Low-GWP Alternative Refrigerant Blends for HFC-134a

WP19-1385

Harrison Skye
P.I.s Piotr A. Domanski, Mark O. McLinden
National Institute of Standards and Technology (NIST)

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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

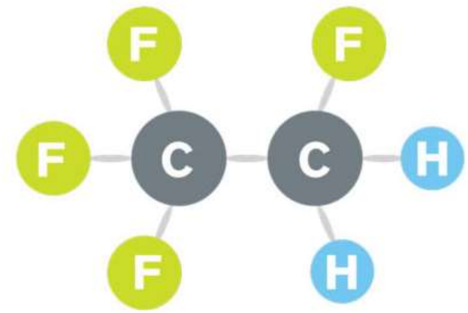
- **NIST, Building Energy and Environment Division, Gaithersburg, MD**

  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

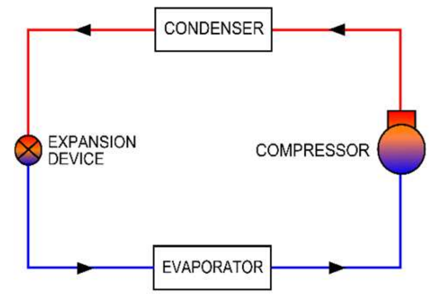
- Transportable units provide cooling in the field
- (10 to 20) kW cooling capacity

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

Technical Objective

Identify replacements for HFC-134a

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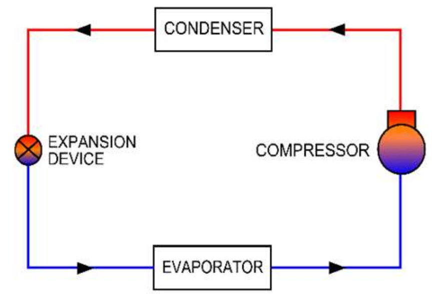
  (tests in environmental chambers at wide range of operating conditions)
- **Extrapolate laboratory results to a 'fully optimized' ECU by detailed ECU simulations**
  (includes machine-learning-based optimization of heat exchangers)



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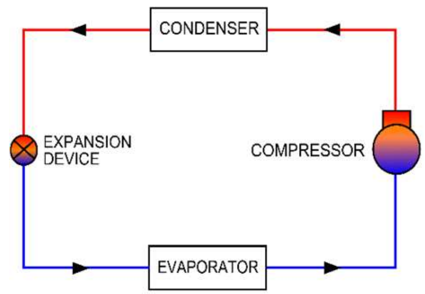
  (includes machine-learning-based optimization of heat exchangers)
- **Simulate ECU operating with carbon dioxide (CO_2)**
  (w/optimization)



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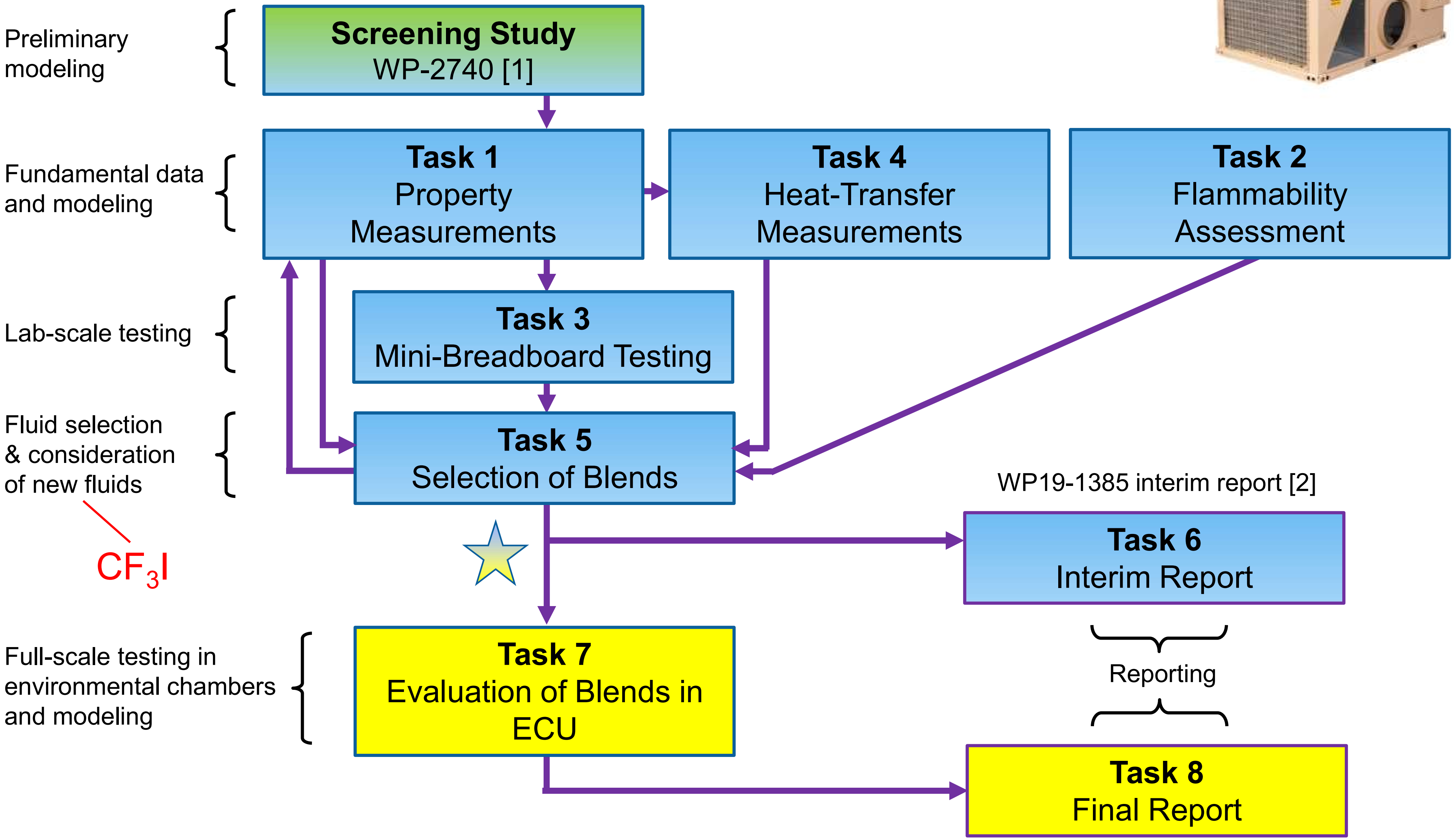
Technical Approach



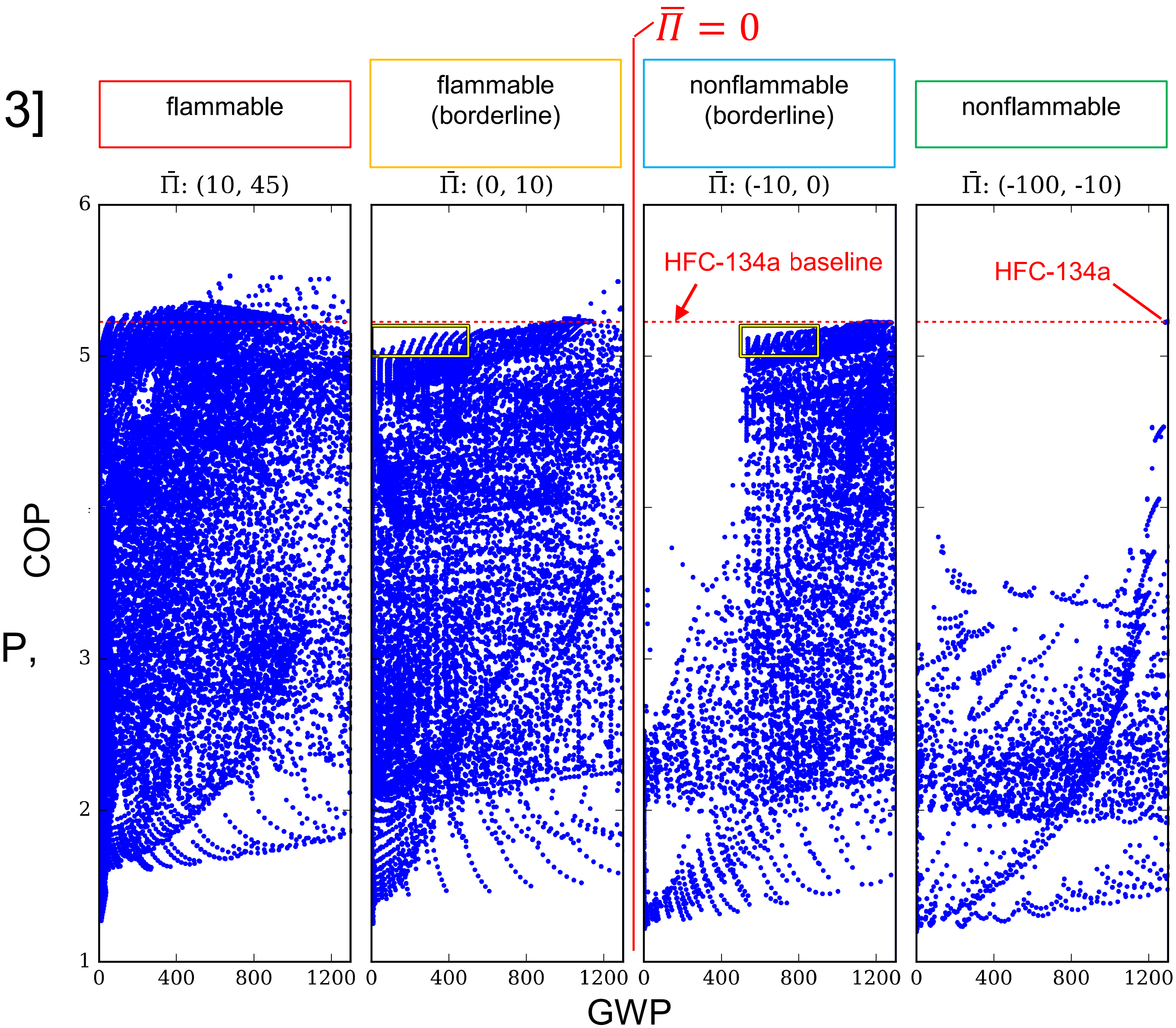
[1] Domanski et al., **2018**, *Low-GWP Alternative Refrigerant Blends for HFC-134a*, WP-2740 https://doi.org/10.6028/NIST.TN.2014

[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-134a}	$Q_{vol}/Q_{vol,\ R-134a}$
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
2. Tern-1
3. R-450A
4. R-515B

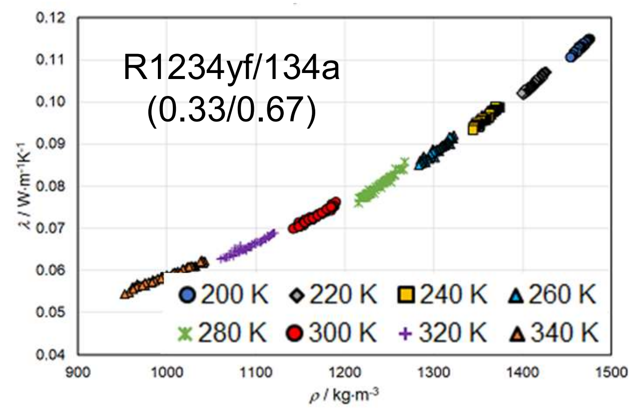
R-450A “like”

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

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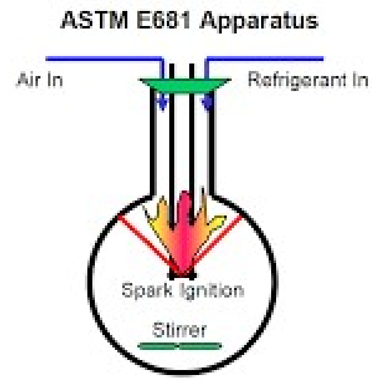
Results

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



12 L vessel

ASTM E681 test

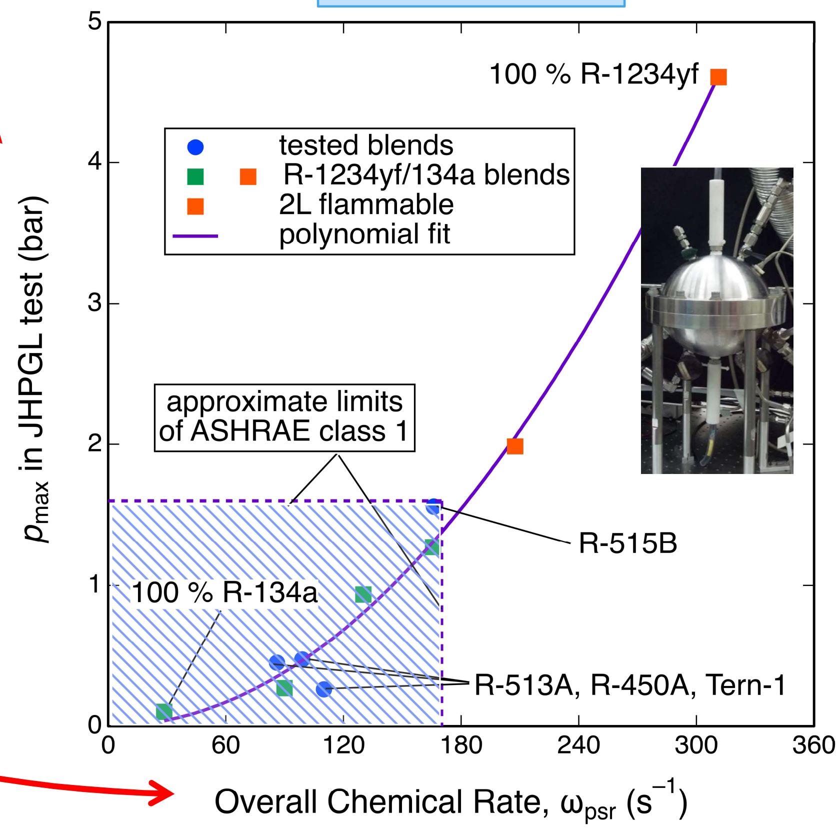
“Non-flame propagating”

“Flame propagating”

- 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

JHGPL test

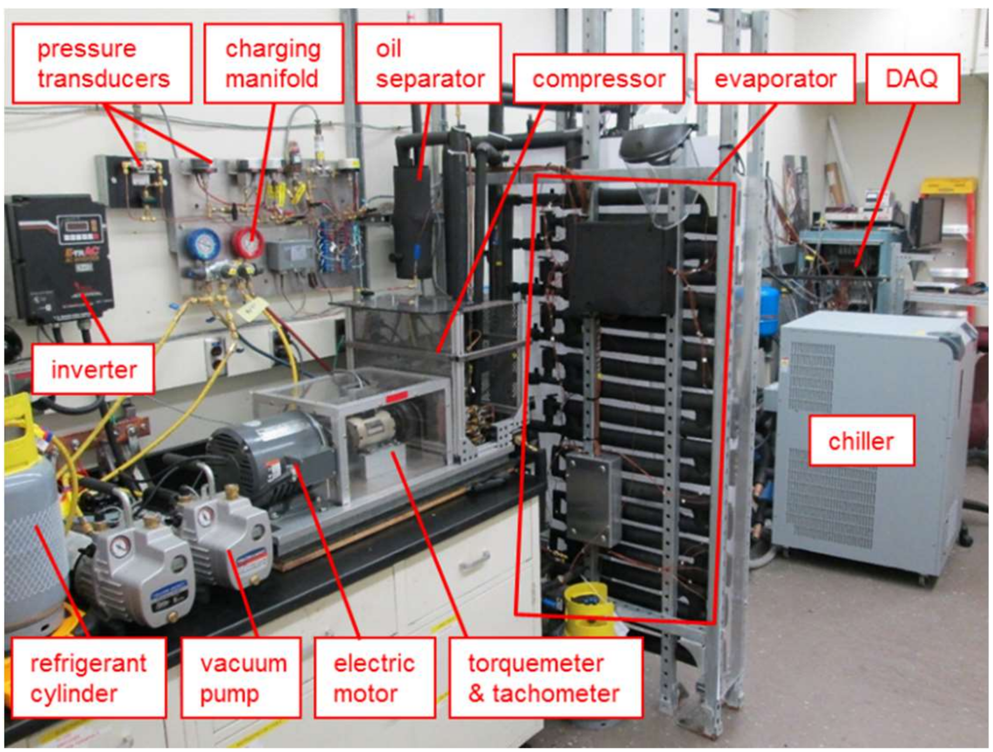


- Chemical kinetic prediction of blend reactivity
  - Predicts experimental flammability behavior
  - After correlation with live-fire test, can be used to predict full-scale behavior
  - Predicts influence of other parameters (humidity, temp, etc.)

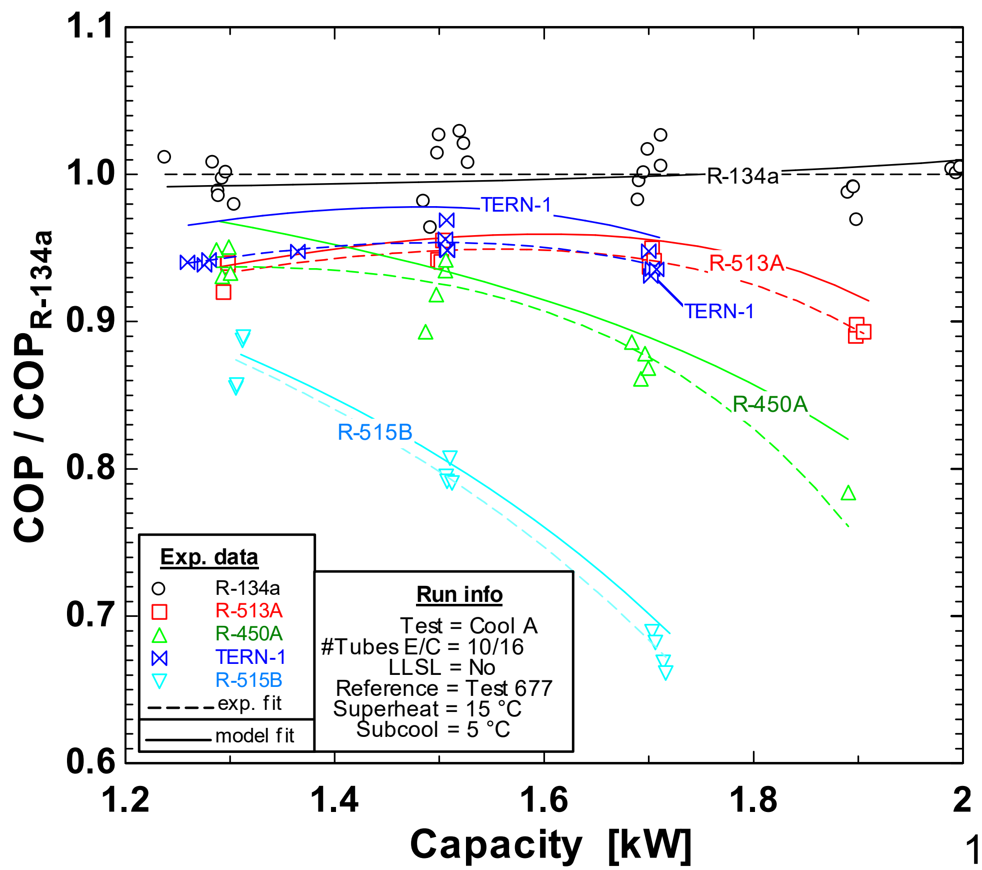
Results

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'

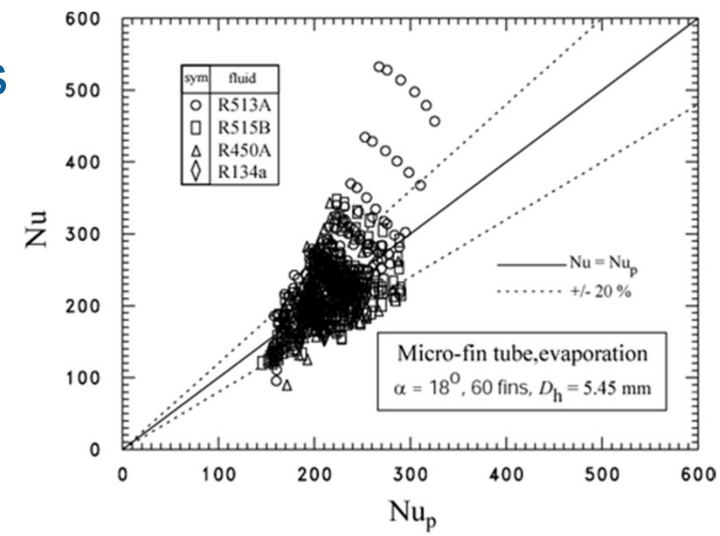


MBHP measurements & simulations



Results

Task 4. Two-Phase Heat-Transfer Measurements



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

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

thermodynamic quality

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

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

used in Task 7 simulations

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

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

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	$\overline{\Pi}^{\dagger}$	COP/ COP_{R-134a}	Q_{vol}/ $Q_{vol,\ R-134a}$
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

*mole fraction
†Flammability index [8]

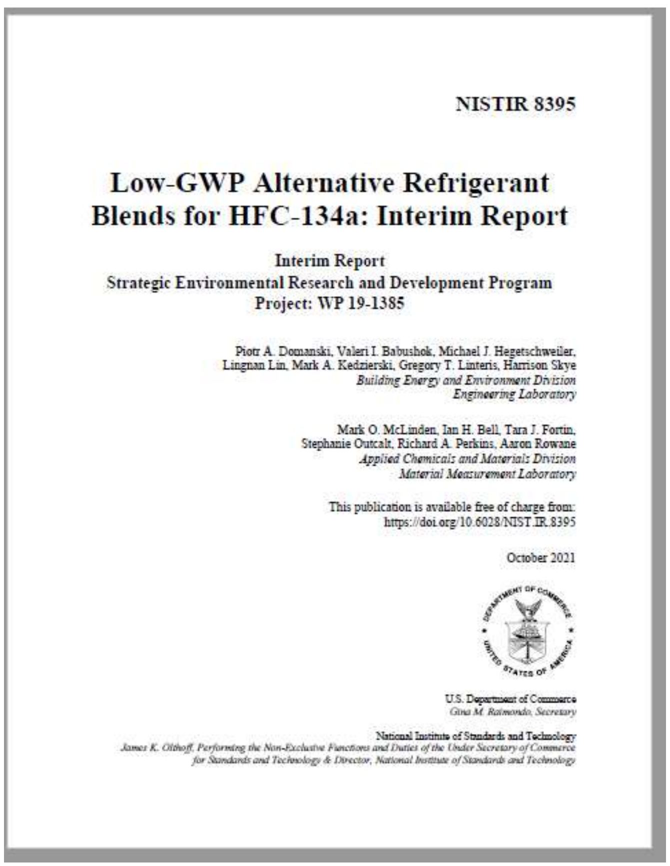
≤50 % GWP of HFC-134a (GWP=1300)

- 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

Piotr A. Domanski, Valeri I. Babushok, Michael J. Hegetschweiler, Lingnan Lin, Mark A. Kedzierski, Gregory T. Linteris, Harrison Skye
Building Energy and Environment Division
Engineering Laboratory

Mark O. McLinden, Ian H. Bell, Tara J. Fortin, Stephanie Outcalt, Richard A. Perkins, Aaron Rowane
Applied Chemicals and Materials Division
Material Measurement Laboratory

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October 2021

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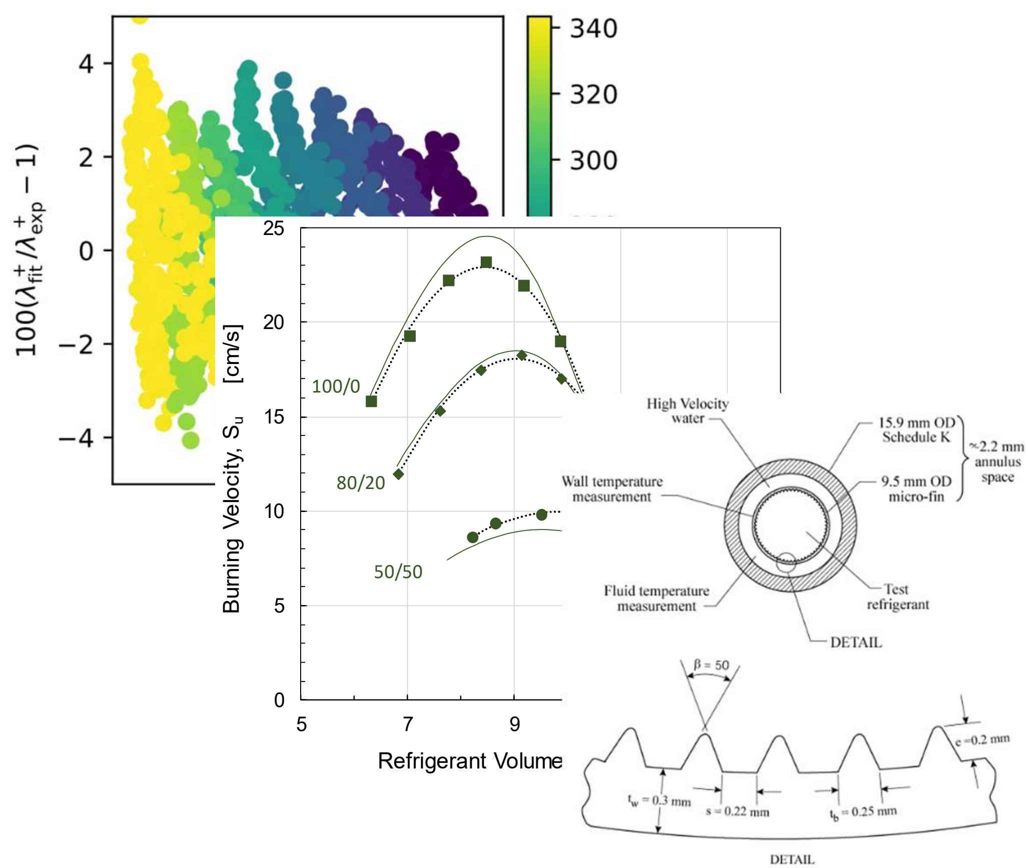


Results

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

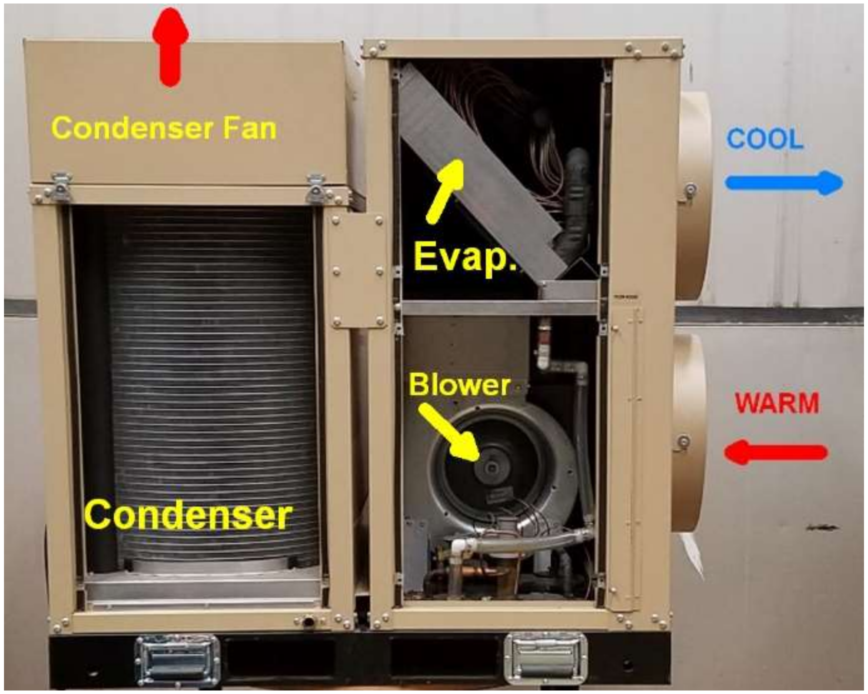
Results

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

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

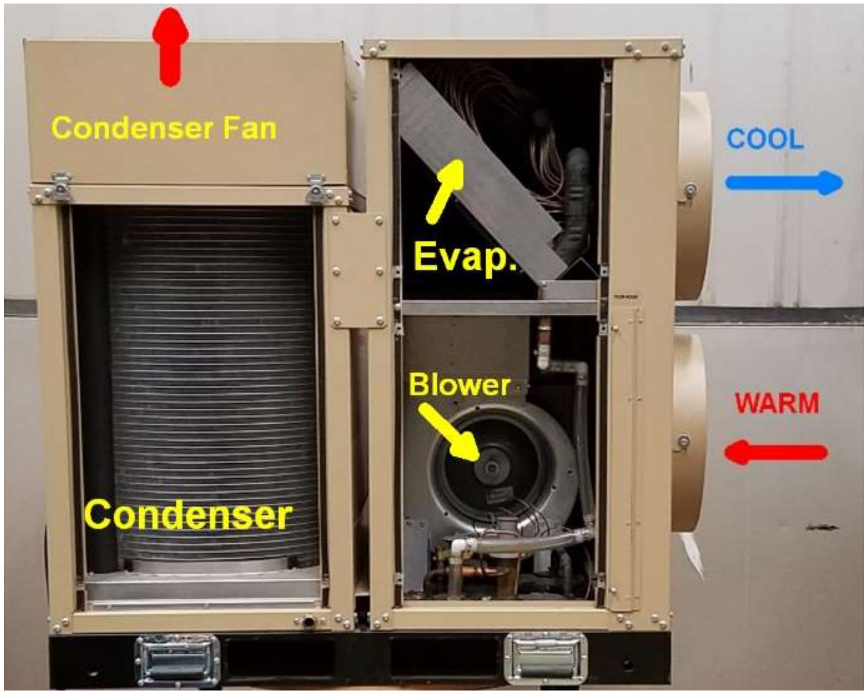
- **Purpose:** Evaluate top refrigerant replacement candidates in a military ECU designed for HFC-134a
  - Tested refrigerants: HFC-134a, R-513A, Tern-1, R-515B
  - ECU specifications: commercially available, ~20 kW cooling capacity, rugged construction, normally powered by a generator
  - ECU components: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

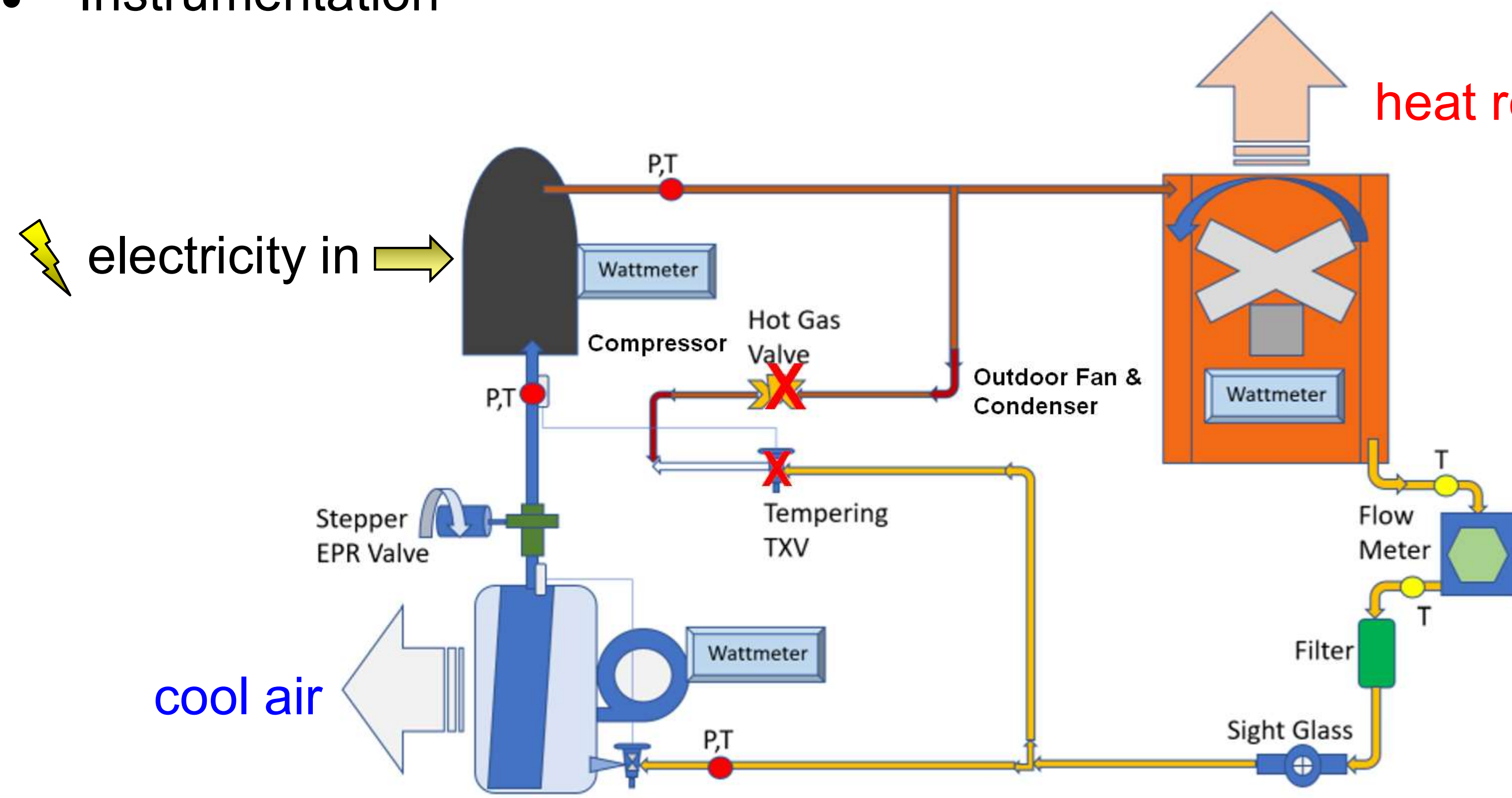


TXV: thermostatic expansion valve EPR: evaporator-pressure regulator

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



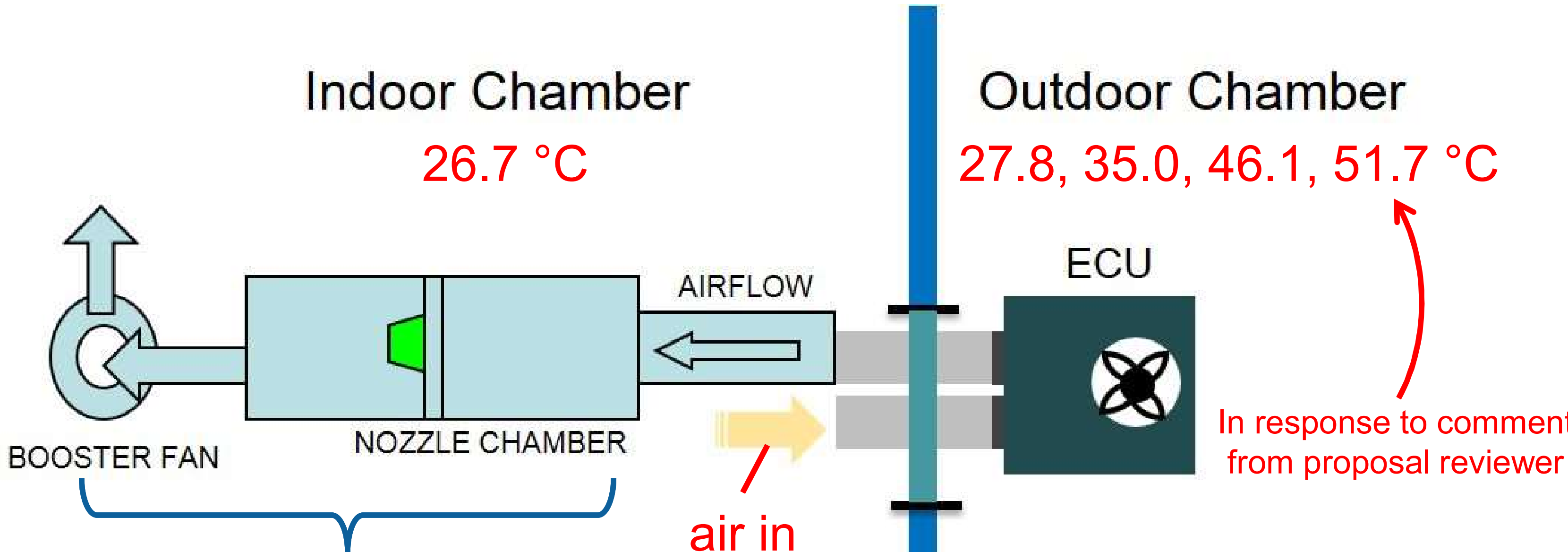
ECU refrigerant schematic

TXV: thermostatic expansion valve EPR: evaporator-pressure regulator

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

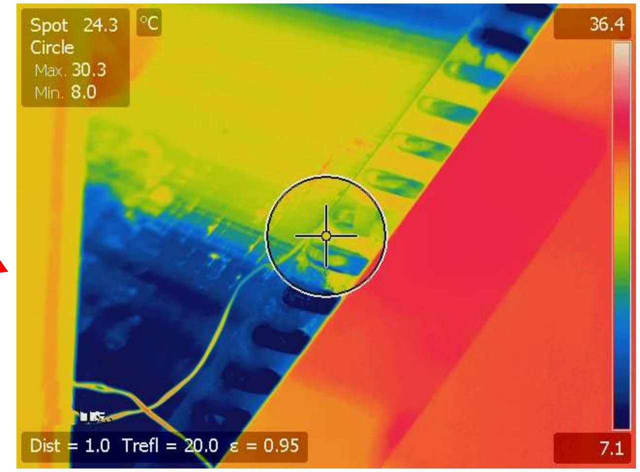
- ECU tested in 2 environmental chambers
- Measured air-side capacity

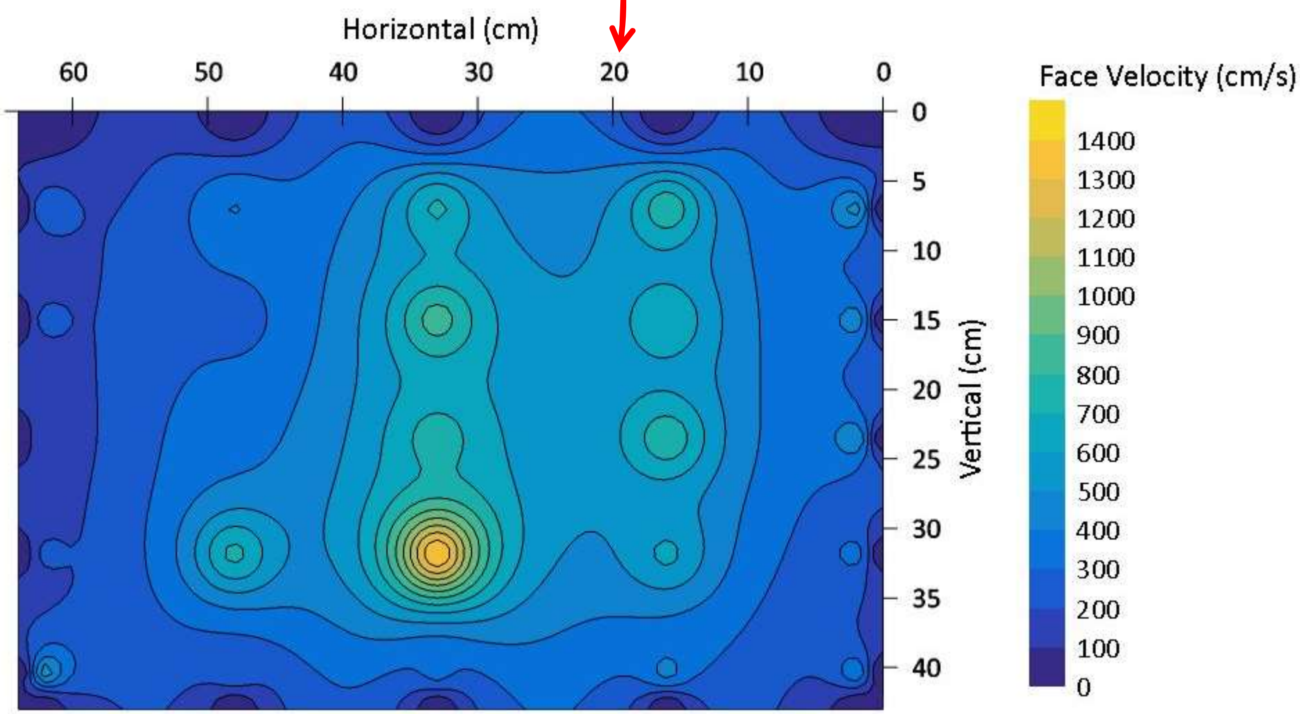


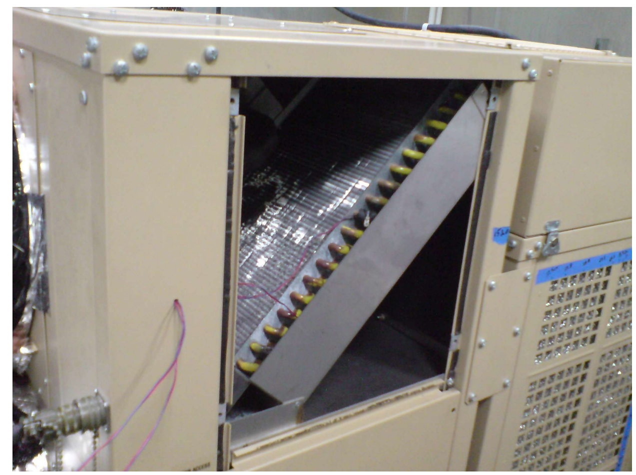
Results

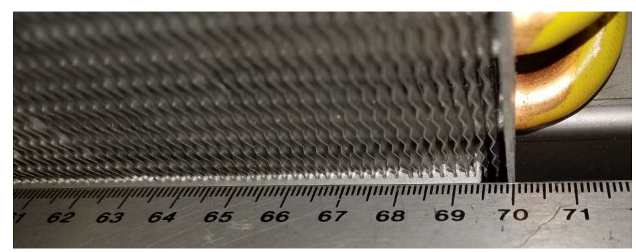
Task 7. Evaluation of Blends in ECU – Exp. Tests

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







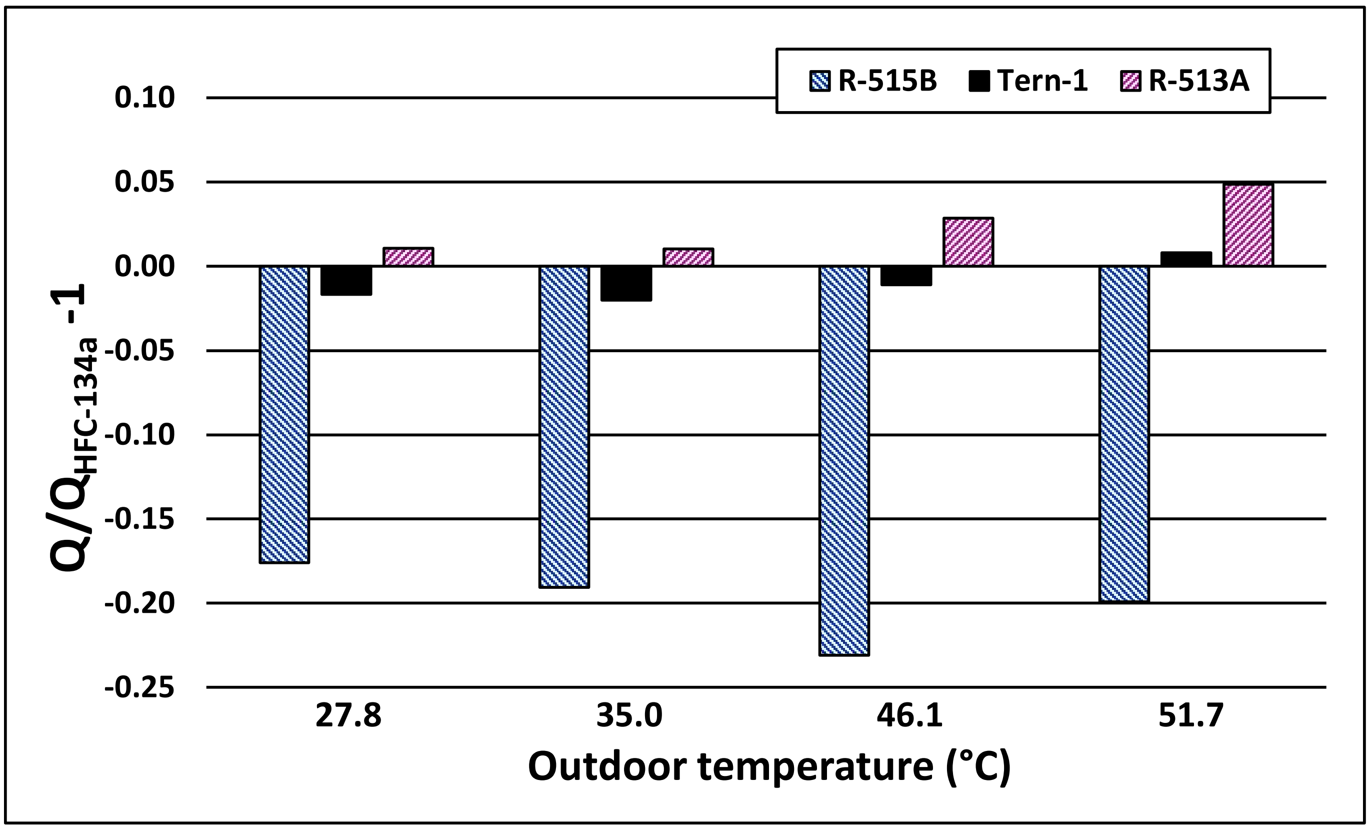


Results

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



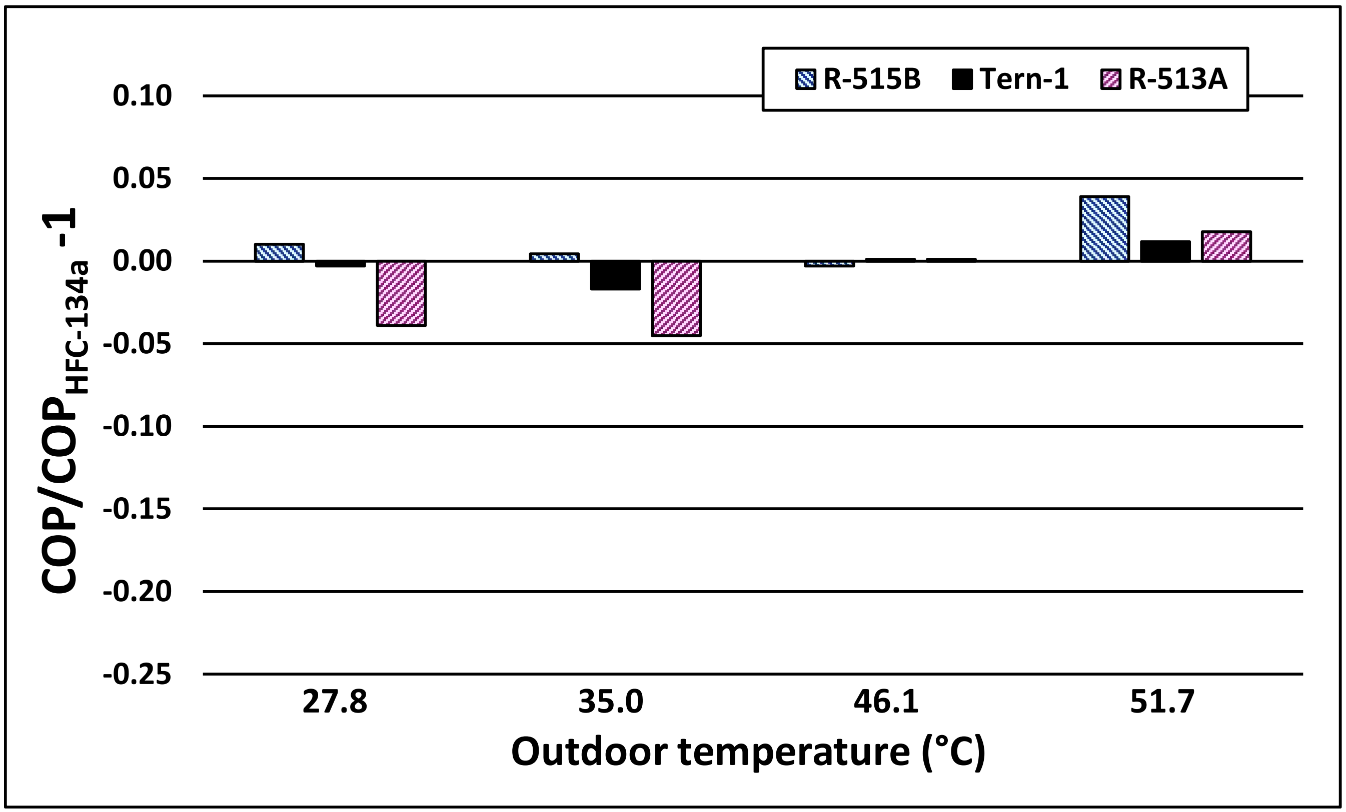
*measured on refrigerant side

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



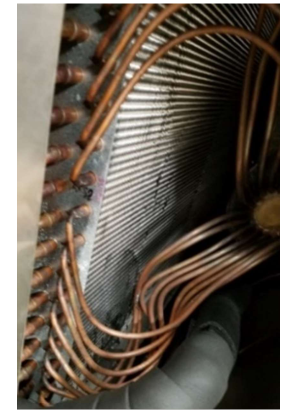
*measured on refrigerant side

Results

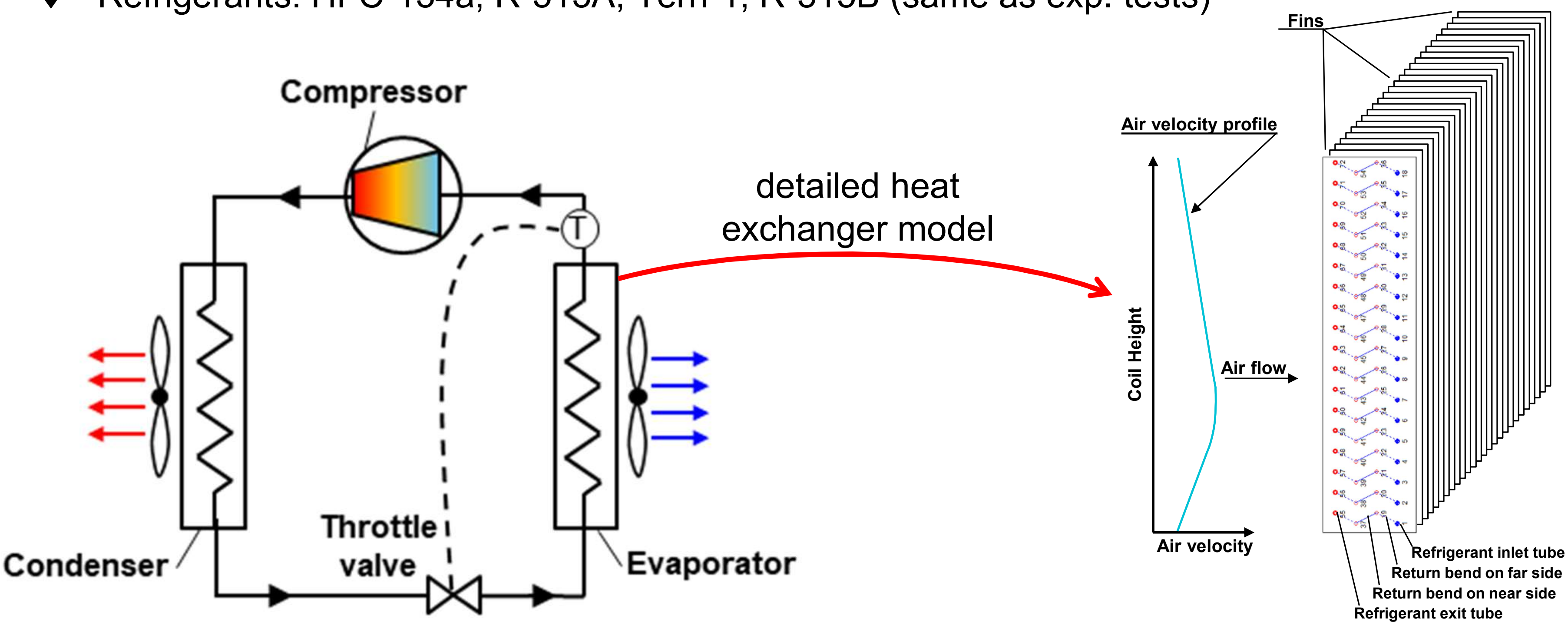
Task 7. Evaluation of Blends in ECU – Simulations with components optimized for each refrigerant

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)

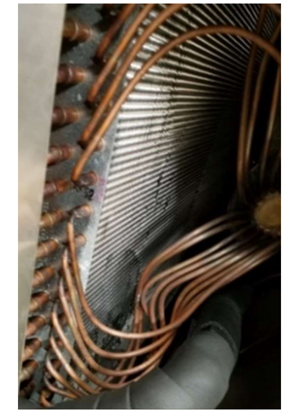


ACSIM - Cycle simulation

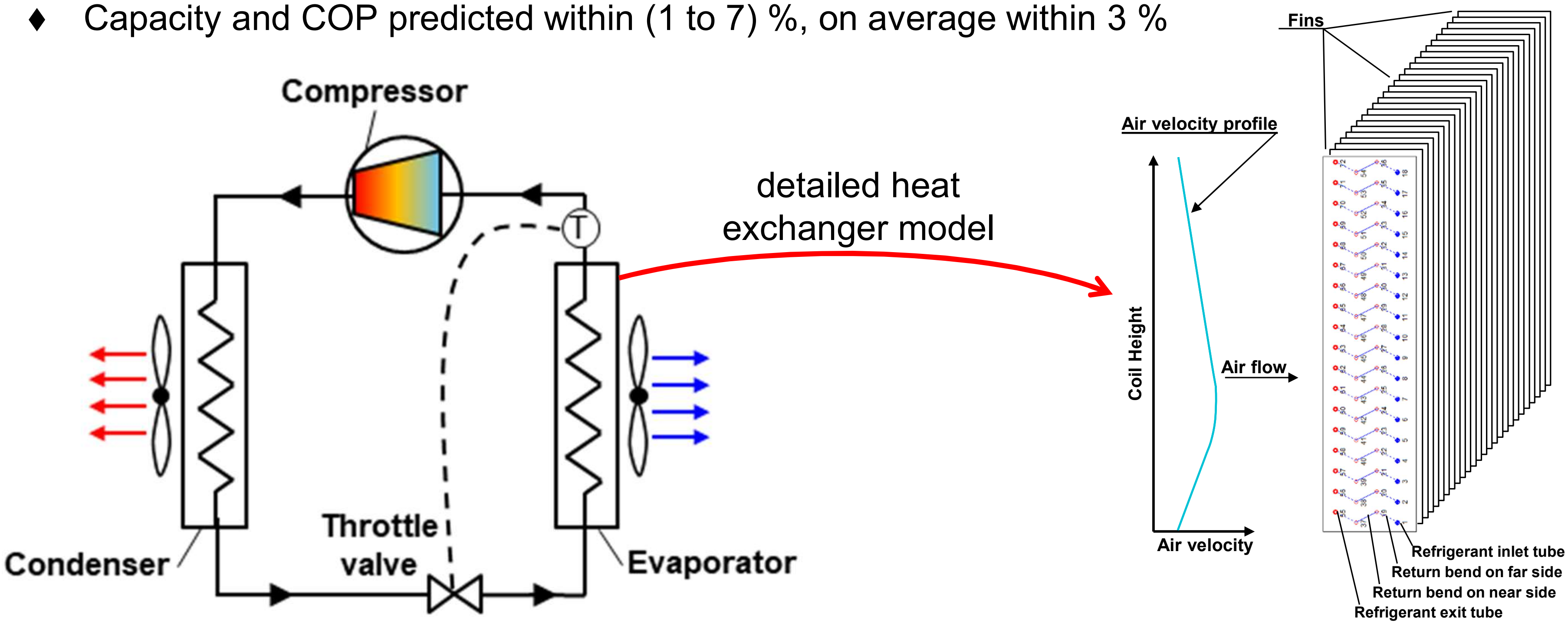
EVAP-COND - Evaporator & condenser simulation

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 %



ACSIM - Cycle simulation

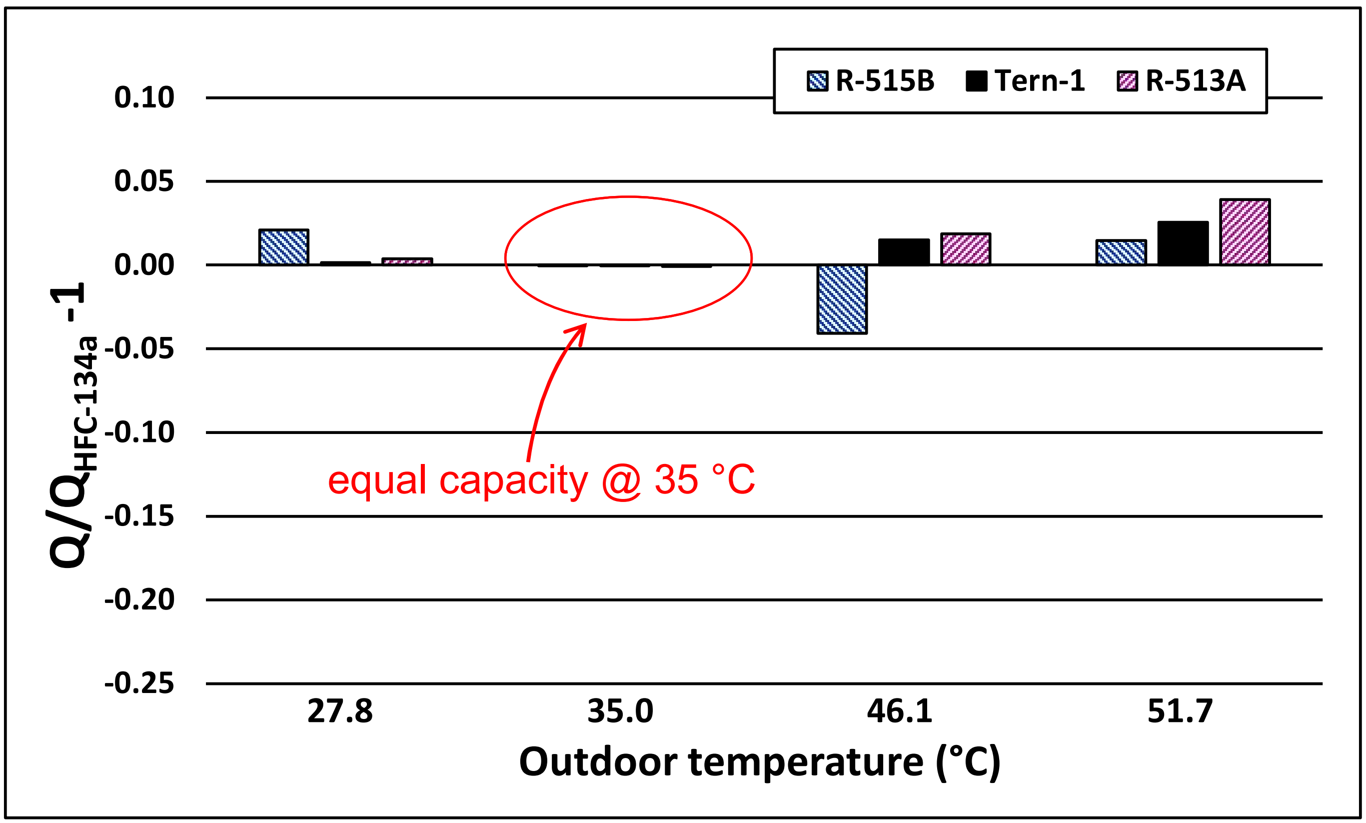
EVAP-COND - Evaporator & condenser simulation

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

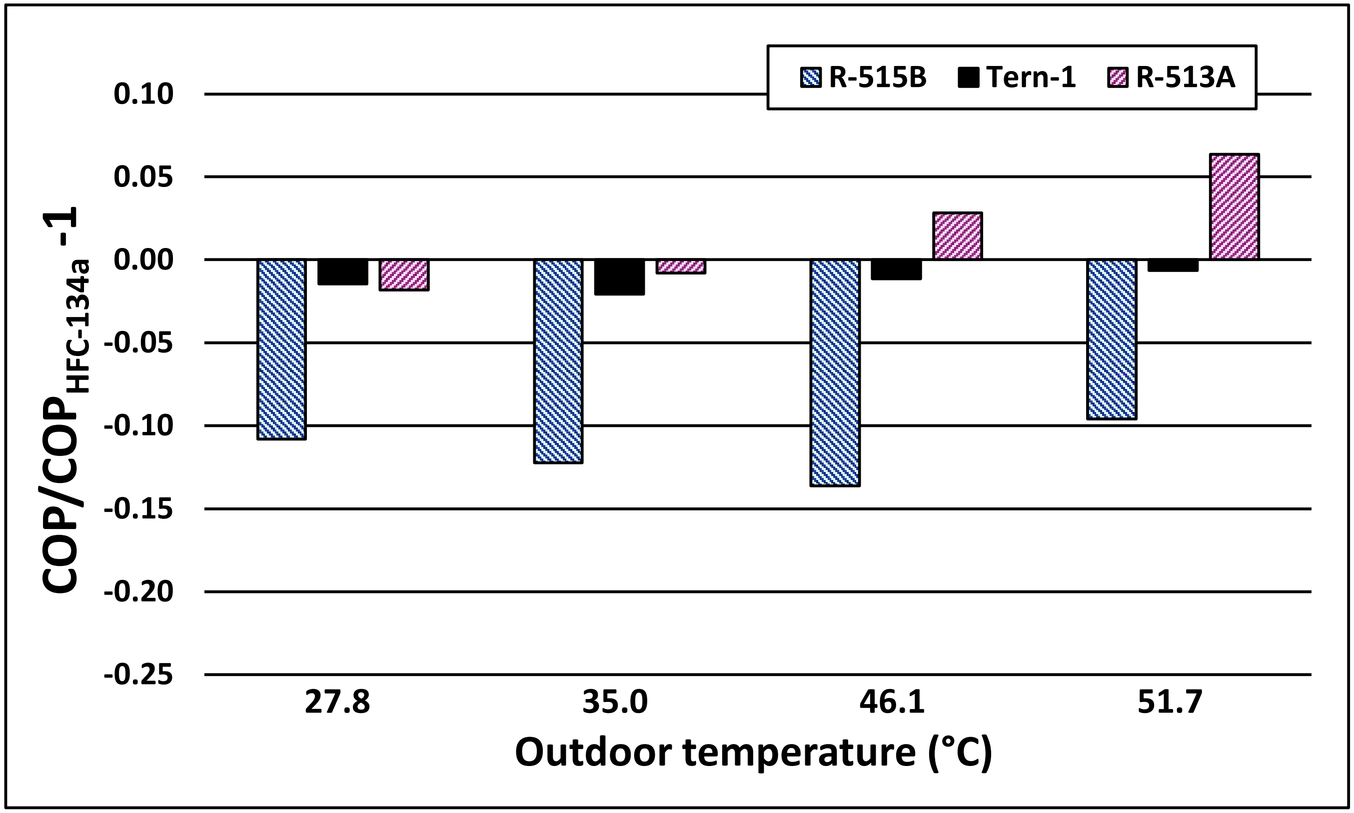


Results

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

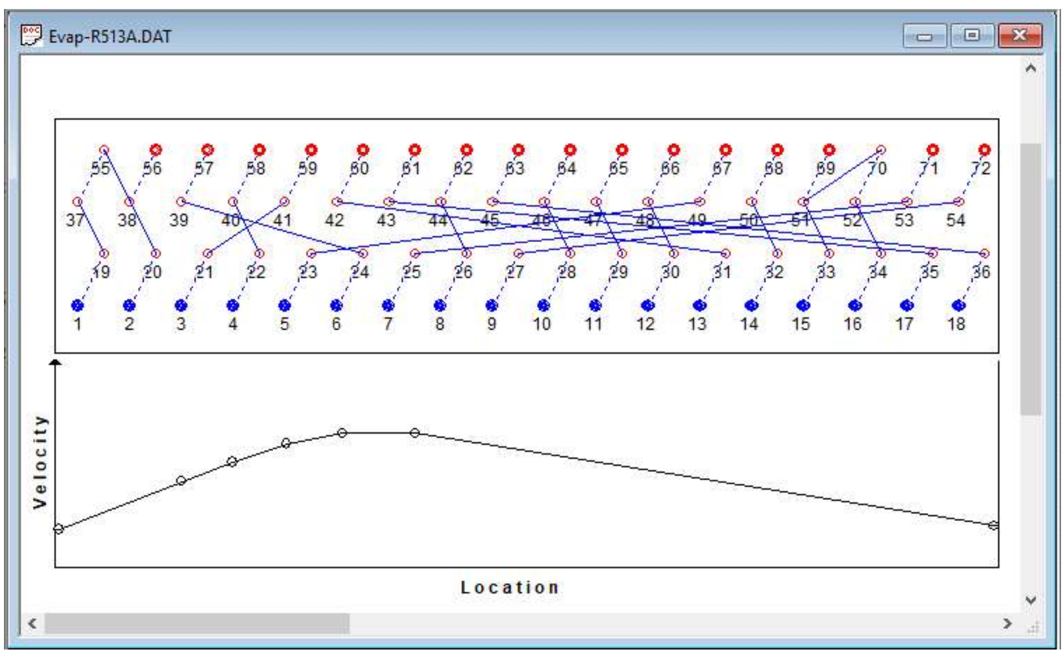


Results

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

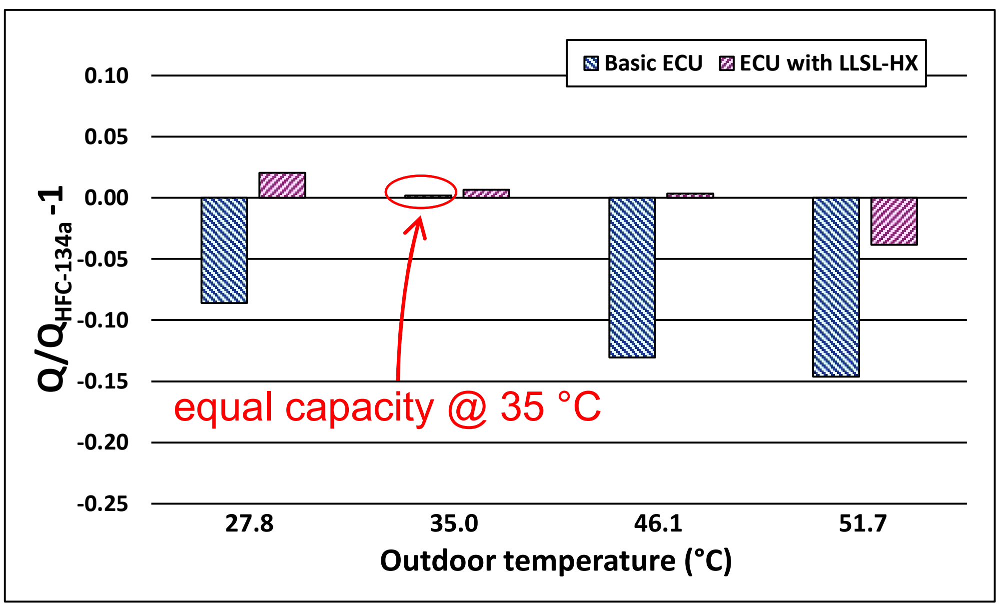
Task 7. Evaluation of Blends in ECU – Simulations

- Evaluated CO_2 as an alternative refrigerant

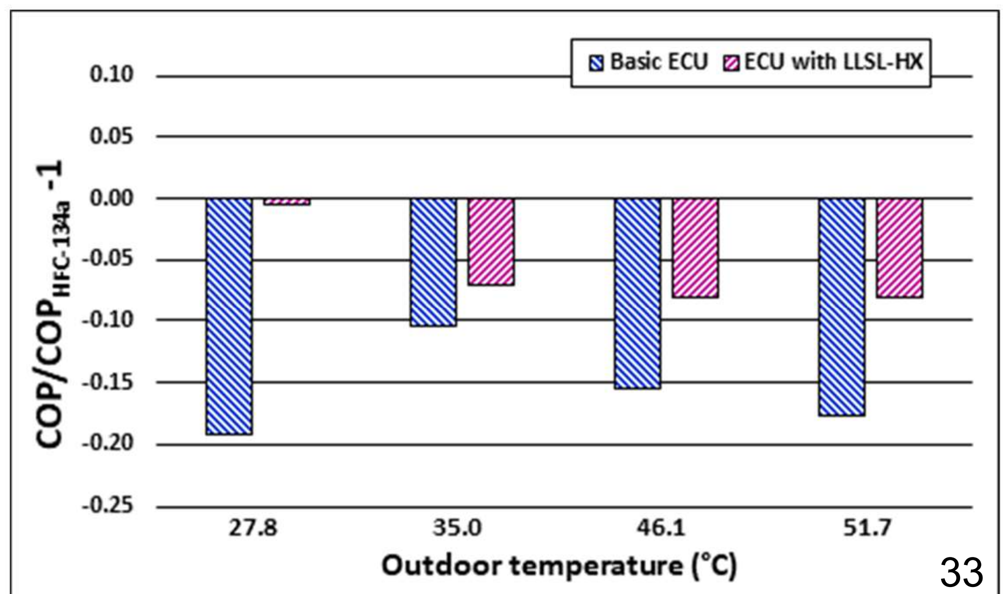
In response to comment from proposal reviewer

- 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

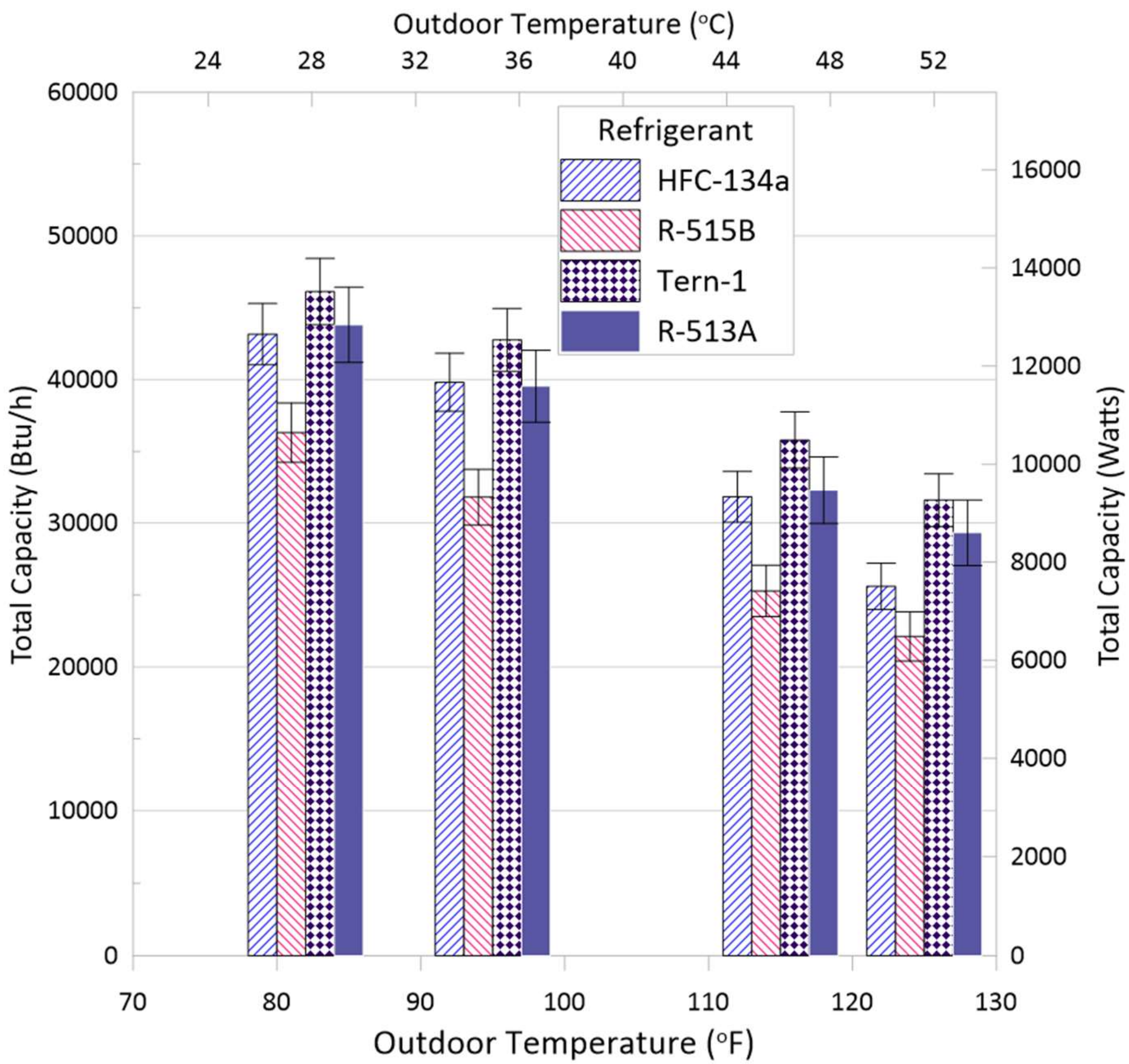
VLE – vapor-liquid equilibrium

$\bar{\Pi}$ - Flammability index

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- Total Capacity

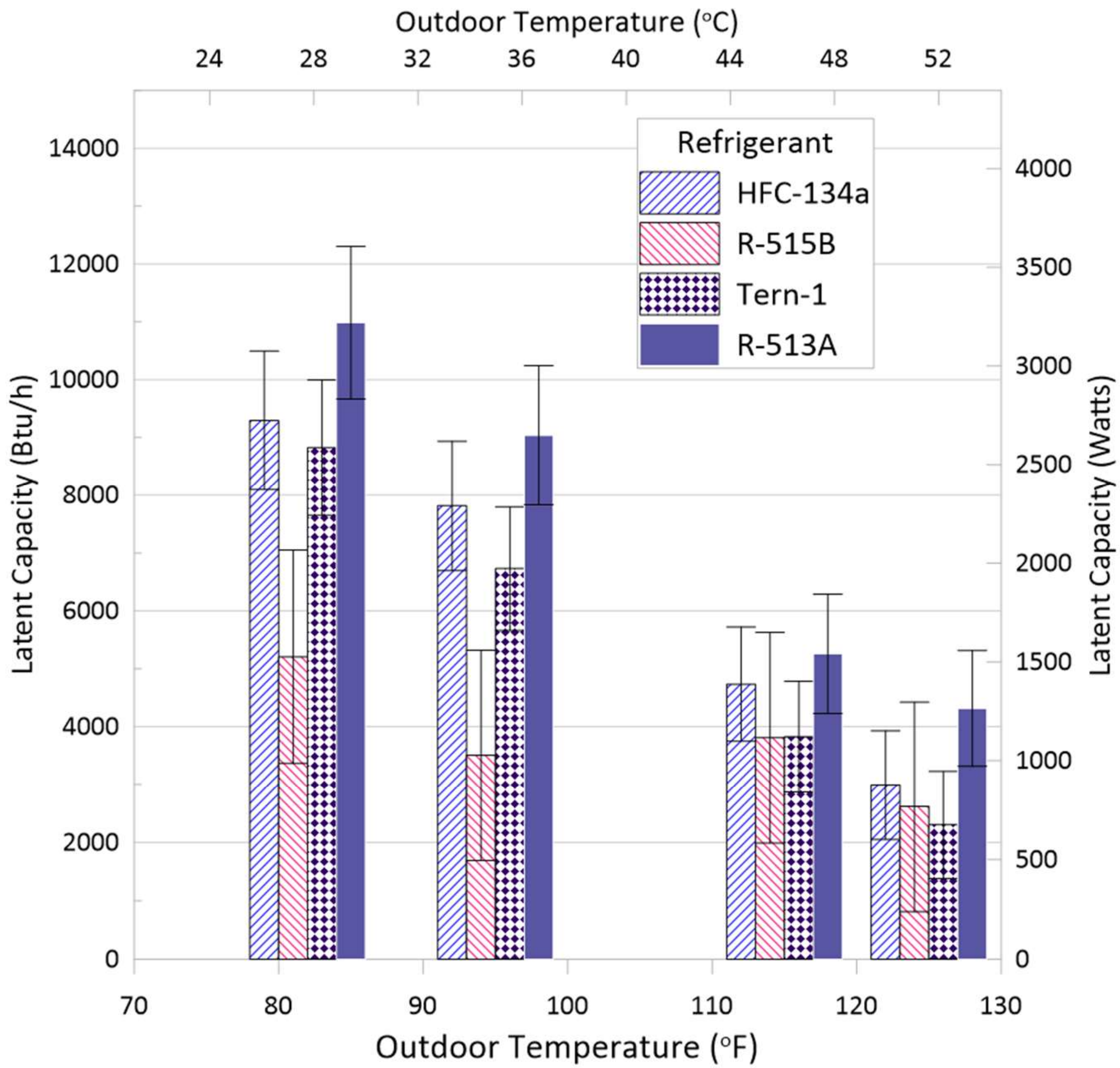


Error bars: *k*=2,
95 % confidence interval

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- Latent Capacity

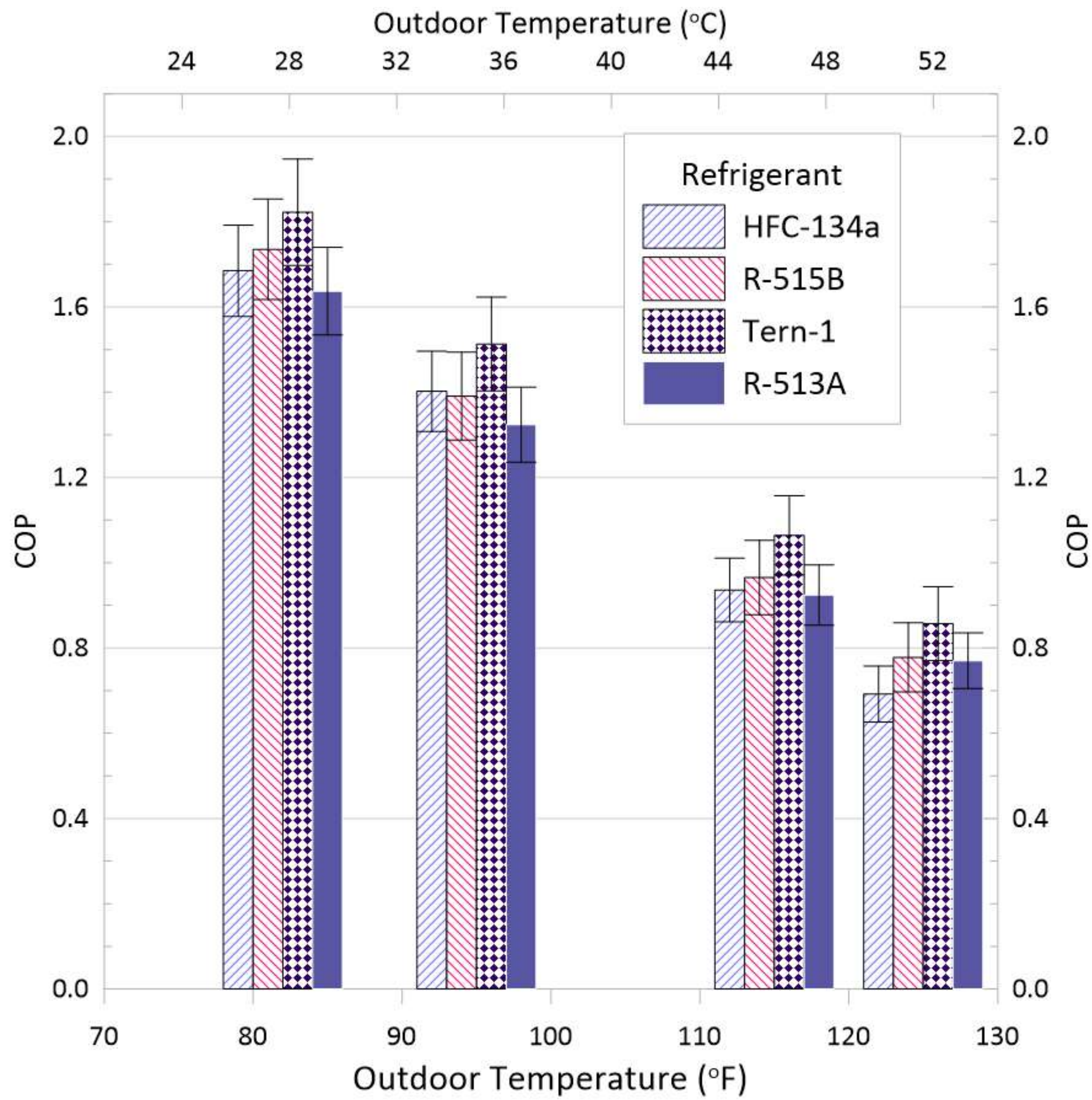


Error bars: *k*=2,
95 % confidence interval

Results

Task 7. Evaluation of Blends in ECU – Experimental Tests

- COP = Capacity / Electricity Input



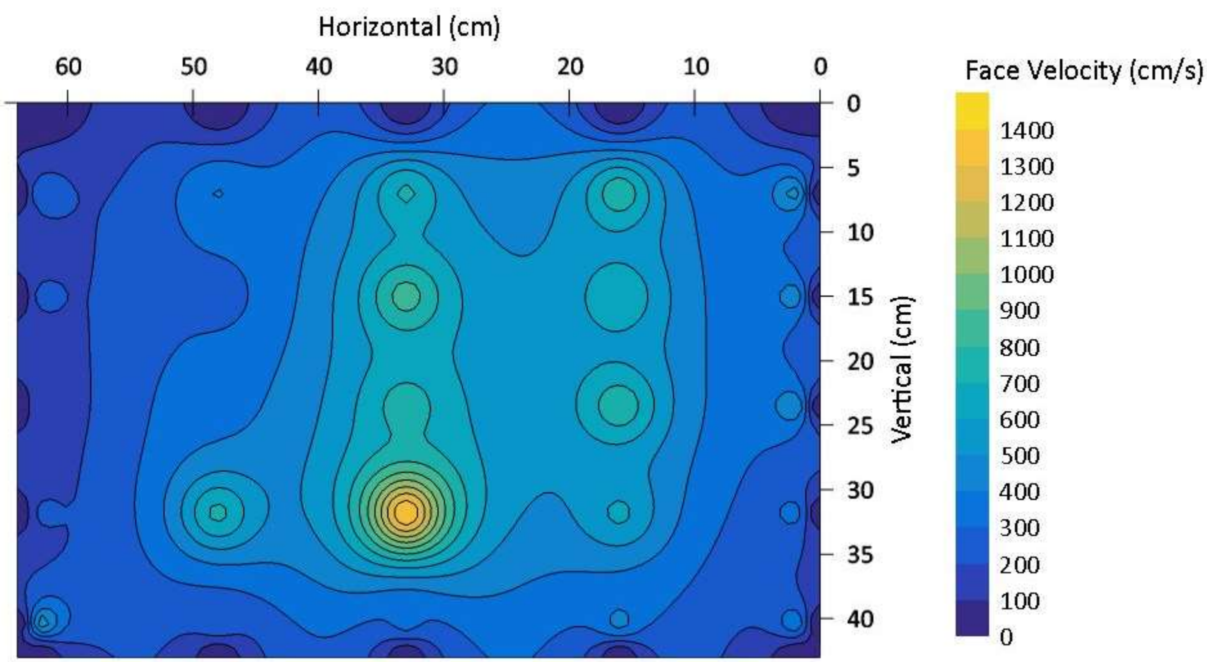
Error bars: *k*=2,
95 % confidence interval

Results

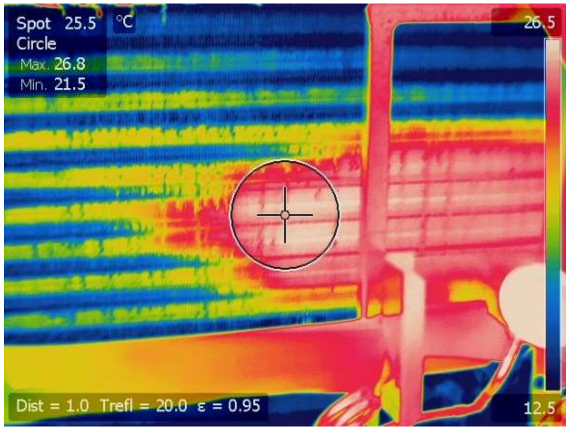
Task 7. Evaluation of Blends in ECU – Experimental Tests

- Evaporator airflow maldistribution reduced capacity and efficiency

Evaporator air velocity



Evaporator refrigerant temperature



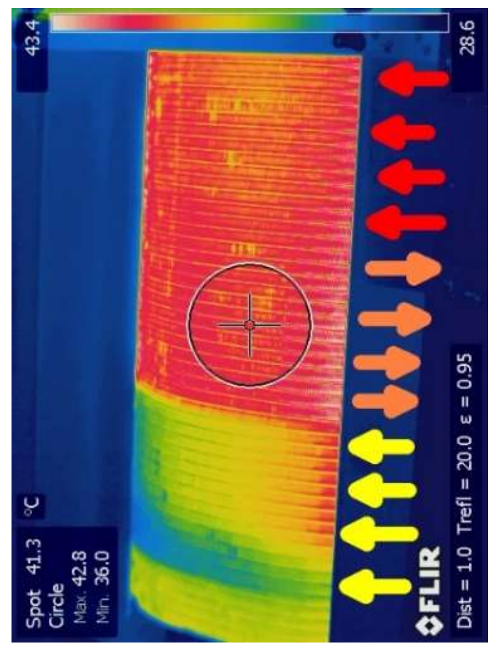
Results

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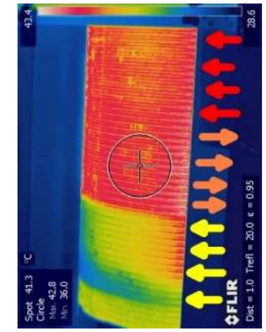
WP19-1385: Low-GWP Alternative Refrigerant Blends for HFC-134a

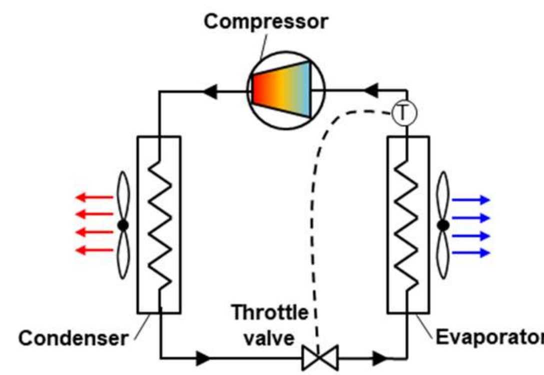


Performers:

- *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)*

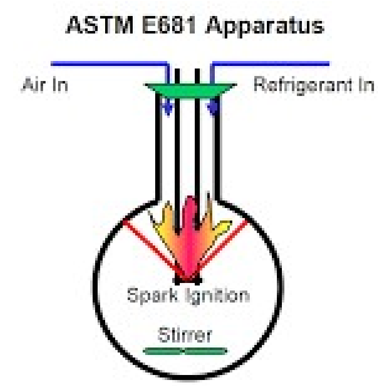


Research Objectives

- *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*