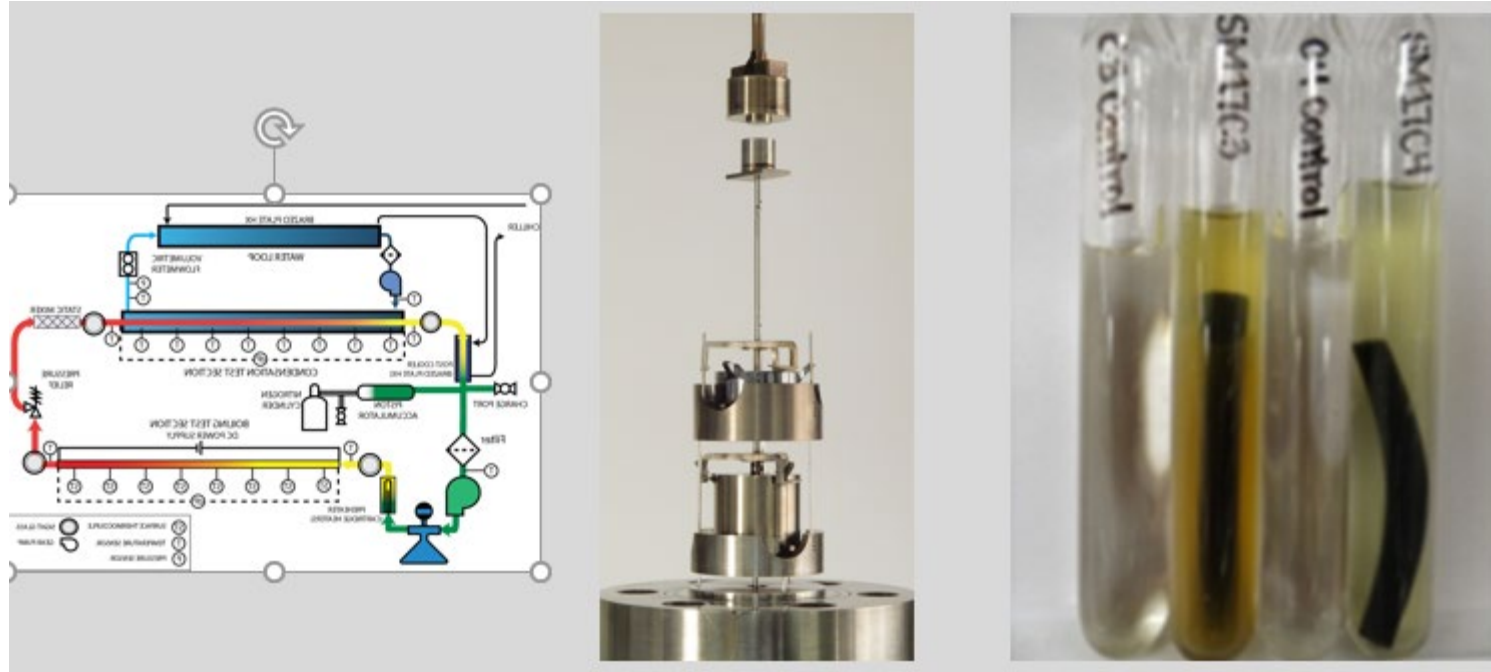


Implementing Low Global Warming Potential (GWP) and Energy Efficient Refrigerant Technologies



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National Institute of Standards and Technology: Mark O. McLinden, Applied Chemicals and Materials Division, markm@boulder.nist.gov
Oak Ridge National Laboratory: Brain A. Fricke, Group Leader, Building Equipment Research, frickeba@ornl.gov

Project Summary

Timeline:

Start date: September 1, 2019

Planned end date: May 31, 2023

Key Milestones

1. development of priority list; July 30, 2021
2. experimental data generation for low GWP refrigerants, March 31, 2022
3. correlations and models development, May 31, 2023

Budget:

Total Project \$ to Date:

- DOE: \$1,111,283
 - AHRTI: \$210,422
 - NIST: \$350,861
 - \$ORNL: \$550,000
- Cost Share: \$129,285

Total Project \$:

- DOE: \$2,101,019
- Cost Share: \$247,117

Key Partners:

Air-Conditioning, Heating and Refrigeration Technology Institute
National Institute of Standards and Technology
Oak Ridge National Laboratory
Air-Conditioning, Heating and Refrigeration Institute
Equipment manufacturers
Chemical producers

Project Outcome:

The program will develop low GWP refrigerants heat transfer and pressure drop correlations, property data, stability and materials compatibility data.

These essential data will overcome the hurdles of implementing new refrigerants and build a foundation for US manufacturers to design and optimize efficient and reliable products.

Team



AHRTI



NIST



OAK RIDGE
National Laboratory



OAK RIDGE
National Laboratory

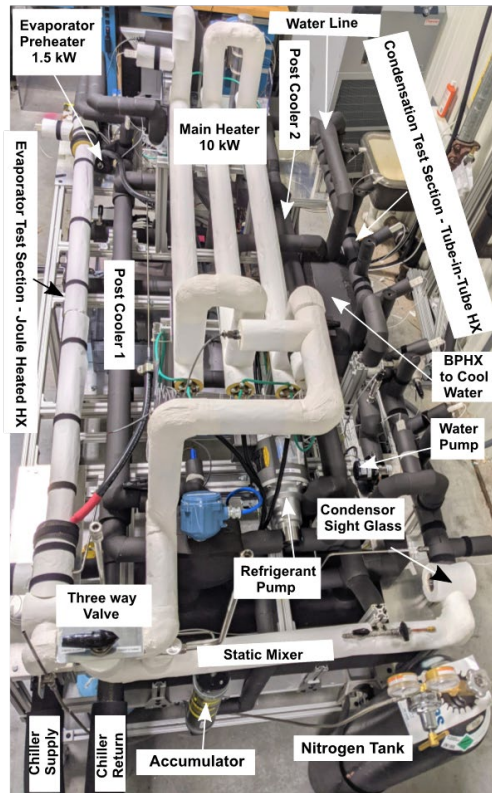


- Testing lab: Trane Technologies
- Industry advisory group (technical experts from major HVACR manufacturers)

Challenge

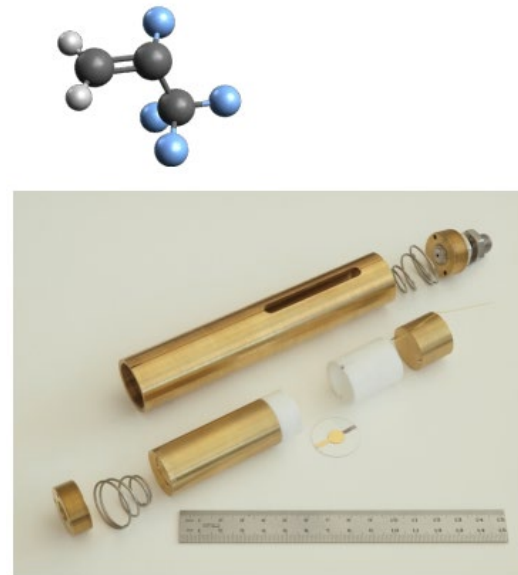
- The US industry is transitioning to next generation equipment using environment-friendly refrigerants
 - new low-GWP refrigerant are primarily blends with multiple components
 - a lack of robust, accurate and accessible refrigerant property and compatibility data leads to:
 - costly product design and optimization (cut-and-try process)
 - potentially premature chemical or electrical failure and the degradation of the system efficiency.
- The project goal is to overcome the hurdles by generating accurate refrigerant properties data and correlations.

Approach



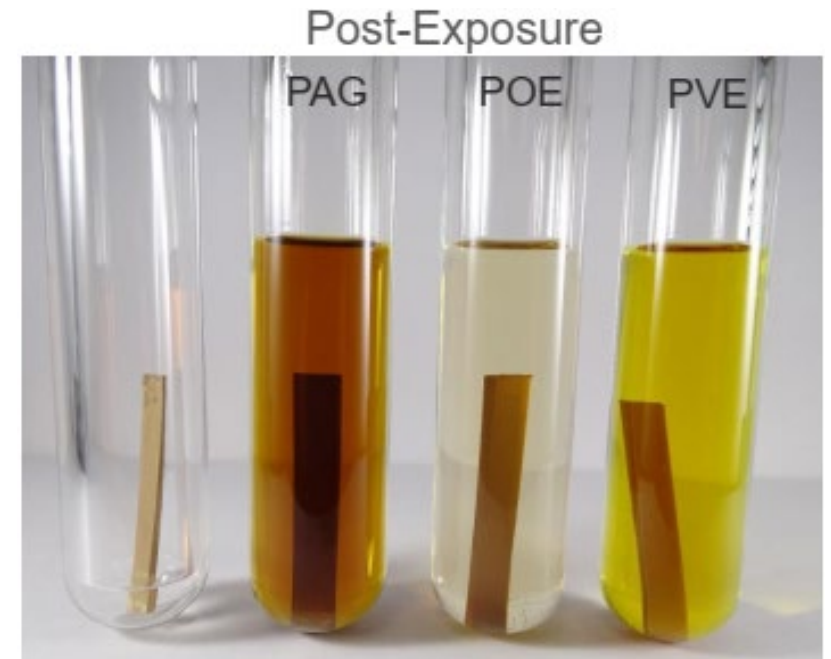
Testing of heat-transfer performance

Two-sinker densimeter



Pulse-echo instrument for liquid-phase speed of sound

Measurement of blend thermodynamic data



Sealed-tube testing for lubricant compatibility

- To develop a critical low-GWP refrigerants database that serves as a stepping stone for US manufacturers' innovation.

Impact

- Supports DOE BTO goal to develop refrigerant solutions to reduce greenhouse gas emissions for space conditioning, water heating, and commercial refrigeration equipment and enable their increased use through laboratory and field validations.
- Generates essential knowledge base to expedite the implementation of low GWP refrigerants in the US market in a timely and less costly way.
- Helps domestic manufacturers to compete in domestic and foreign markets:
 - efficient and effective design and optimization
 - ensured product efficiency and reliability
- Avoids further duplication of effort within the industry which is beneficial to all the US manufacturers and their customers

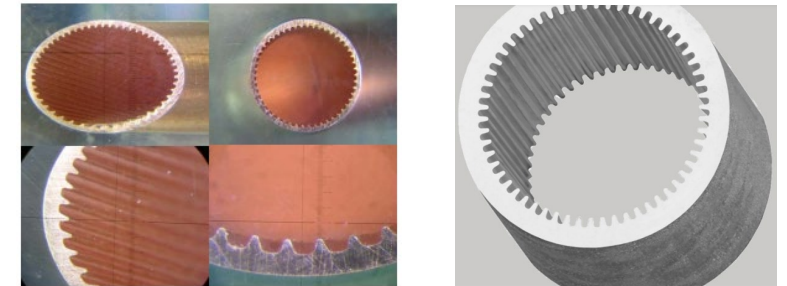
Progress – ORNL (refrigerants and tubing selection)

- Several meetings with the AHRTI Working Group within the past year
 - Selection of refrigerants for evaluation
 - Selection of refrigerant tubing for evaluation

– Refrigerant Selection –

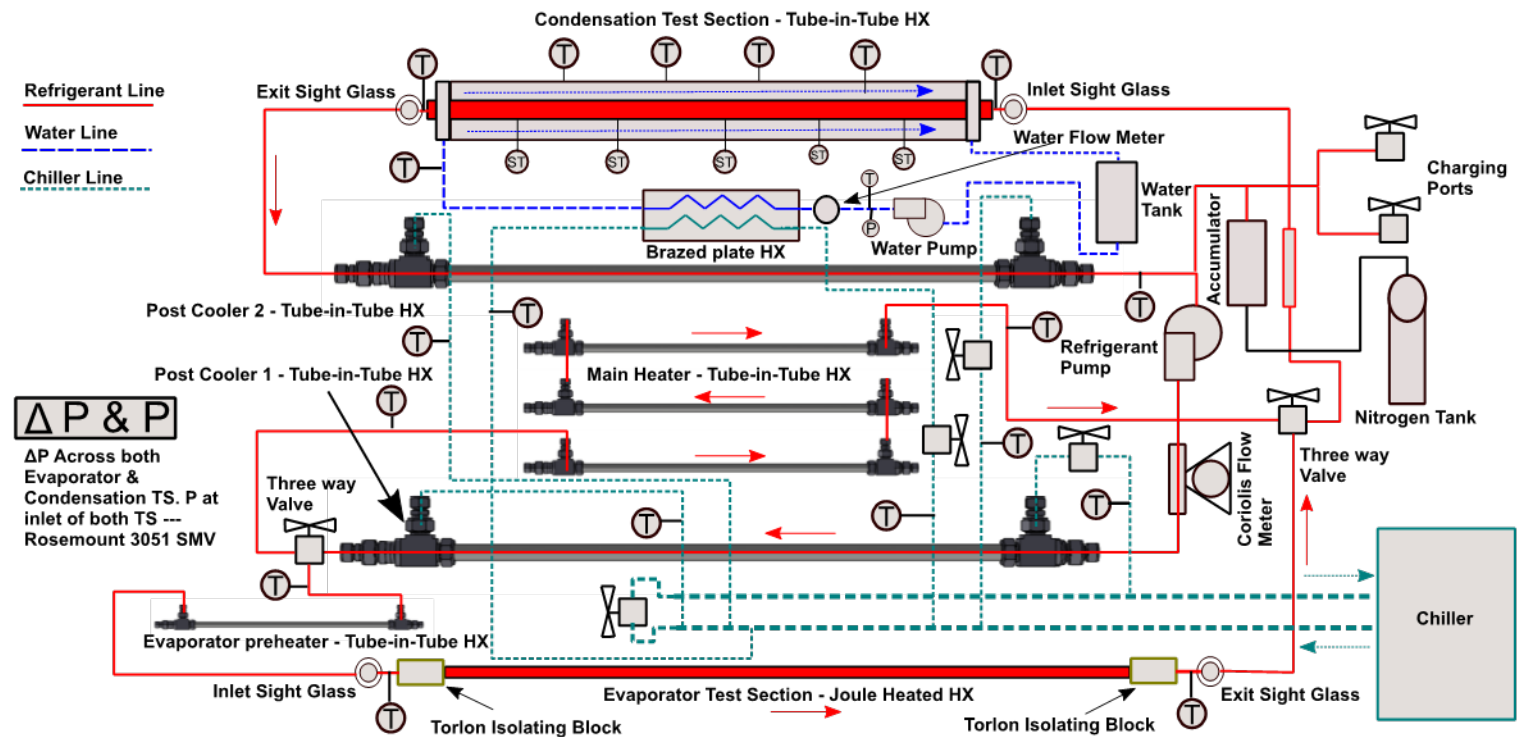
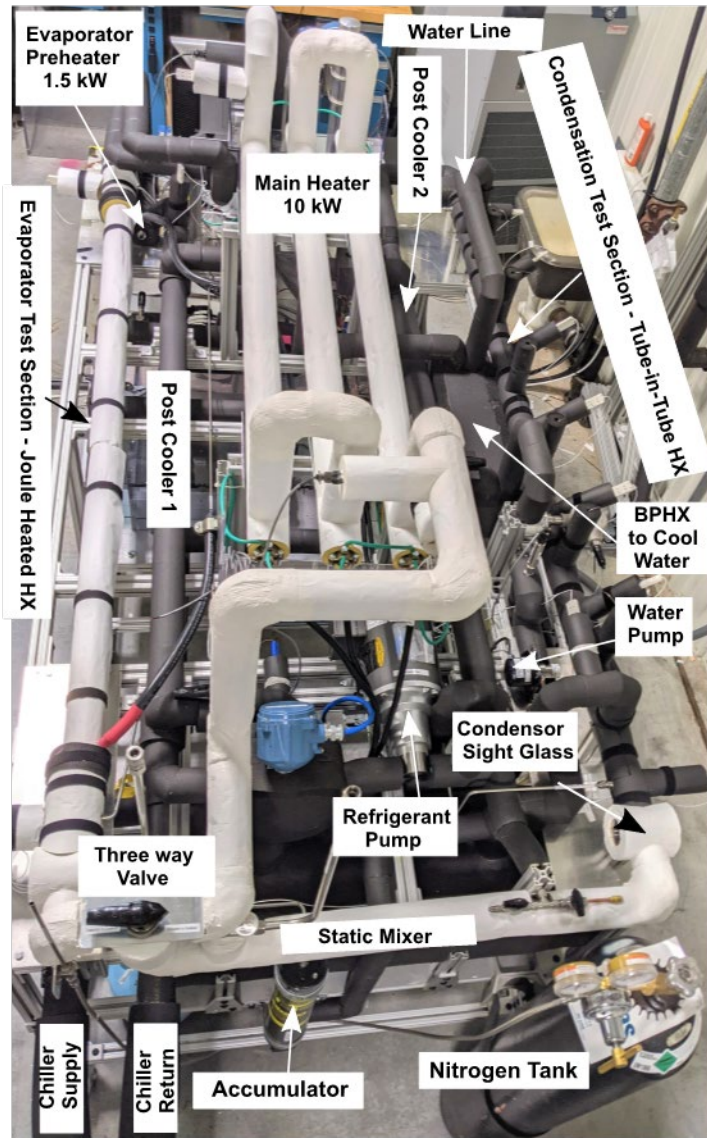
Refrigerant	Composition (Mass %)	Safety Classification	Bubble Point (°C), 101.3 kPa	Dew Point (°C), 101.3 kPa	GWP
R-410A (baseline)	R-32/125 (50.0/50.0)	A1	-51.6	-51.5	2088
R-32	--	A2L	-51.7	-51.7	675
R-454B	R-32/1234yf (68.9/31.1)	A2L	-50.9	-50.0	466

– Tube Selection –



Internal Surface	Diameter	Material
Smooth (baseline)	3/8 inch	Copper
Rifled	3/8 inch	Copper
Axial	7 mm	Aluminum

Progress – ORNL (refrigerant test loop fabrication)

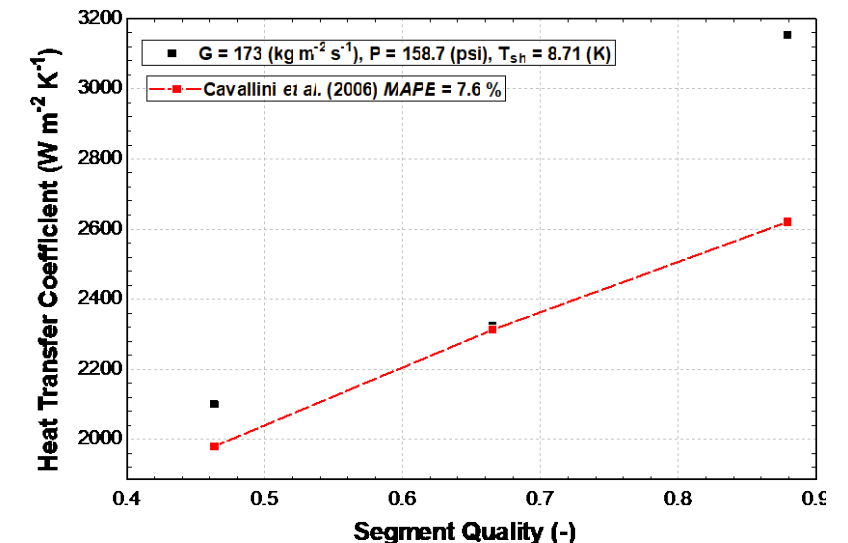
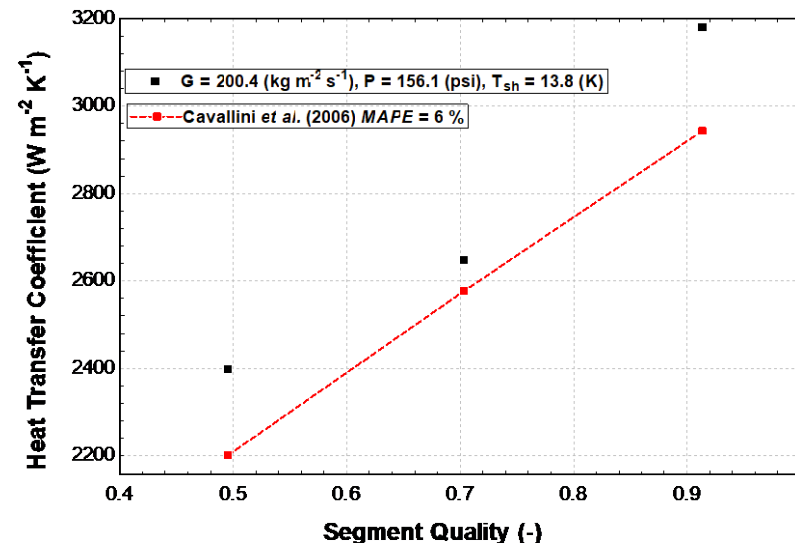
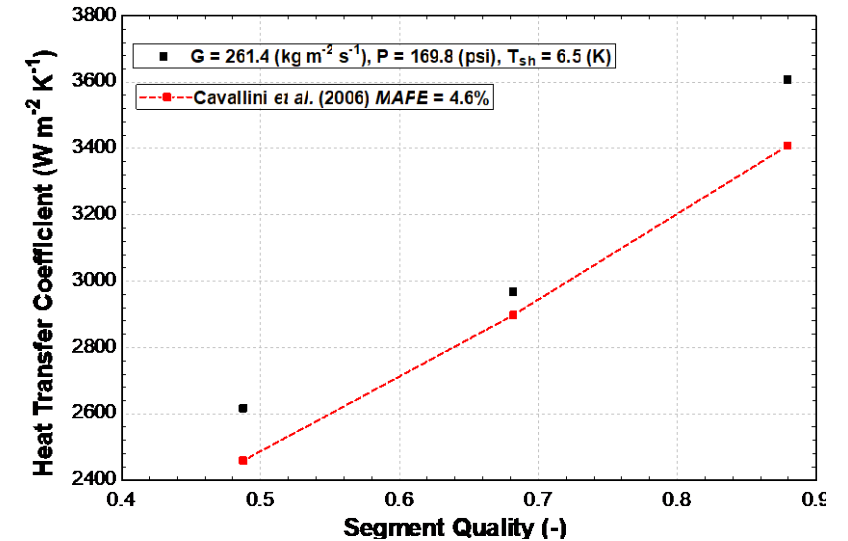
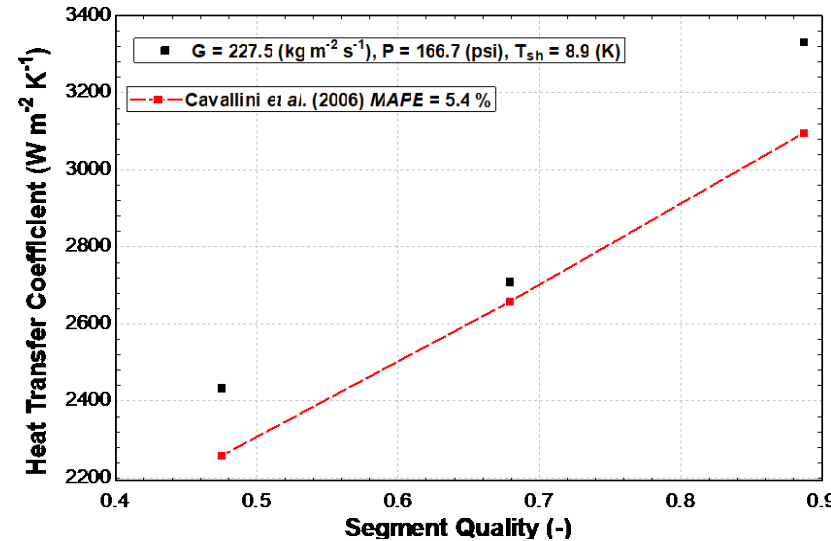


Completed fabrication of refrigerant test loop

- Condensation test section (tube-in-tube method)
- Evaporation test section (Joule heating method)

Progress – ORNL (preliminary results)

- Comparison of measured data for R-134a with correlation from Cavallini et al., “Condensation in Horizontal Smooth Tubes: A New Heat Transfer Model for Heat Exchanger Design,” *Heat Transfer Engineering*, vol. 27. no.8 (2006)
- Overall energy balance within 3%
- Mean absolute percentage error (MAPE) within 7.6%



Remaining Project Work – ORNL

- **Validate condensation and evaporation test sections**
 - R-410A, 3/8” smooth copper tube
 - Compare with published literature
- **Complete condensation and evaporation studies**
 - Determine heat transfer coefficient and pressure drop
 - Refrigerants: R-32 and R-454B
 - Tubing: 3/8” smooth copper, 3/8” rifled copper, 7 mm axial aluminum
- **Develop heat transfer and pressure drop correlations**

Progress – NIST (Thermo Property Measurements, subtasks 2.1 & 5.1)

Objective: Develop the experimental database needed for equation of state development

- Late stage, on-time, on-budget
- Mixture priorities selected by working group (parallel Army-sponsored project at NIST has measured some high-priority mixtures)
- Vapor-liquid equilibria (VLE):
 - most important for model development (e.g., reveals existence of azeotropes)
- “Comprehensive” comprising:
 - density as a $f(T, p)$ [(p, ρ, T, x)]
 - & speed of sound as a $f(T, p)$
 - needed for accurate enthalpies, etc.
- Why speed of sound?
 - thermo properties are interconnected
 - SoS related to heat capacity, but can be measured more accurately

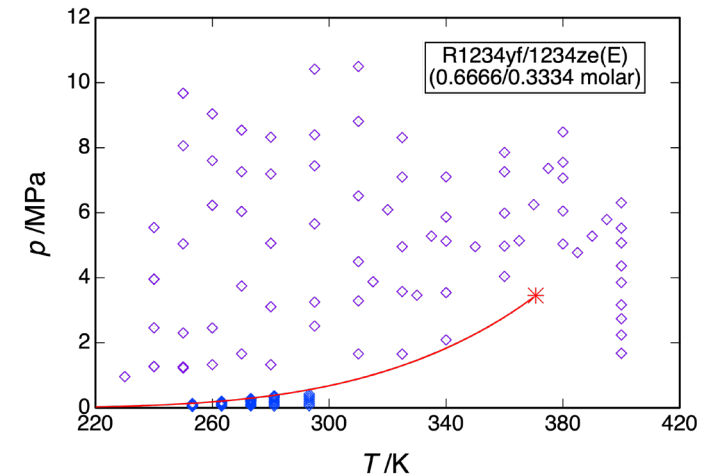
(p, ρ, T, x) (liq, vap, supercrit)	Speed of sound (liquid)	VLE (bubble point)	Budget period
32+1234yf	32+1234yf	32+1234yf	1
32+1234ze(E)	32+1234ze(E)	32+1234ze(E)	1
152a+1234yf	152a+1234yf	152a+1234yf (parallel project)	2
(literature data avail.)	125+1234yf	125+1234yf (parallel project)	2
227ea+1234ze(E)	227ea+1234ze(E)	227ea+1234ze(E) (parallel project)	2
	1132a (pure)	R1132a/1234yf	2

Color code:
completed in progress

Speed of sound related to C_V

$$w^2 = \left(\frac{\partial p}{\partial \rho} \right)_T + \frac{T}{\rho^2 C_V} \left[\left(\frac{\partial p}{\partial T} \right)_\rho \right]^2$$

Sample measurements for density (p - ρ - T - x)



Progress – NIST (Equation of State Development, subtasks 2.2 & 5.2)

Objective: Develop thermodynamic models (i.e., equations of state or EOS), disseminated via REFPROP, needed by industry for equipment design and optimization

- Mid stage, on-time, on-budget
- Literature survey of blends with HFOs (HFCs, HCs)
 - 120 data sources identified and data compiled (only a single speed of sound data set)
 - very sparse data for HFO/HFO blends (this project will fill that in)
 - data compared to present REFPROP models range from spot-on to significant deviations
 - Bell, et al., *J. Chem. Eng. Data* 66:2335 (2021) (open source)
- These data, together with new measurements, will form basis for EOS development
- EOS development now underway

Journal of
Chemical & Engineering Data

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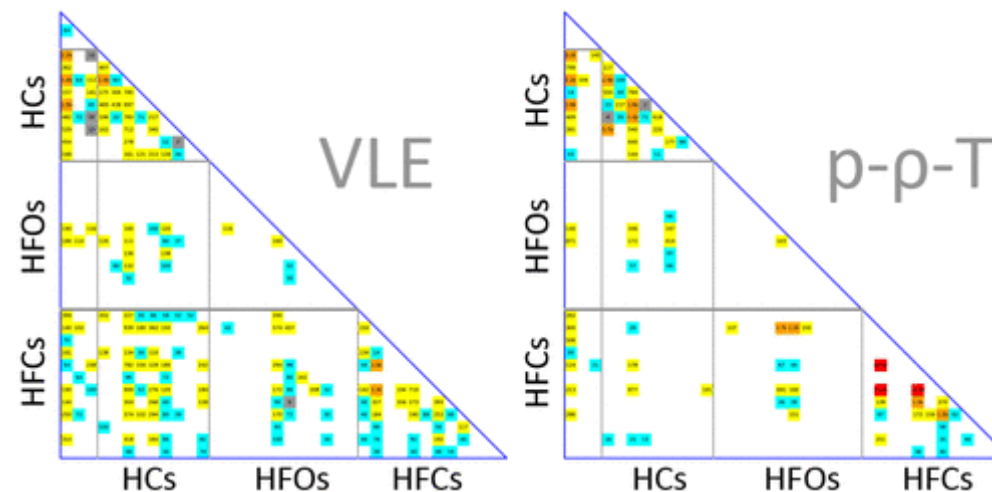
Review

Survey of Data and Models for Refrigerant Mixtures Containing Halogenated Olefins

Ian H. Bell,* Demian Riccardi, Ala Bazyleva, and Mark O. McLinden

Cite This: *J. Chem. Eng. Data* 2021, 66, 2335–2354

Read Online



Remaining Project Work – NIST

Goal: Develop a mixture model for low-GWP blends that will serve industry in the way that the HFC model of Lemmon & Jacobsen has done for 20 years

- Remaining measurements completed by October 2021
- Development of mixture equation of state
 - current EOS model in REFPROP cannot simultaneously fit VLE and speed of sound data
 - explore: “departure function” and “reducing functions”
- Implement new model in NIST REFPROP
 - preference is for same functional forms
 - will revise REFPROP, if needed, for new functional form
- Working group has identified additional high-priority pure fluids [including R1132(E), R1336mzz(E)] and blends
 - will propose additional measurements in continuation application to DOE

Equations of State for Mixtures of R-32, R-125, R-134a, R-143a, and R-152a

Eric W. Lemmon^{a)}

*Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway,
Boulder, Colorado 80305-3328*

Richard T Jacobsen

Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415-2214

(Received 30 December 2002; revised manuscript received 16 December 2003; accepted 31 December 2003; published online 2 June 2004)

Mixture models explicit in Helmholtz energy have been developed to calculate the thermodynamic properties of refrigerant mixtures containing R-32, R-125, R-134a, R-143a, and R-152a. The Helmholtz energy of the mixture is the sum of the ideal gas contribution, the compressibility (or real fluid) contribution, and the contribution from mixing. The independent variables are the density, temperature, and composition. The model may be used to calculate the thermodynamic properties of mixtures, including dew and bubble point properties, within the experimental uncertainties of the available measured properties. It incorporates the most accurate equations of state available for each pure fluid. The estimated uncertainties of calculated properties are 0.1% in density and 0.5% in heat capacities and in the speed of sound. Calculated bubble point pressures have typical uncertainties of 0.5%. © 2004 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [DOI: 10.1063/1.1649997]

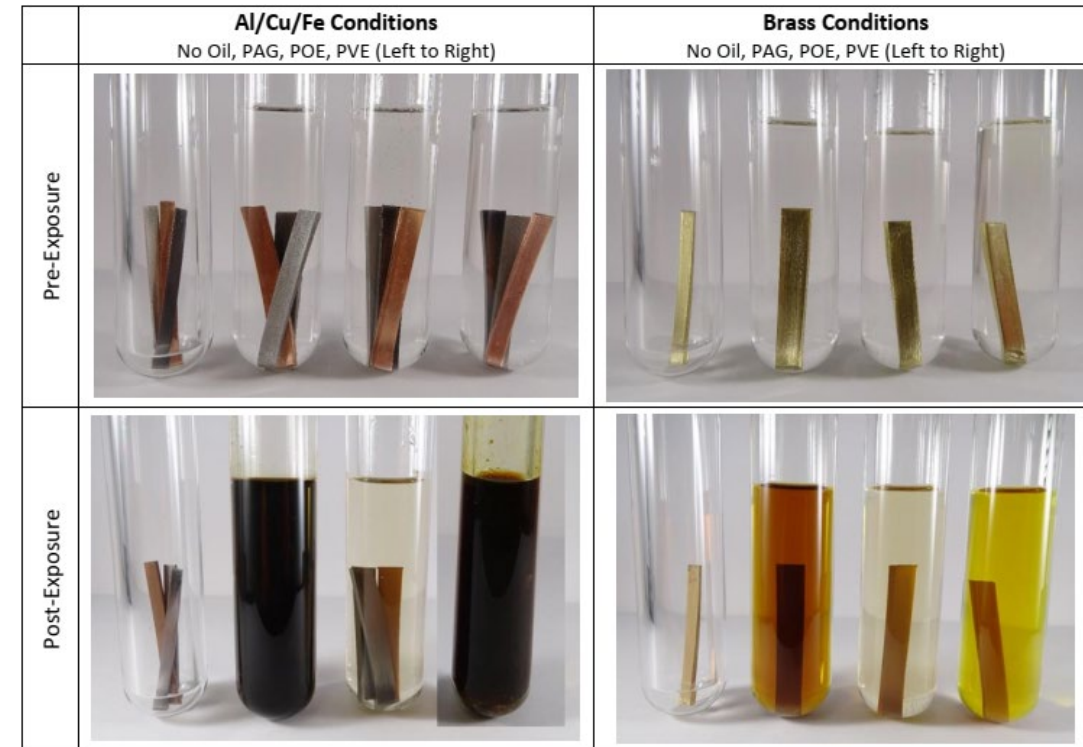
Key words: density; equation of state; heat capacity; HFC-32; HFC-125; HFC-134a; HFC-143a; HFC-152a; R-404A; R-407C; R-410A; R-507; refrigerant mixtures; speed of sound; thermodynamic properties; VLE.

J. Phys. Chem. Ref. Data **33**:593 (2004)

Progress – AHRTI (Chemical Stability Testing , Task 3)

Goal: determine the thermal and chemical stability of several low GWP refrigerant blends with lubricants.

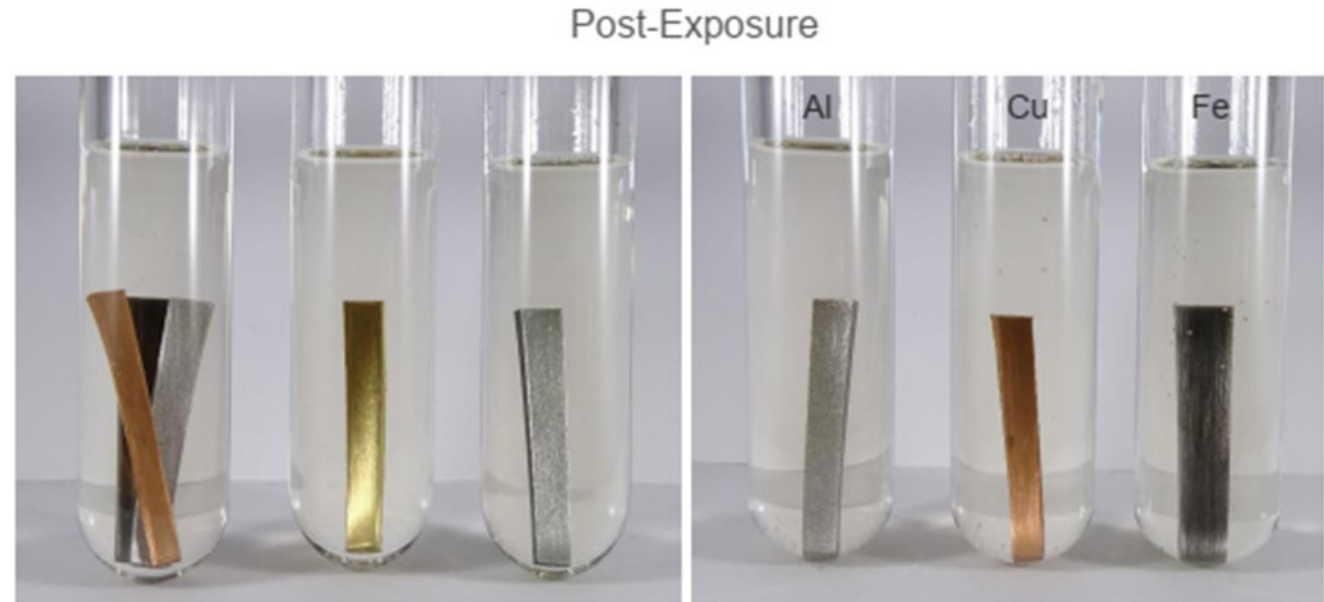
- Late stage, on-budget, six months delay due to COVID-19
- Phase I testing completed (159 total test tubes):
 - Low Pressure Refrigerants: R-123, R-1233zd(E), R-1224yd(Z), R-514A, R-1336mzz(Z), R-1336mzz(E)
 - Medium Pressure Refrigerants: R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, R-516A
 - High Pressure Refrigerants: R-454C, R-455A, R-468A, R-466A,
 - Lubricants: Polyol ester (POE), Polyvinyl ether (PVE), Polyalkylene Glycol (PAG).
 - Metal Catalysts: Aluminum, Iron, Copper, Zinc and Brass.
 - Good chemical stability found across all refrigerants evaluated, except R-466A
 - PVE has unique interactions with each HFO
 - PAG had similar results to PVEs with the generation of fluoride, however no unknown components found by GCMS to suggest reaction between lubricant and refrigerant
 - POE showed consistent increases in reactivity in the presence of zinc



R-466A Pre and Post Exposure Observations with Metal Coupons.

Progress – AHRTI (Chemical Stability Testing , Task 3)

- Phase II testing is near completion (207 test tubes):
 - R-466A with additized POE
 - Further study of reactivities with standard oil additives/stabilizers
 - R-454B to round out full spectrum of R32/yf blends (understanding ratios vs. stability)
 - Pure Materials used in Blends (R152a, R227ea components of R-516A since R-516A showed fluoride formation w/PAG and PVE
 - A filter drier/desiccant materials study (3A, 4A Molesieve and Activated Alumina as catalysts)



*R-466A with additized POE post exposure observations
(Substantial reduction in reactivity vs Phase I.)*

Remaining Project Work – AHRTI

Goal: to determine low GWP refrigerant blends with lubricants long-term material compatibility with materials commonly used in stationary air-conditioning and refrigeration systems.

- Remaining stability testing and report completed by November 2021, and compatibility type testing completed by December 2022
- Work with industry representatives to select refrigerants, lubricants and materials for testing including state of the art and emerging materials
- Conduct material compatibility tests using Parr pressure vessels or other industry accepted methods

Stakeholder Engagement

- Industry-wide engagement and collaboration
 - three industry advisory committees
 - refrigerant heat transfer/pressure drop correlations
 - refrigerant blends property data
 - refrigerant compatibility and lubricant
 - 50+ industry experts from 26 companies
 - access to new refrigerant blends and materials
- Stakeholders
 - Chemical producers to supply new refrigerants and lubricants
 - Manufacturers to guide the work direction for industry needs and interest

Thank You

Air-Conditioning, Heating and Refrigeration Technology Institute:

Xudong Wang, Vice President, Research, xwang@ahrinet.org

National Institute of Standards and Technology:

Mark O. McLinden, Applied Chemicals and Materials Division, markm@boulder.nist.gov

Oak Ridge National Laboratory:

Brain A. Fricke, Group Leader, Building Equipment Research, frickeba@ornl.gov

Kashif Nawaz, Group Leader, Multifunctional Equipment Integration, nawazk@ornl.gov

REFERENCE SLIDES

Project Budget

Project Budget: \$2,348,136 (DOE: \$2,101,019 Cost share: \$247,117)

Variances: A 12 months no-cost extension was granted due to the COVID-19 pandemic.

Cost to Date: \$1,240,568 (DOE: \$1,111,283 Cost share: \$129,285)

Additional Funding: None

Budget History			
Sep 2019 – FY 2021 (current)		FY 2022 – 3/31/2023 (planned)	
DOE	Cost-share	DOE	Cost-share
\$953,311	\$117,349	\$1,147,708	\$129,768

Project Plan and Schedule

	completed				ongoing/planned													
	Budget Period 1								Budget Period 2									
	FY2020				FY2021				FY2022				FY2023					
Task	Q1 (Oct-Dec)	Q2 (Jan-Mar)	Q3 (Apr-Jun)	Q4 (Jul-Sep)	Q1 (Oct-Dec)	Q2 (Jan-Mar)	Q3 (Apr-Jun)	Q4 (Jul-Sep)	Q1 (Oct-Dec)	Q2 (Jan-Mar)	Q3 (Apr-Jun)	Q4 (Jul-Sep)	Q1 (Oct-Dec)	Q2 (Jan-Mar)	Q3 (Apr-Jun)	Q4 (Jul-Sep)		
1. Low GWP refrigerants heat transfer and pressure drop correlation development																		
1.1. design of the test setup	■	■	■															
1.2. construction of the test setup				■	■	■	■											
1.3~1.5 Measure heat transfer and pressure drop in tube sections								■	■	■								
2. Low GWP refrigerant property data generation																		
2.1 Experimental Data on Key Binary Mixtures																		
2.1.1 top priority mixtures selection (first three binary pairs)	■	■																
2.1.2 measure mixtures' thermodynamic properties (VLE only)		■	■	■														
2.1.3 measure mixtures' thermodynamic properties (comprehensive)		■	■	■	■	■												
2.1.4 2nd tier mixture selection (final binary pairs selected)						■												
2.2 Mixture Model Optimized for Low-GWP Fluids							■											
2.2.1 develop preliminary model for two mixtures							■											
3. Low GWP refrigerant material compatibility and lubricant research																		
3.1 Refrigerant and Lubricant Stability Testing																		
3.1.1 complete the design of experiment and test matrix	■	■	■															
3.1.2 select subcontract laboratories for testing				■														
3.2 Refrigerant and lubricant stability testing				■	■	■	■	■										
3.2.1 design and construction of the test setup					■													
3.2.2-3.2.5 chemical stability testing						■	■	■										
Future work in budget period 2																		
4. Low GWP refrigerants heat transfer and pressure drop correlation development												■	■	■	■	■		
5: Low GWP refrigerant property data generation												■	■	■	■	■		
6: Low GWP refrigerant material compatibility testing												■	■	■	■	■		

The schedule reflects the current and projected timeline that has included a 12 months no-cost extension.

While making a good progress in Budget Period 1 (BP1), we have experienced a delay due to nation-wide labs shut-down, reduced operational capacity and disrupted supply chains caused by the COVID-19 pandemic.

We expect to complete all tasks in BP1 by March 31 2022. This will have no impact to overall budget and tasks.