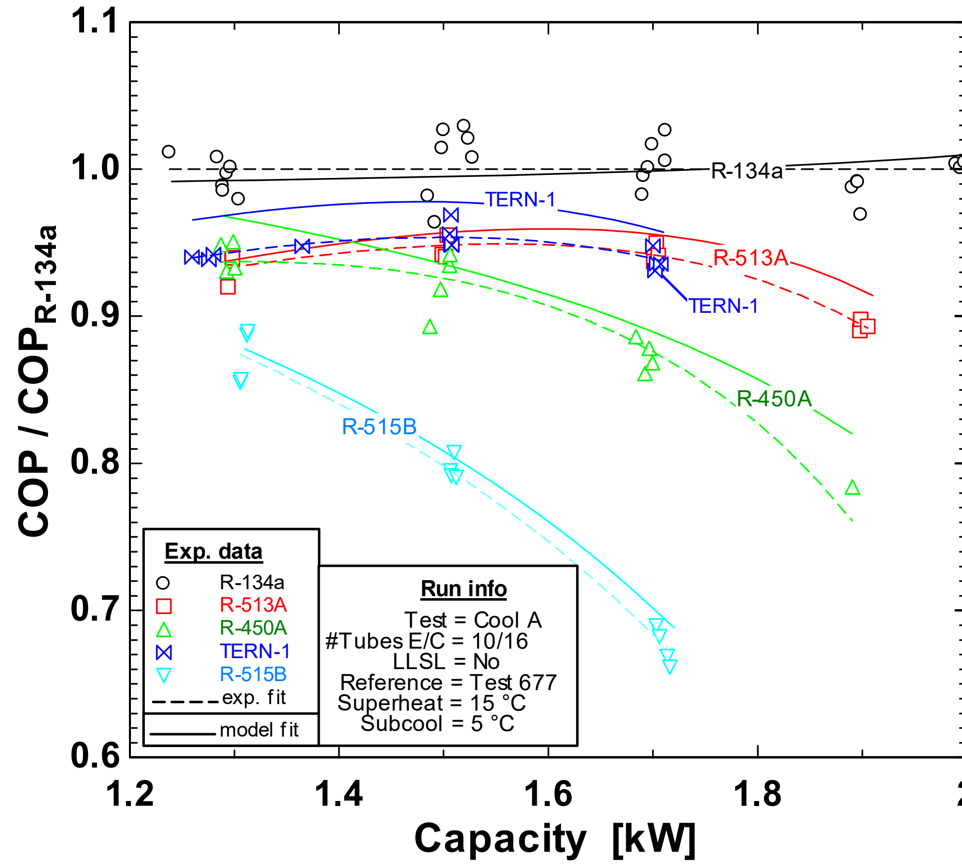
Results

Task 3. Testing of Best Blends in Mini-Breadboard Heat Pump (MBHP)

- Measured cycle performance in laboratory heat pump
- Qualified blends for ECU tests
- Validated CYCLE_D-HX [5] → used in preliminary blend screening [1]
  - ♦ Simulations predicted COP within ±(1.5 to 3) %
  - ♦ Correctly predicted 'ranking'

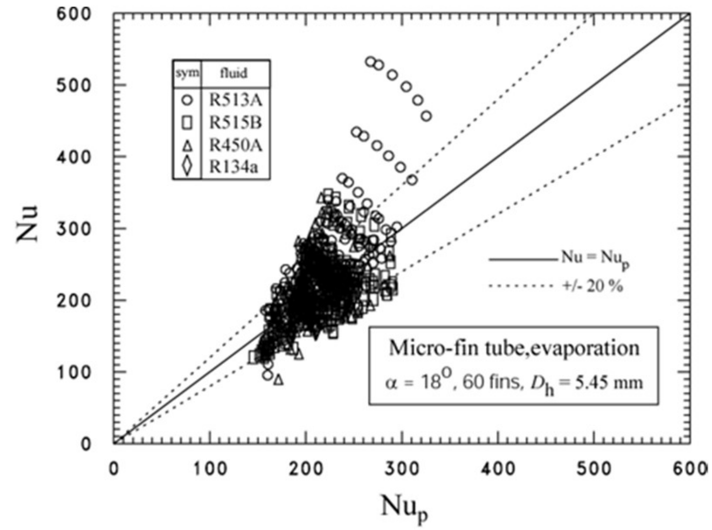


MBHP measurements & simulations



Results

Task 4. Two-Phase Heat-Transfer Measurements



- 432 local convective-boiling measurements were taken and correlated.

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

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

thermodynamic quality (x_q)

Bond number $= \dfrac{(\rho_l-\rho_v)geD_h}{\sigma N}$

Reynolds number $= \dfrac{G_r D_h}{\mu_{r,l}}$

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

used in Task 7 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 %

Results

Task 5. Selection of Final Blends for Testing in ECU

- Selected 3 blends (and HFC-134a as baseline)

Refrigerant Designation	Blend Composition*	GWP	$\bar{\Pi}^{\dagger}$	COP/ $COP_{R\text{-}134a}$	Q_{vol}/ $Q_{vol,\,R\text{-}134a}$
R-513A	R-134a/1234yf (46.8/53.2)	573	-0.4	0.988	1.027
Tern-1	R-134a/1234yf/1234ze(E) (52/32/16)	640	-1.2	0.987	0.989
R-515B	R-1234ze(E)/227ea (93.85/6.15)	344	2.0	0.973	0.738
R-450A	R-134a/1234ze(E) (53.3/44.7)	457	-0.2	0.983	0.867

ECU tests (R-513A, Tern-1, R-515B)

*mole fraction
†Flammability index [8]

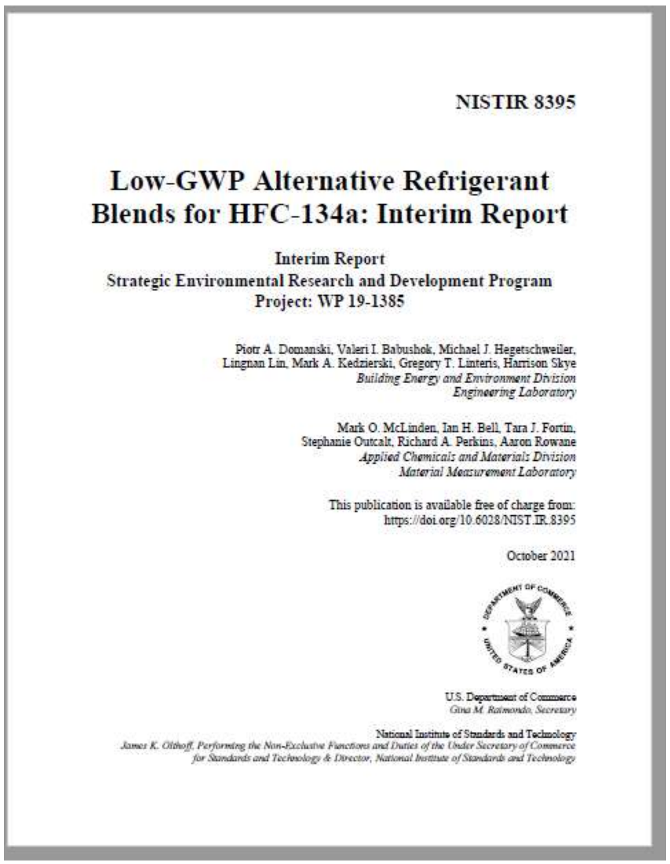
≤50 % GWP of HFC-134a (GWP=1300)

- Rationale for selection:
  - R-513A: azeotrope, very close in performance to HFC-134a
  - Tern-1: performance close to that of HFC-134a; farther from flammability boundary than R-513A
  - R-515B: the lowest GWP; lower COP and capacity, more flammable
  - Other blends can be simulated as needed, with good accuracy
  - Considered, but didn't test blends with R-13I1 (CF_3I), R-1132(E). Possible future use. [2]

Results

Task 6. Interim report

- Published October 2021
- Details Tasks 1-5
- Domanski et al., 2021, Low-GWP Alternative Refrigerant Blends for HFC-134a: Interim Report, WP 19-1385 https://doi.org/10.6028/NIST.IR.8395 [2]


NISTIR 8395

Low-GWP Alternative Refrigerant Blends for HFC-134a: Interim Report

Interim Report
Strategic Environmental Research and Development Program
Project: WP 19-1385

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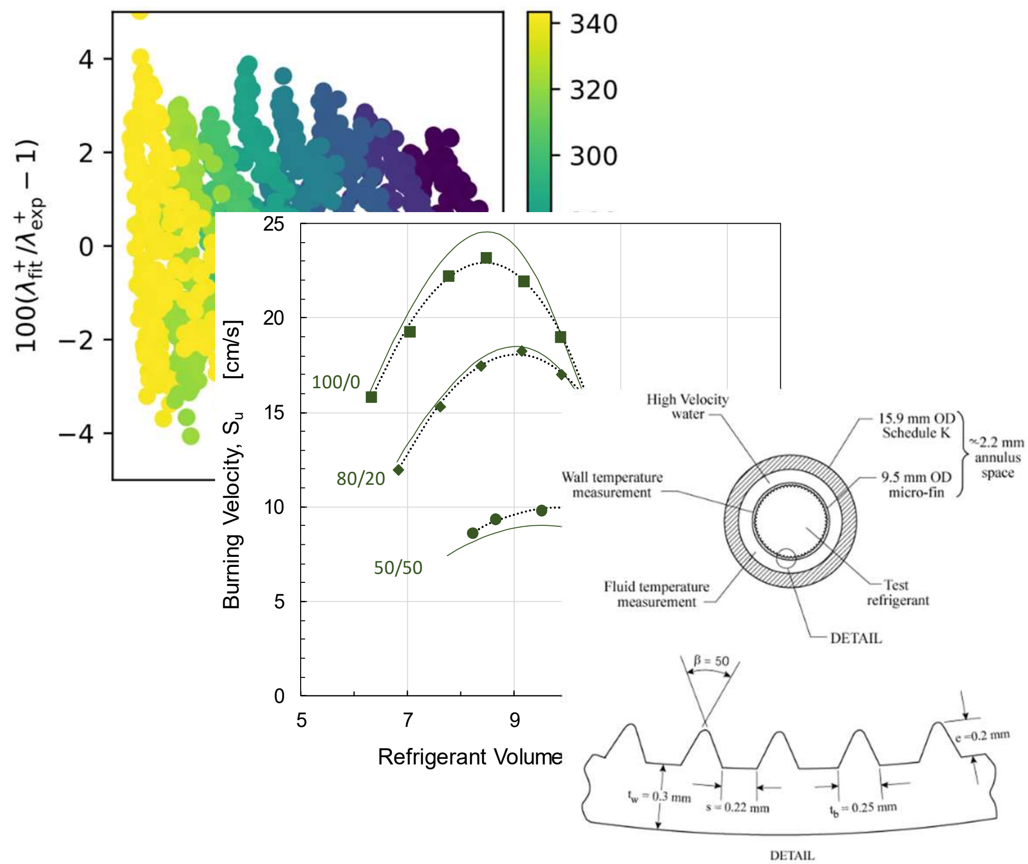


Results

Task 7. Evaluation of Blends in ECU

New work (since interim presentation)

Results

Task 7. Evaluation of Blends in ECU - Overview

1. Experimental full-scale “Drop-in” tests
2. Simulations with components optimized for each refrigerant
   a. Preliminary evaluation of CO_2

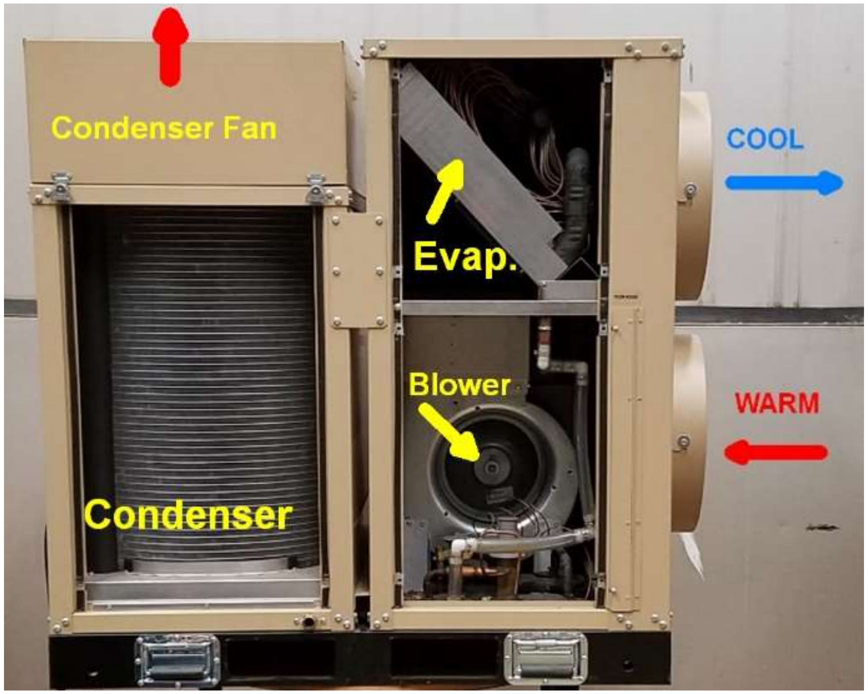
Results

Task 7. Evaluation of Blends in ECU – Experimental "Drop-in" Tests

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

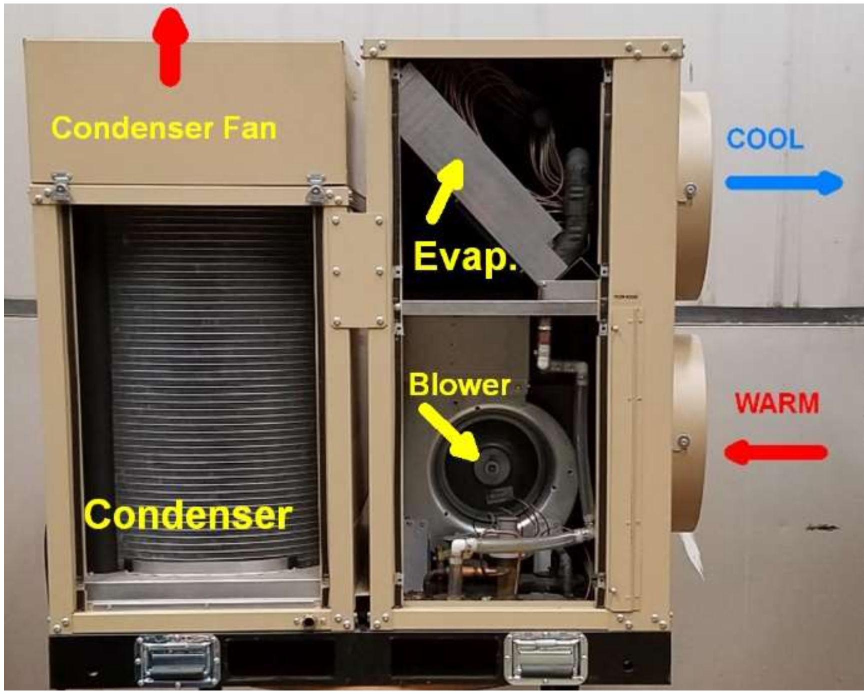
- **Purpose:** Evaluate top refrigerant replacement candidates in a military ECU designed for HFC-134a
  - Tested refrigerants: HFC-134a, R-513A, Tern-1, R-515B
  - ECU specifications: commercially available, ~20 kW cooling capacity, rugged construction, normally powered by a generator
  - ECU components: scroll compressor, finned-tube evaporator, microchannel condenser



Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- **Methods:** Tested ECU under controlled environmental conditions
- "Drop-in" tests
- Soft-optimized cycle for each refrigerant:
    - ♦ Adjusted refrigerant charge to get target subcooling
    - ♦ Adjusted (or replaced) TXV to get target superheat

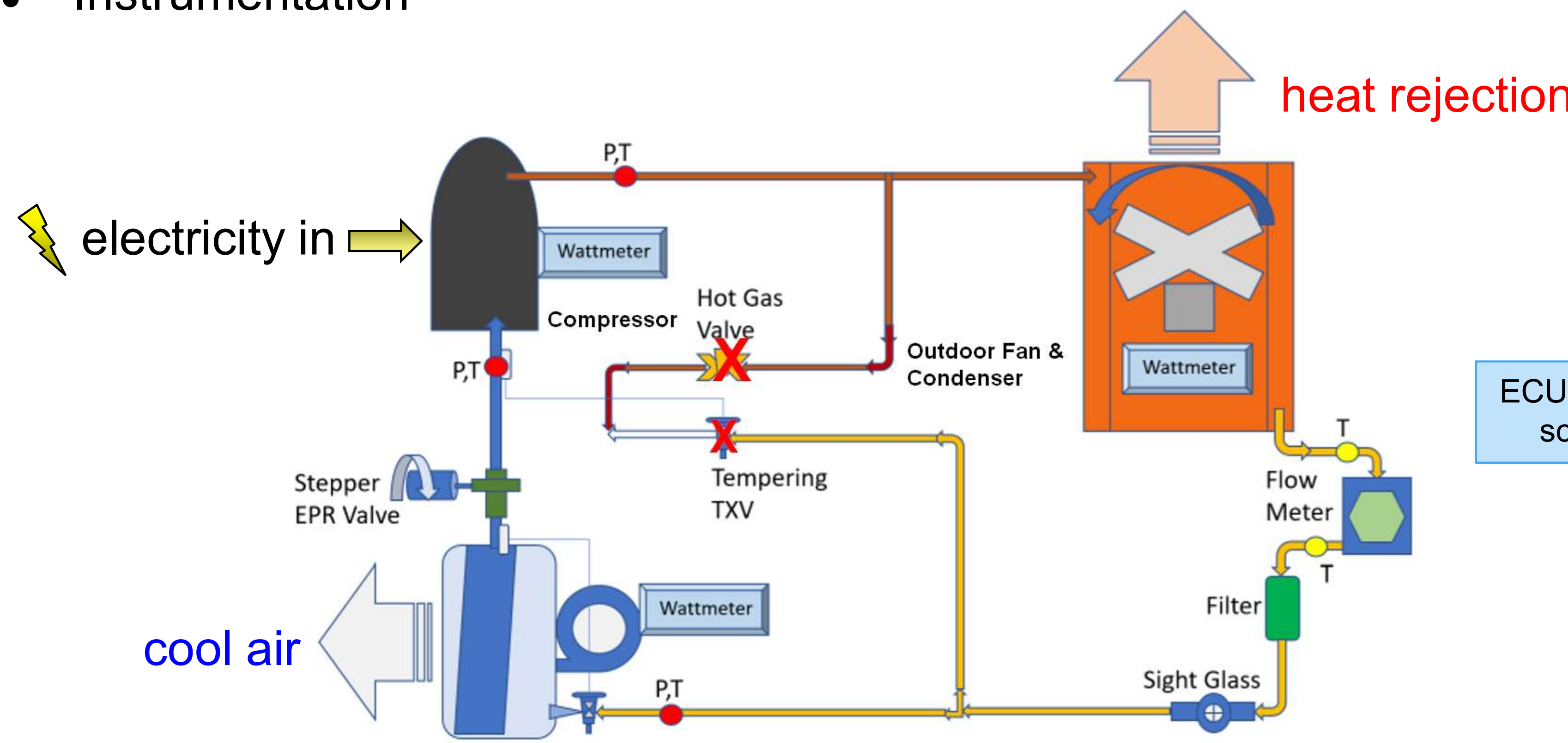


TXV: thermostatic expansion valve EPR: evaporator-pressure regulator

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- Basic vapor-compression cycle
- Bypassed/disabled components normally used to modulate capacity
  - hot-gas bypass valve, tempering TXV, EPR valve
- Instrumentation



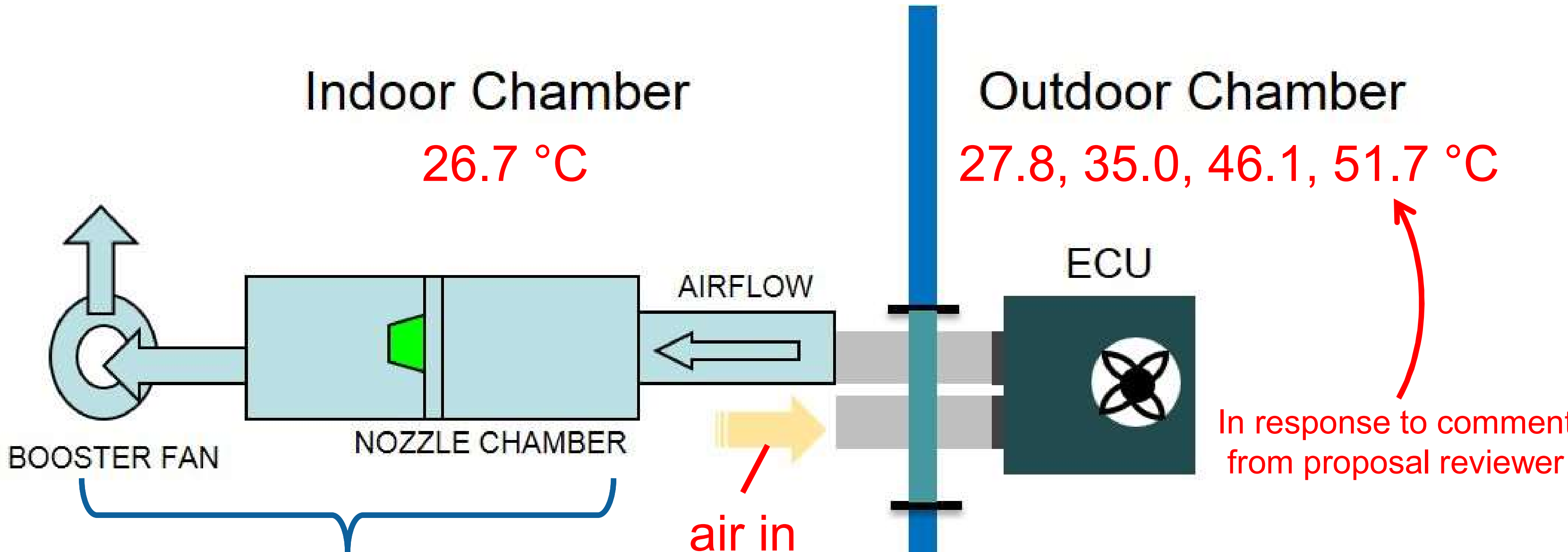
ECU refrigerant schematic

TXV: thermostatic expansion valve EPR: evaporator-pressure regulator

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

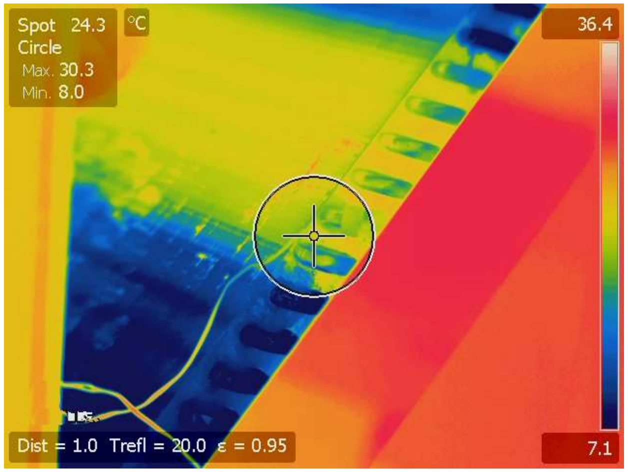
- ECU tested in 2 environmental chambers
- Measured air-side capacity

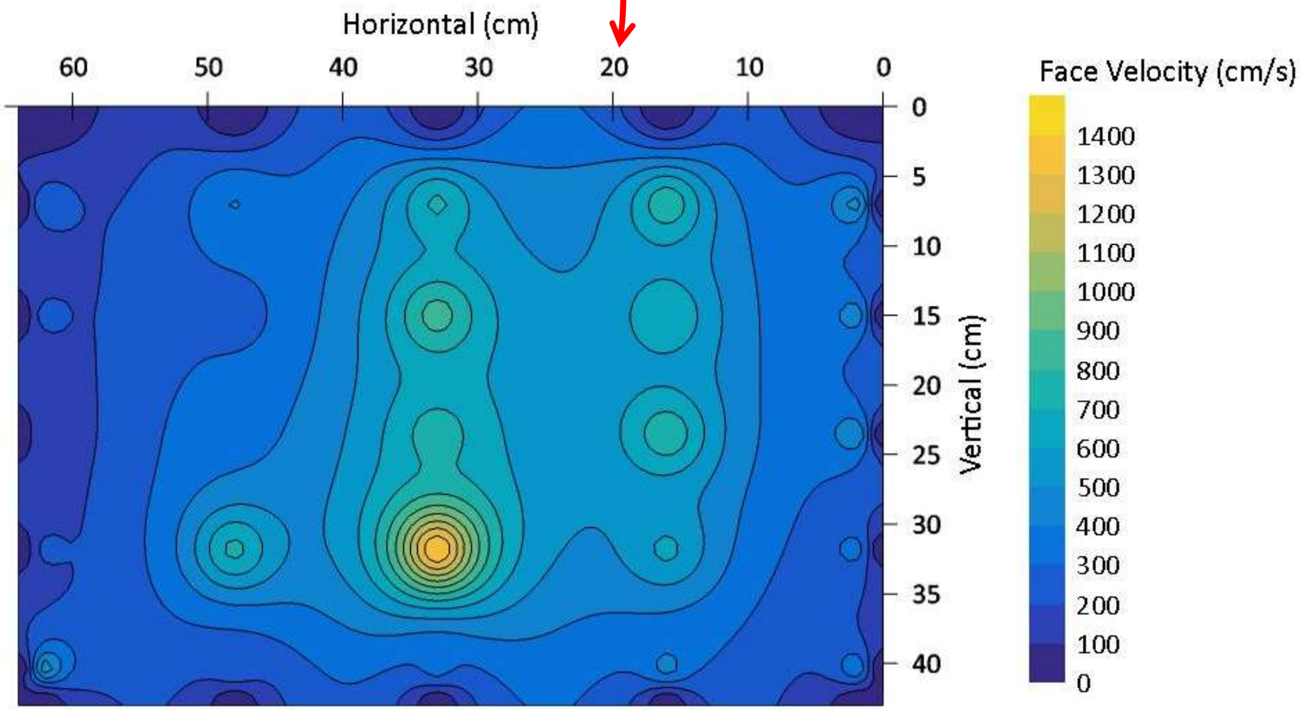


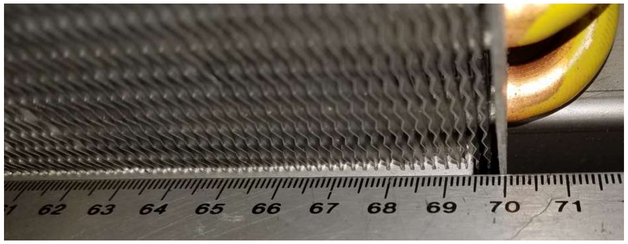
Results

Task 7. Evaluation of Blends in ECU – Exp. Tests

- Additional heat exchanger measurements
  - ♦ Thermal imaging with infrared camera
  - ♦ Airflow distribution with hot-wire anemometer





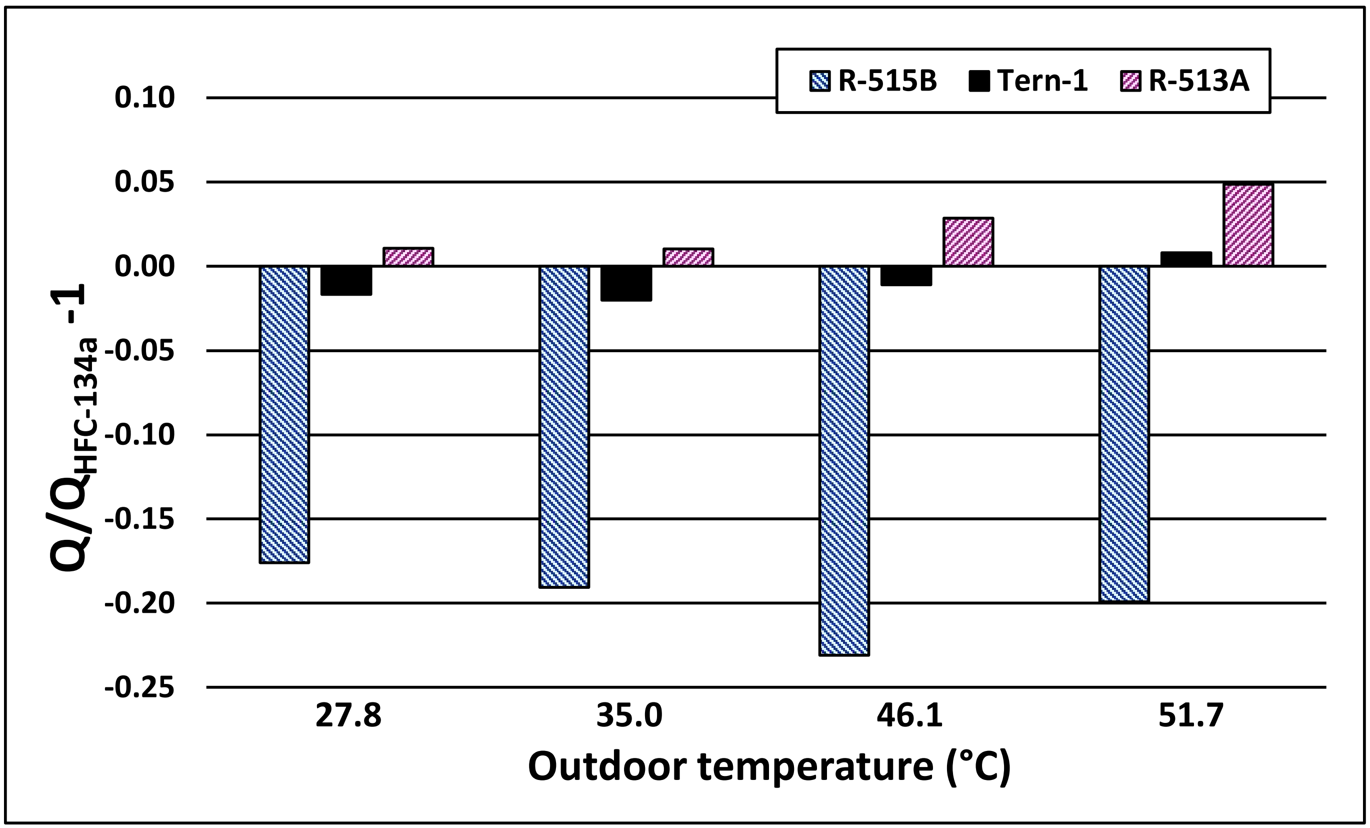


Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- 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



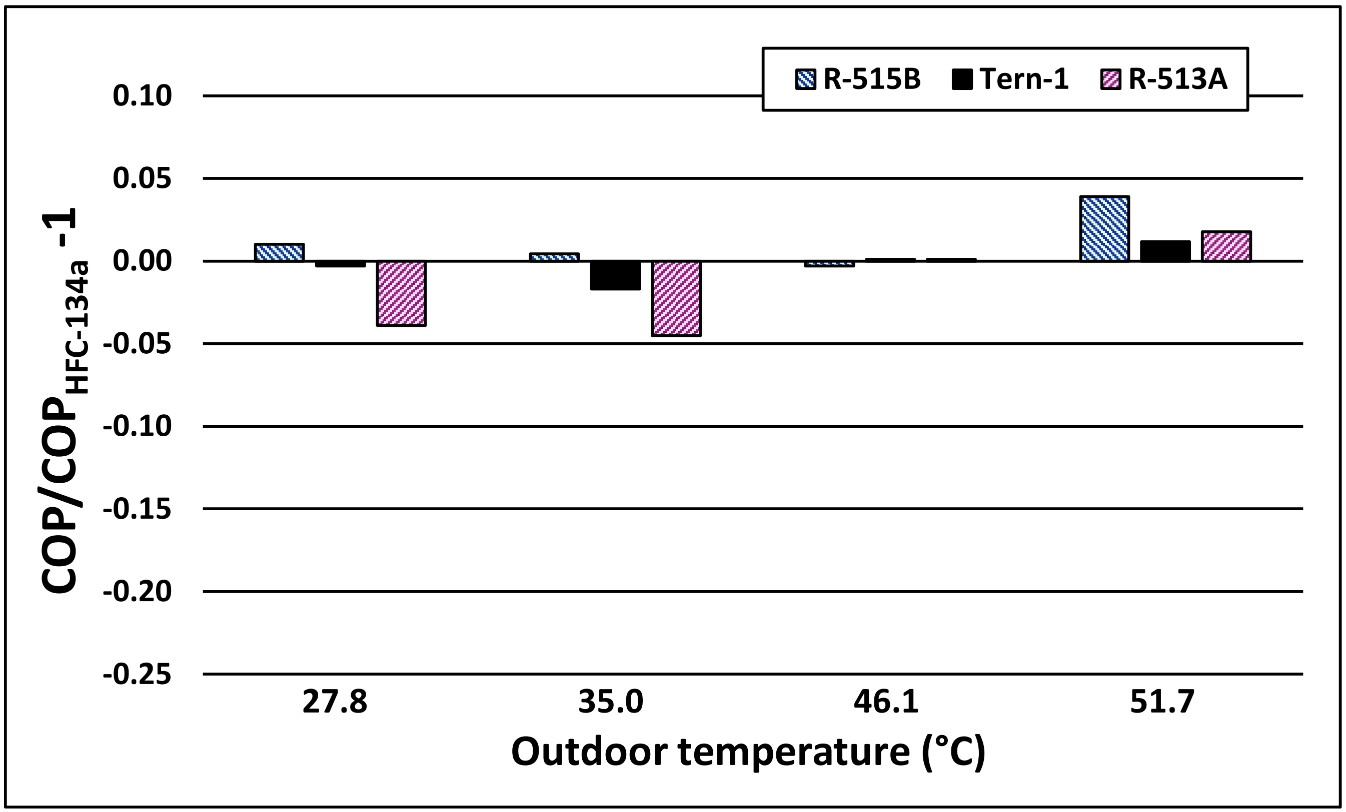
*measured on refrigerant side

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- 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

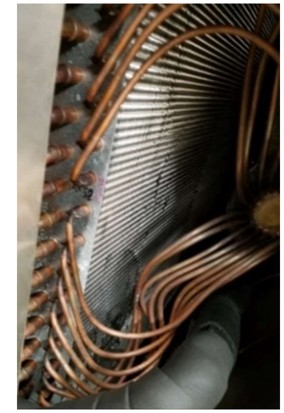
Results

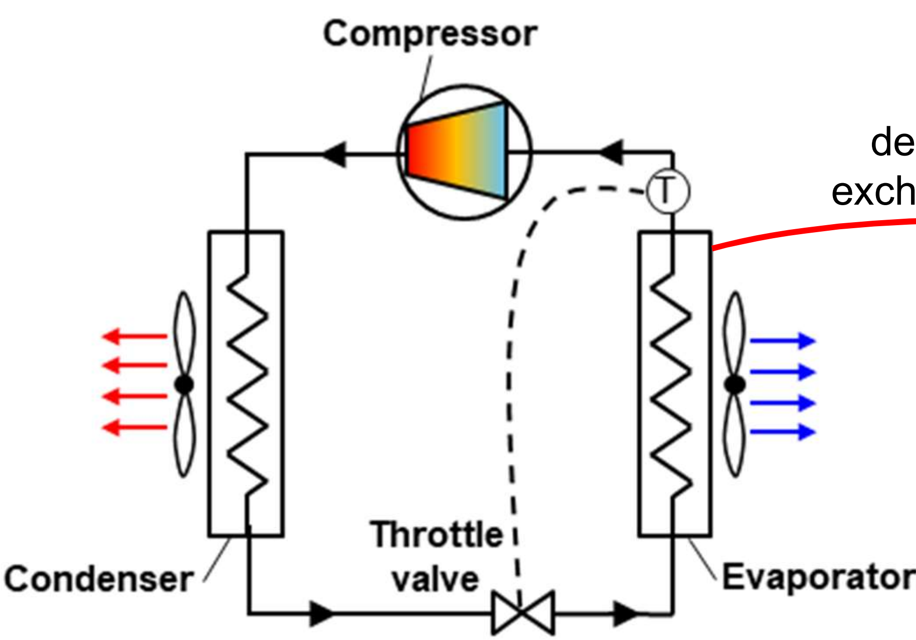
Task 7. Evaluation of Blends in ECU – Simulations with components optimized for each refrigerant

Results

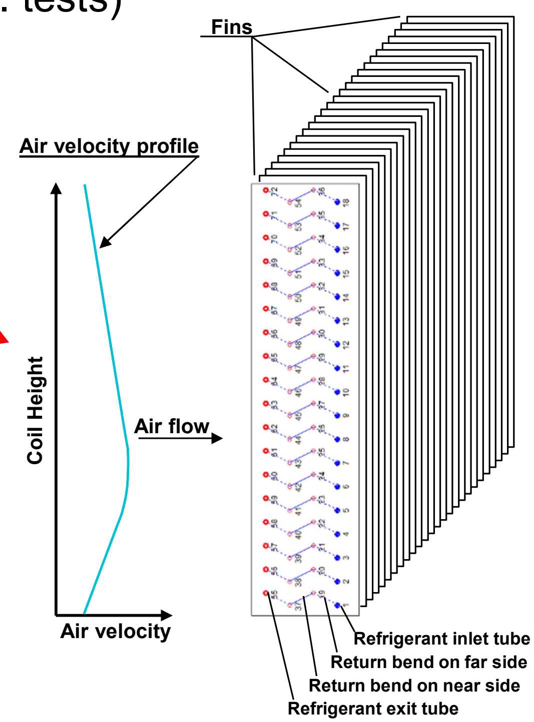
Task 7. Evaluation of Blends in ECU – Simulations

- **Purpose:** evaluate HFC-134a alternatives in ECU tailored to each refrigerant
  - ♦ Provide fairer comparison than experimental that had fixed hardware designed for HFC-134a (e.g., compressor and heat exchangers)
  - ♦ Allows imposing the same capacity
  - ♦ Refrigerants: HFC-134a, R-513A, Tern-1, R-515B (same as exp. tests)





detailed heat exchanger model

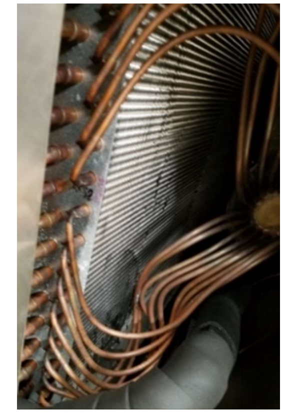


ACSIM - Cycle simulation

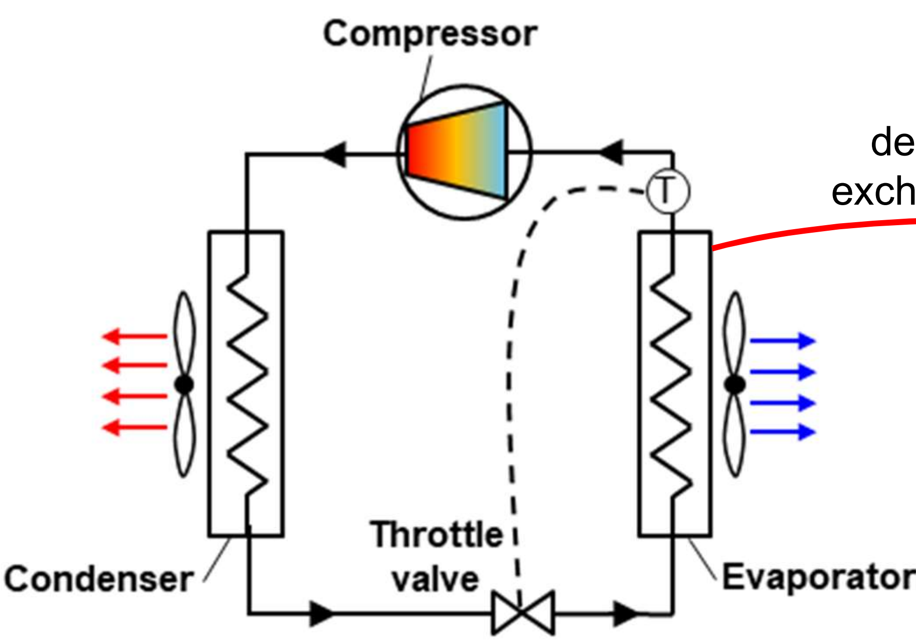
EVAP-COND - Evaporator & condenser simulation

Results

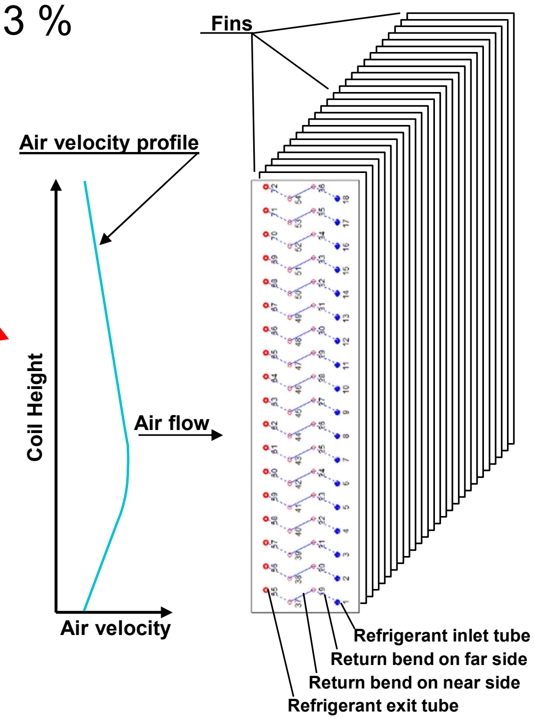
Task 7. Evaluation of Blends in ECU – Simulations



- **Methods:** Experimentally-tuned simulations using NIST 'in-house' air-conditioning cycle simulation (ACSIM)
  - ♦ Property data from Task 1 and heat-transfer correlation from Task 4
  - ♦ Compressor: Performance map w/ correction for high-ambient. Equal efficiency.
  - ♦ Heat exchanger: tube-by-tube simulation of refrigerant & air flow (EVAP-COND) [6]
  - ♦ Capacity and COP predicted within (1 to 7) %, on average within 3 %



detailed heat exchanger model



ACSIM - Cycle simulation

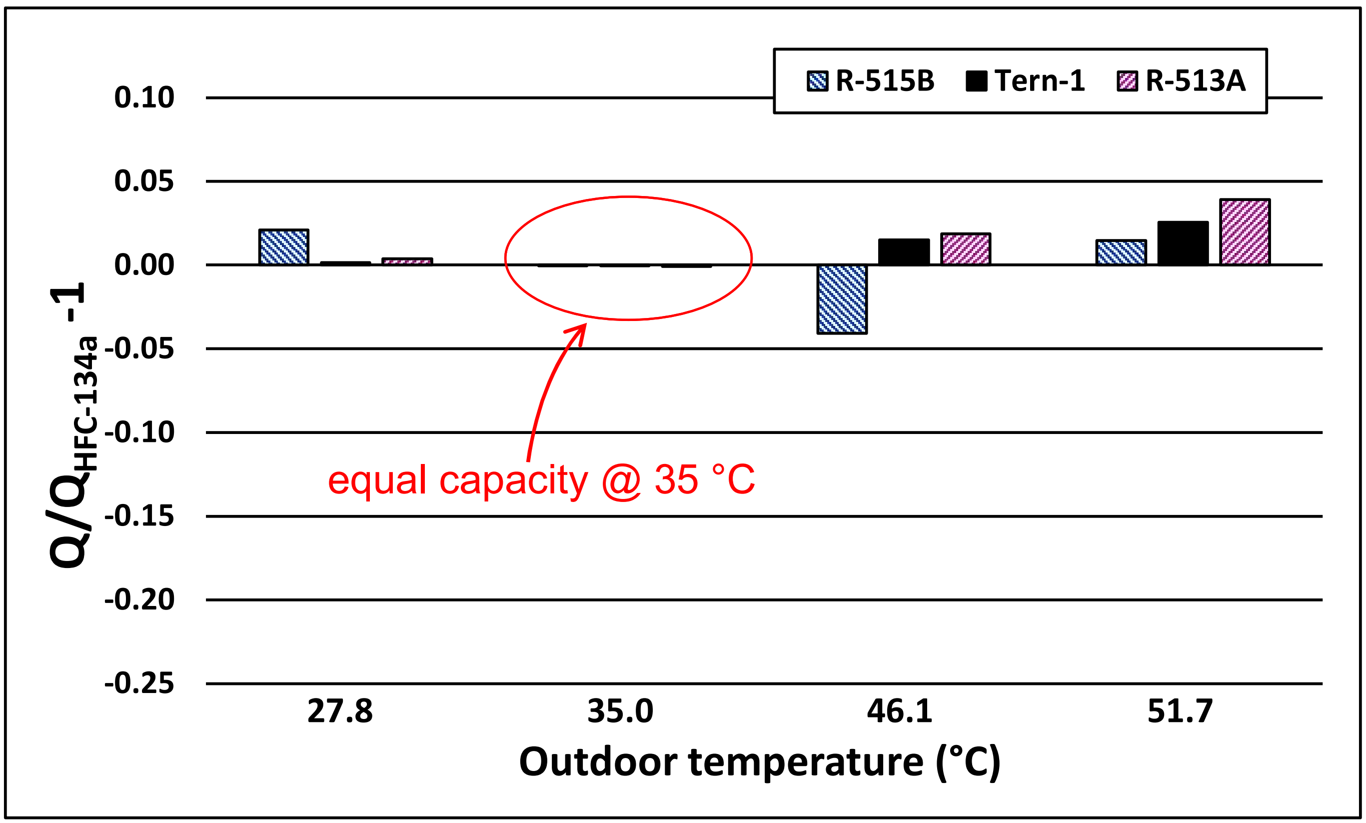
EVAP-COND - Evaporator & condenser simulation

Results

Task 7. Evaluation of Blends in ECU – Simulations

- 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

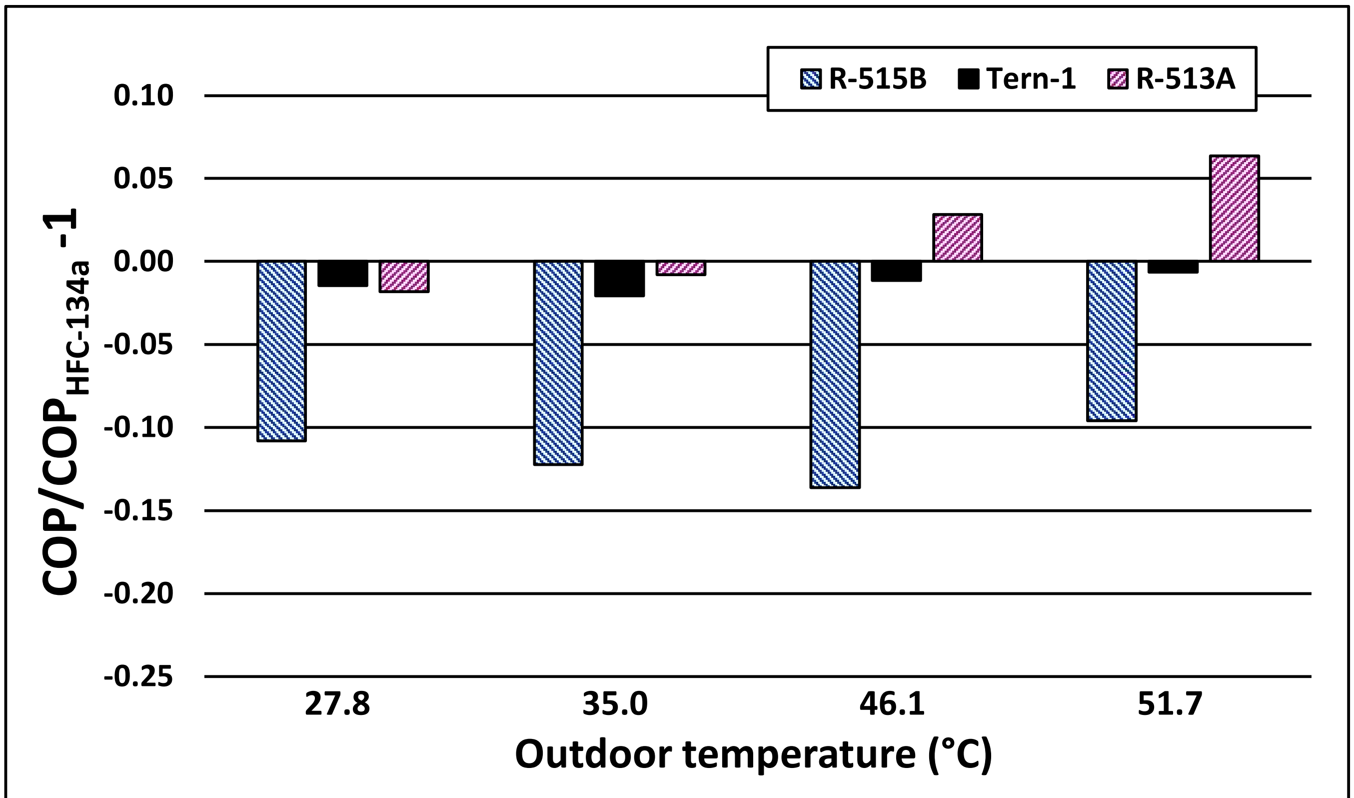


Results

Task 7. Evaluation of Blends in ECU – Simulations

- 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

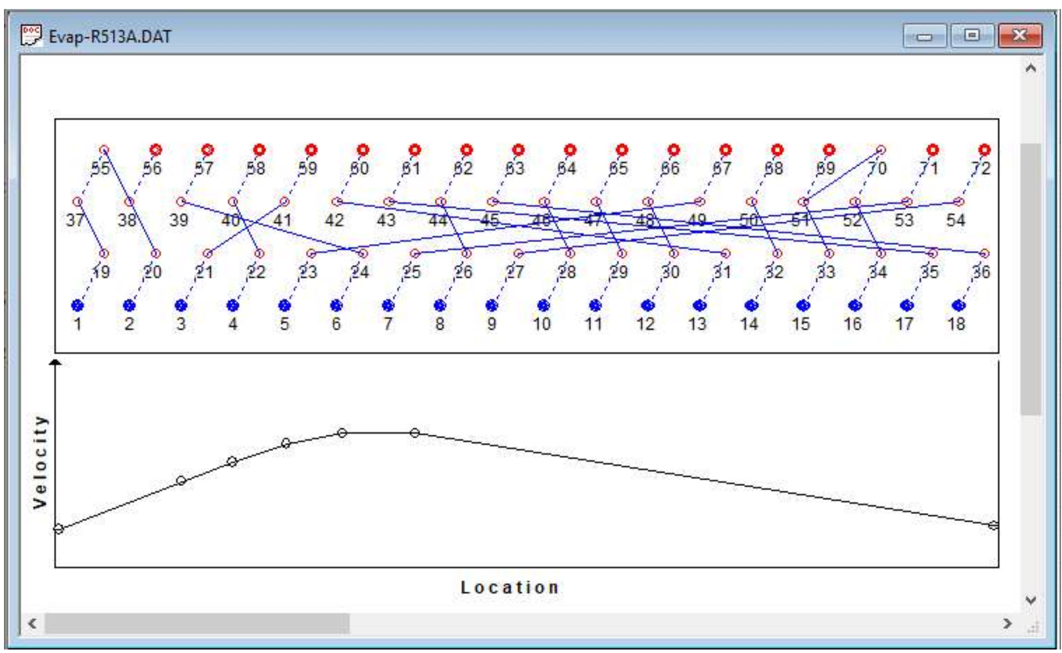


Results

Task 7. Evaluation of Blends in ECU – Simulations

- Circuit optimization in EVAP-COND [6]
  - ♦ Genetic algorithm evaluated 8000 circuit architectures for evaporator & condenser
  - ♦ Adjusted refrigerant tube connections to balance refrigerant exposure to high & low air velocity
  - ♦ Increased capacity (0.1 to 0.6) %, didn't change refrigerant ranking
  - ♦ Didn't change refrigerant ranking, so used original configuration for comparisons

Evaporator with optimized tube circuitry



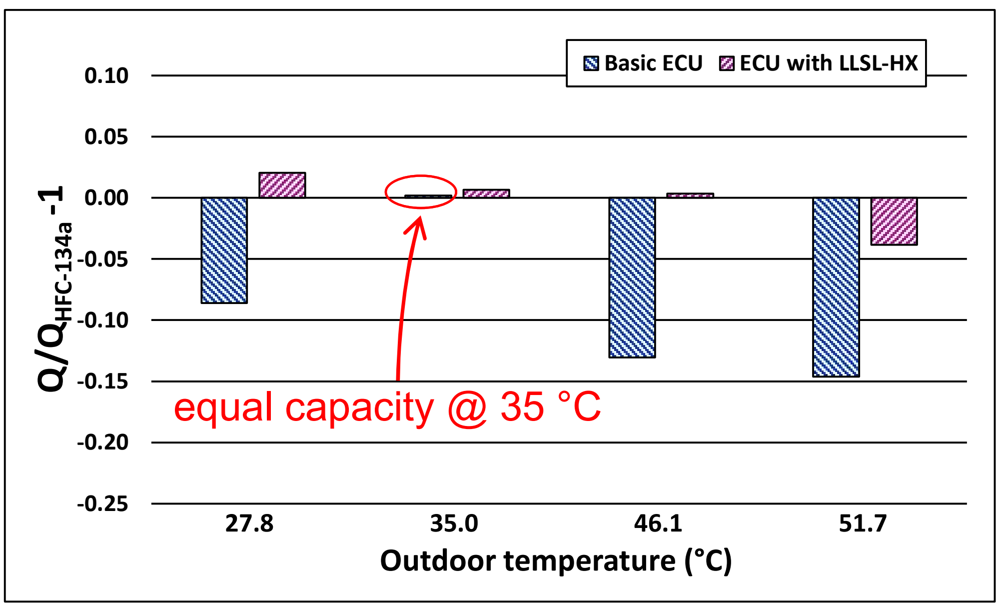
ECU evaporator

Results

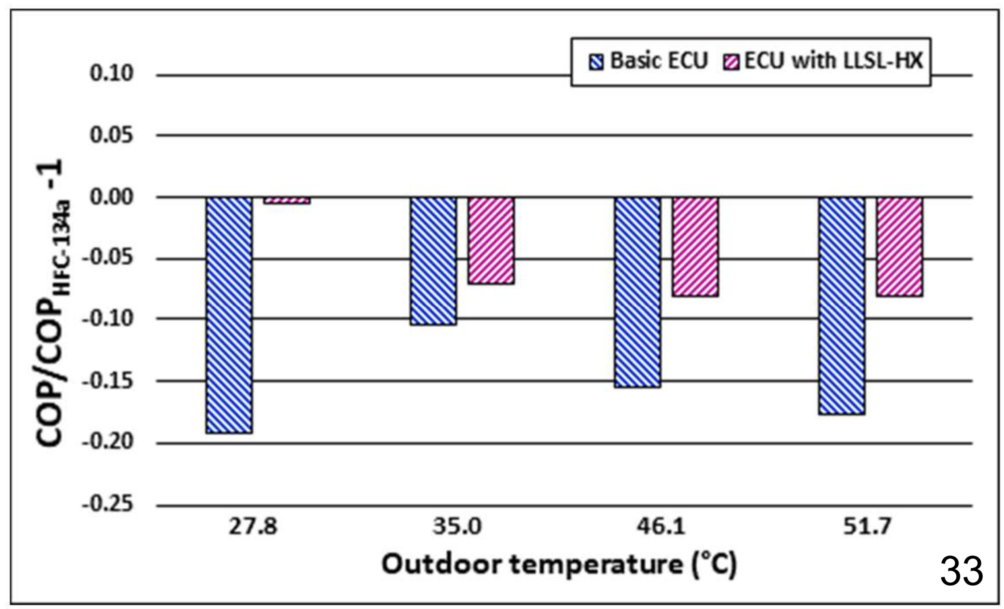
Task 7. Evaluation of Blends in ECU – Simulations

- Evaluated CO_2 as an alternative refrigerant ← In response to comment from proposal reviewer
- Modified "ACSIM" simulation (ACSIM.CO_2)
    - ♦ Transcritical operation w/ optimized gas-cooler pressure
    - ♦ Correlation for heat transfer above critical point [7]
    - ♦ Basic cycle and cycle with liquid-line/suction-line heat exchanger (LLSL-HX)
- COP (10 to 20) % lower in basic cycle, (1 to 8) % lower in LLSL-HX cycle

Capacity (Q) – relative to HFC-134a



Coefficient of Performance (COP) – relative to HFC-134a



Key Points *from the search for non-flammable, Low-GWP Alternative 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

- R-513A and Tern-1:
  - Capacity and COP comparable to HFC-134a
  - GWP reductions of 66 % (R-513A) and 51 % (Tern-1)
  - Can be implemented without major redesign of current components
  - Might pass more-stringent military flammability criteria
- R-515B and CO_2:
  - If greater reduction in GWP is desirable, 74 % GWP reduction (R-515B) and CO_2 (GWP = 1) can be considered, but they require further research and development
  - If flammability criteria for military is more stringent than ASTM E681, R-515B likely fail
  - CO_2 is a fire suppressant and would pass military flammability test
- Flammability:
  - R-513A, Tern-1, R-515B, and R-450A pass ASTM E681, but some more easily
  - If R-513A and Tern-1 fail military test, can use simulation tools of this project to identify less-flammable & higher-GWP blends, e.g., those from the preliminary study [1]
  - **Recommend live-fire tests to establish flammability criteria for military threats and correlate with lab-scale tests and model predictions**

Technology Transfer

- Keynote presentation "*Finding a Non-Flammable, Low-GWP Replacement for R-134a*", M. McLinden, at HFO 2021, 2nd IIR Conference on HFOs and Low-GWP Blends, 16-18 June 2021; Osaka, Japan (virtual)
- Updates to property data in REFPROP [4] for HFO-HFC blends ← most popular NIST download
- Developed flammability index based on the adiabatic flame temperature and the fluorine to hydrogen ratio [8]
- Improvements to flame kinetic model
- Validated CYCLE_D-HX simulation software [5]
- Correlations for HFO-HFC blend two-phase heat-transfer and pressure drop, used in EVAP-COND heat exchanger simulation software [6]

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Questions?

BACKUP SLIDES

Acronyms 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

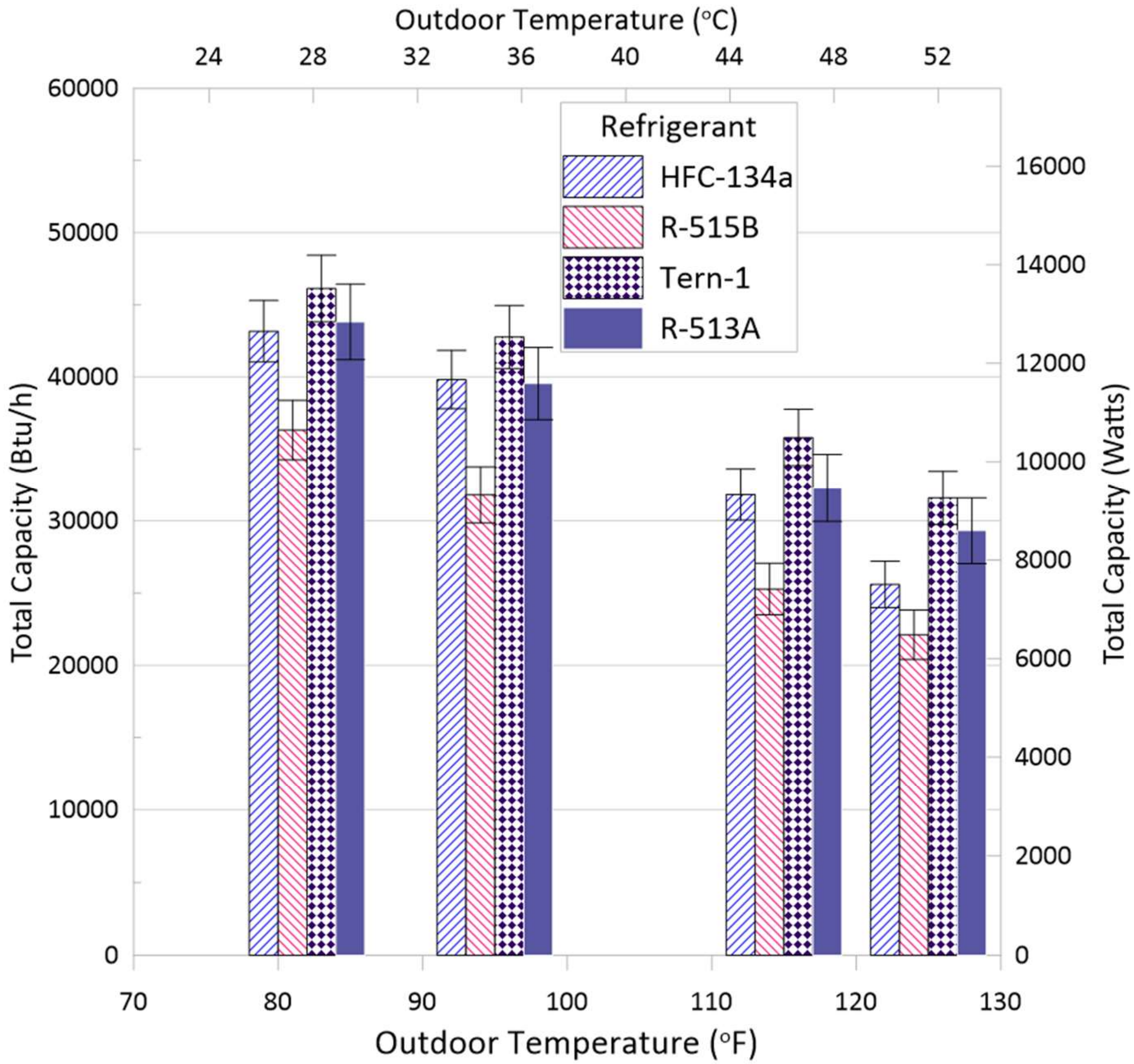
VLE – vapor-liquid equilibrium

$\overline{\Pi}$ - Flammability index

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- Total Capacity

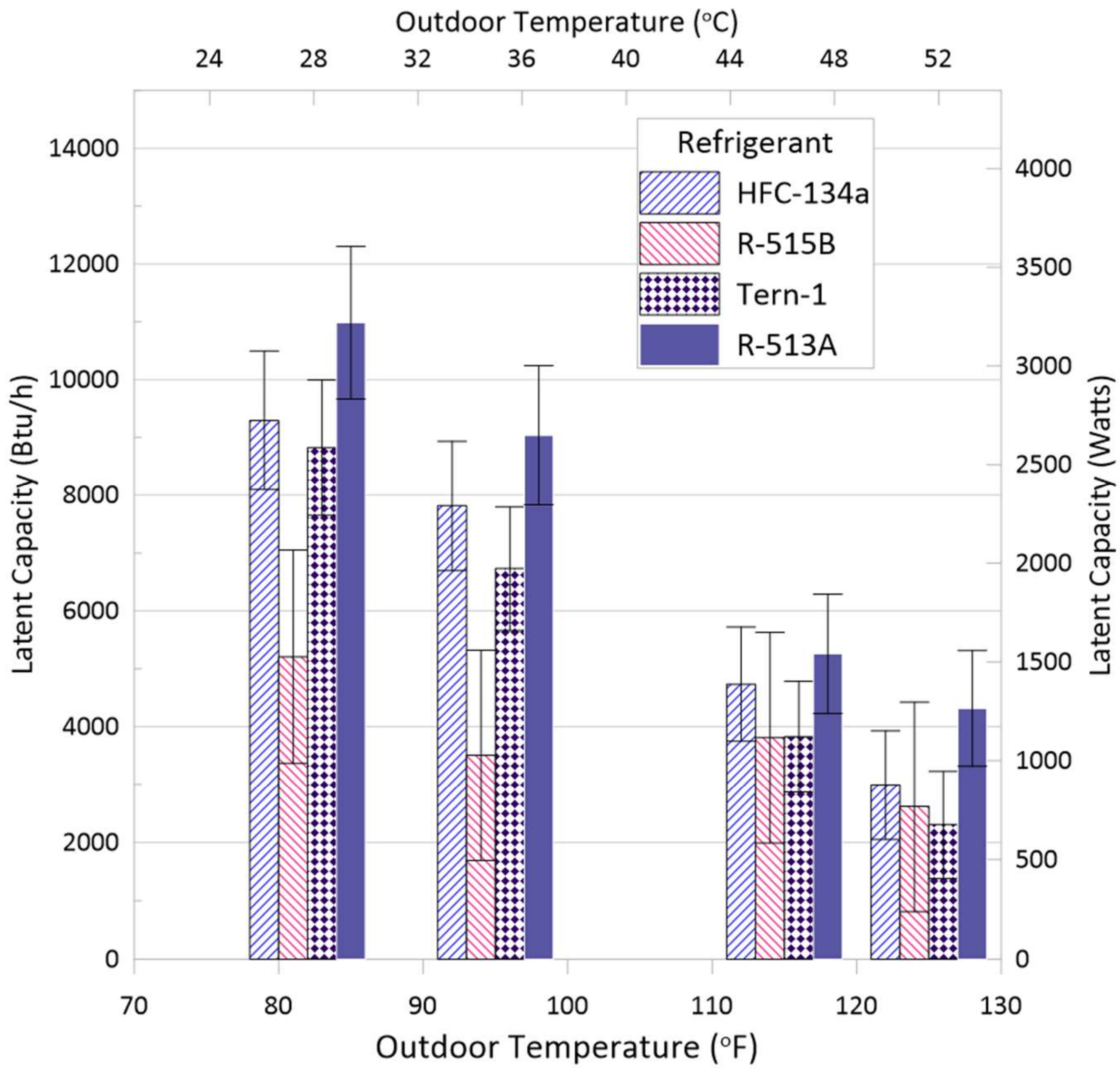


Error bars: *k*=2,
95 % confidence interval

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- Latent Capacity

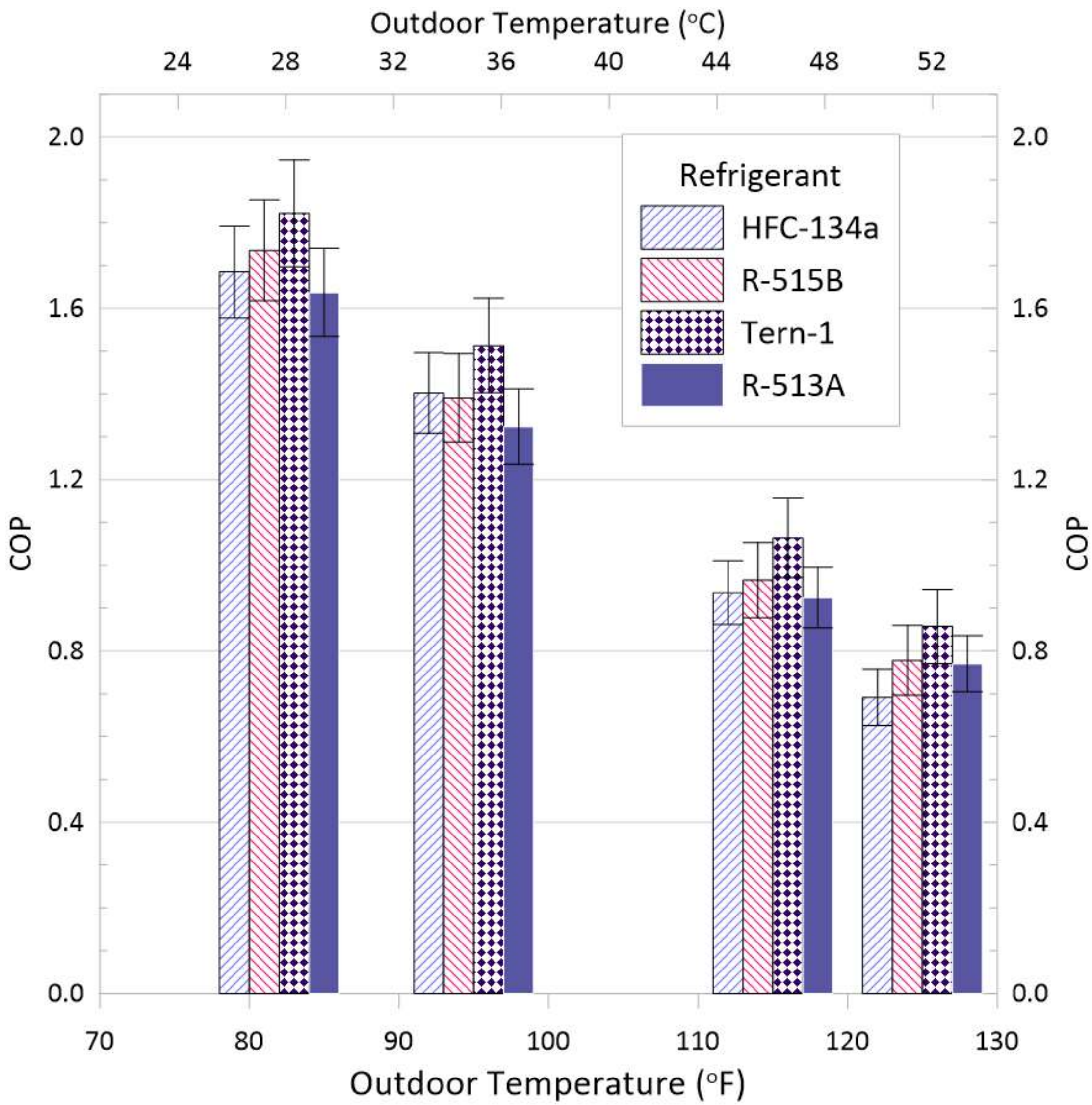


Error bars: *k*=2,
95 % confidence interval

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- COP = Capacity / Electricity Input



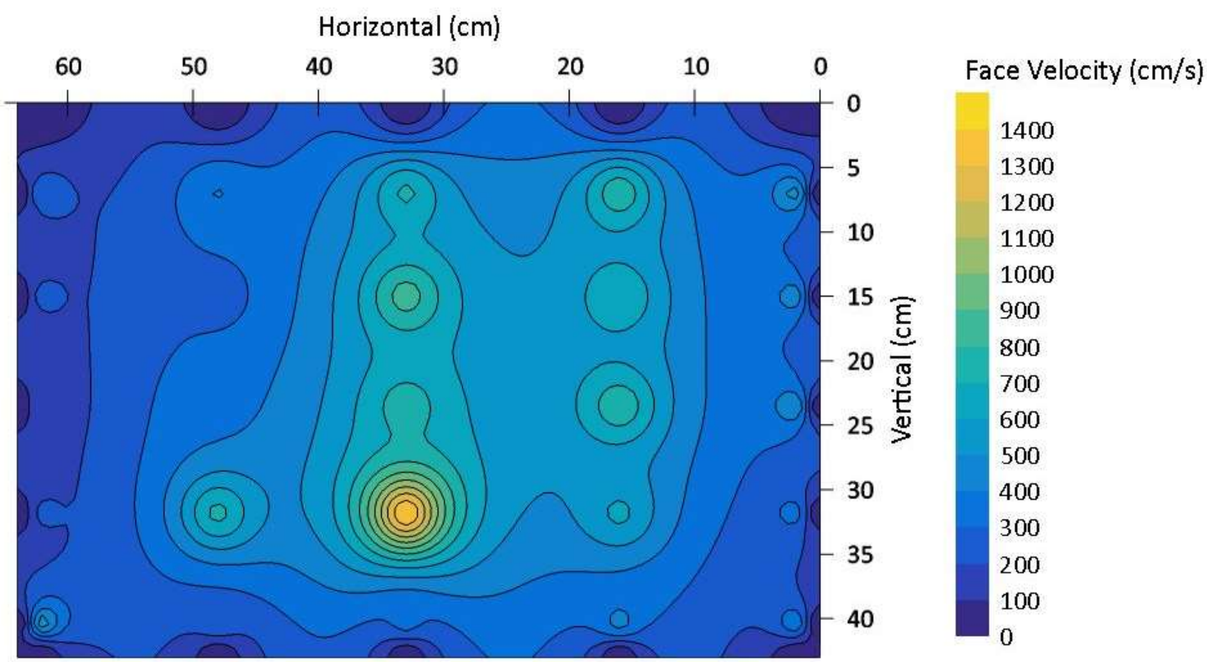
Error bars: *k*=2,
95 % confidence interval

Results

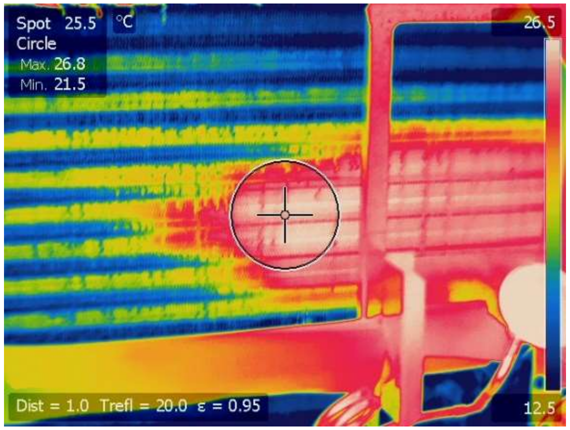
Task 7. Evaluation of Blends in ECU – Experimental Tests

- Evaporator airflow maldistribution reduced capacity and efficiency

Evaporator air velocity



Evaporator refrigerant temperature



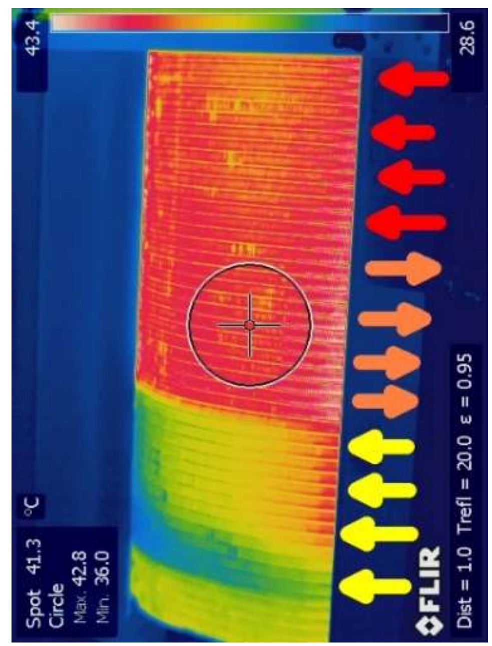
Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- Condenser – channels at bottom may not fully condense refrigerant

Microchannel condenser

Condenser refrigerant temperatures



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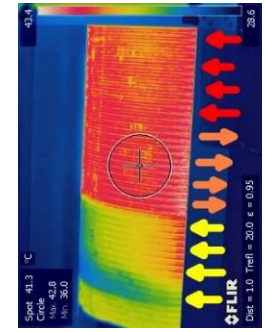
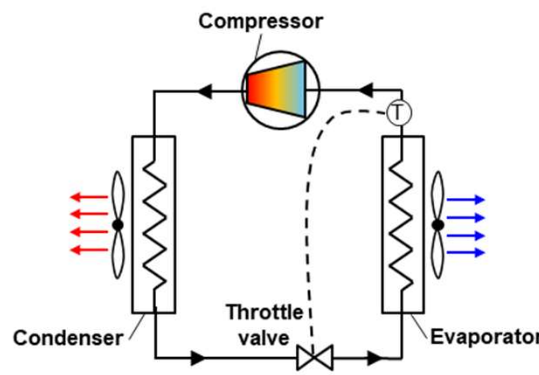
WP19-1385: Low-GWP Alternative Refrigerant Blends for HFC-134a

Performers:
- *National Institute of Standards and Technology (NIST)*

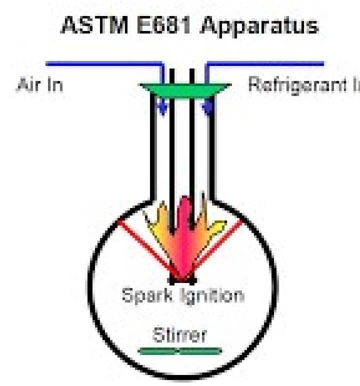


Technology Focus
- *Military air-conditioning systems using refrigerant HFC-134a, in particular, field-deployable Environmental Control Units (ECU)*



Research Objectives
- *Identify non-flammable low Global Warming Potential (GWP) replacement for refrigerant HFC-134a*

Project Progress and Results
- *Low-GWP refrigerants (R-513A, Tern-1) w/ similar performance to HFC-134a, likely to pass military flammability requirements*
- *A third option, R-515B has even lower GWP, but requires additional research & development. It may not pass military flammability test if more stringent than ASTM E681*



Technology Transition
- *Recommend live-fire tests and modeling to establish representative test of 'non-flammability' for military*