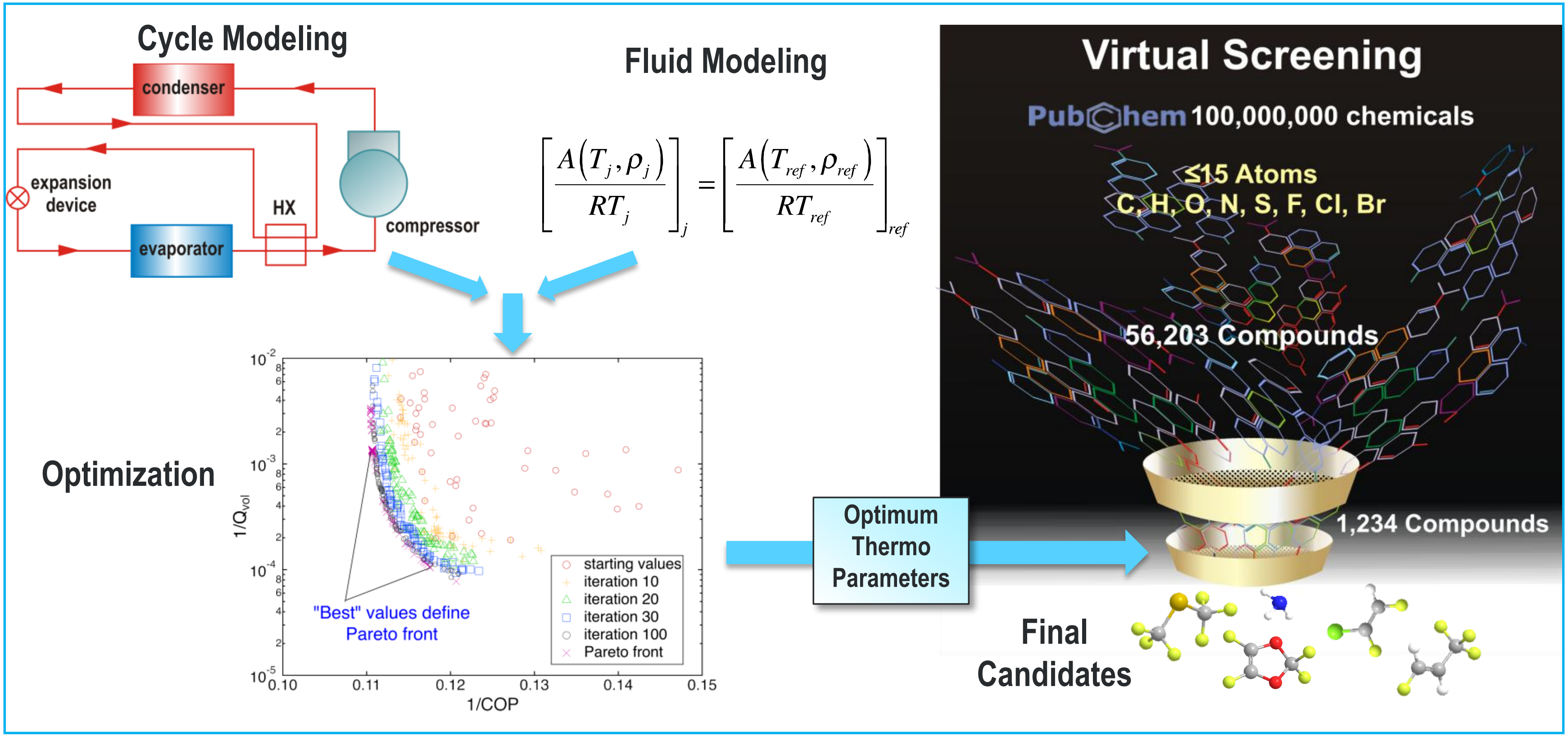
Thermodynamic Evaluation of Low-GWP Refrigerants

2014 Building Technologies Office Peer Review



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Project Summary

Timeline:
Start date: February 1, 2011
Planned end date: March 31, 2015

Key Milestones
1. Selection of top 20 candidate low-GWP fluids; Sep 30, 2014
2. Complete simulations of top 20 candidate fluids February 28, 2015
3. Technical paper with project conclusions March 31, 2015

Budget:
Total DOE $ to date: $1350 k
Total future DOE $ (FY2014): $400 k

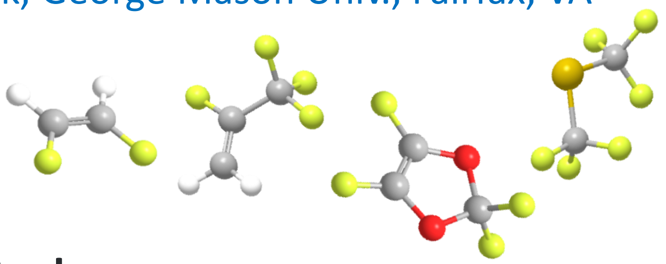
Target Market:
Space conditioning and refrigeration

Audience:
Equipment manufacturers, refrigerant producers, government regulators

Key Partners:

J. S. Brown, Catholic Univ. of America, Wash., DC

J. Wojtusiak, George Mason Univ., Fairfax, VA



Project Goal:
- Systematically and exhaustively search for and evaluate potential low-GWP refrigerants
- Recommend 20 fluids with tradeoffs identified
- Develop novel cycle simulation model for refrigerant screening accounting for thermodynamic and transport properties

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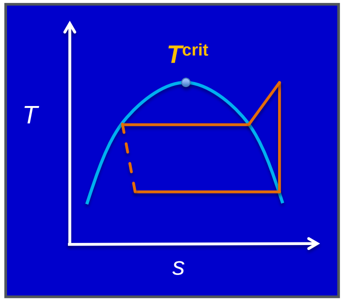
Purpose and Objectives

Problem Statement: HFC refrigerants face phase down:

European Parliament approved F-gas regulation on March 2, 2014 (79 % cut by 2030)
U.S./Canada/Mexico proposal to Montreal Protocol (85 % cut by 2033)

Low-GWP refrigerants must be found and implemented while maintaining efficiency, safety, and reliability.

Target Market: Air conditioning, refrigeration, and heat pumping is the largest consumer of primary energy in U.S. buildings (over 20 %). Refrigerant choice affects system efficiency.



Audience: Equipment manufactures, refrigerant producers, regulators.

Impact of Project:

The project will:

- Identify most promising low-GWP refrigerants and trade-offs between them
- 'Close the book' on available low-GWP refrigerants
- Provide a novel simulation tool for evaluating merits of refrigerants based on thermodynamic and transport properties

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Approach

Multi-Pronged Approach:

Screening of candidate molecules:

What are the possibilities for low-GWP fluids?

Thermodynamic analysis:

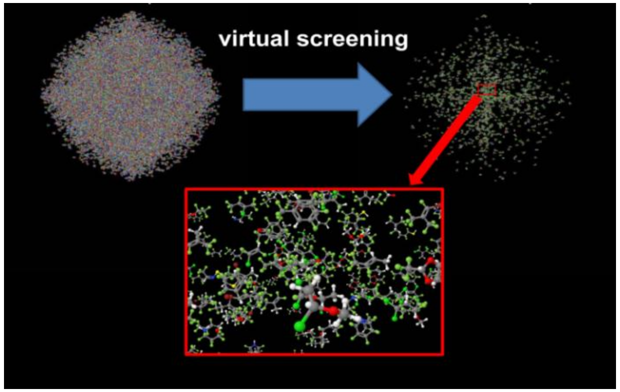
What are the limits to performance?

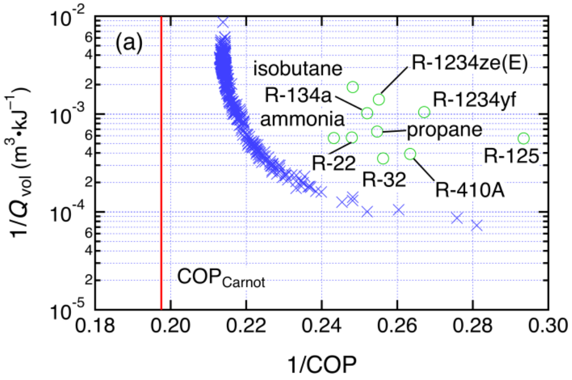
What fluid parameters result in approach to limits?

Combining the approaches:

Optimum parameters guide screening of candidates

COP prediction (cycle simulation detail) and refrigerant property representation improve as the screening narrows the pool of considered refrigerants





Key Issue: Identification of a substitute for R410A (high-pressure refrigerant)

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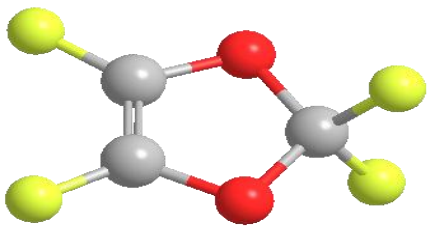
Approach

Distinctive Characteristic:



Refrigerant screening

Use PubChem database; 100 million compounds

Screening considerations (screens)

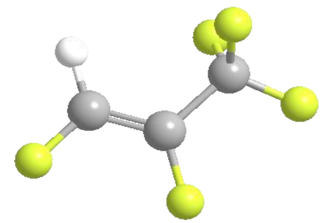
- Component atoms; only C, H, N, O, S, F, Cl, Br ← PubChem
- Max. number of atoms in the molecule ← PubChem
- Global Warming Potential (GWP) ← NIST estimation method (Kazakov, *et al.,* 2012)
- Toxicity ← Markers/groups (Lagorce, *et al.,* 2008)
- Flammability ← NIST estimation method (Kazakov, *et al.,* 2012)
- Critical temperature (T^{crit}) ← NIST estimation method (Kazakov, *et al.,* 2010)
- Stability ← E.g., peroxides (O-O), 3-member rings

Detailed evaluation of merits of top low-GWP candidates

- Develop representation of thermophysical properties
- Detailed cycle simulations accounting for heat transfer (includes model development)

Progress and Accomplishments

Lessons Learned:



Screen	Compound Count
• PubChem Compound Database	100 000 000
• Component atoms; only C, H, N, O, S, F, Cl, Br • Max. number of atoms in the molecule: 15	56203
• Global Warming Potential: GWP < 200	52265
• Toxicity	30135
• Flammability: lower flammability limit LFL > 0.1 kg/m^3	20277
• Critical temperature: 300 K < T^{crit} < 550 K (80 °F - 530 °F)	1728
• Stability	1234
• Critical temperature: 300 K < T^{crit} < 400 K (80 °F - 260 °F)	62

Note: the group of 62 dominated by molecules with a C=C bond

(39 halogenated olefins and 11 halogenated ethers)

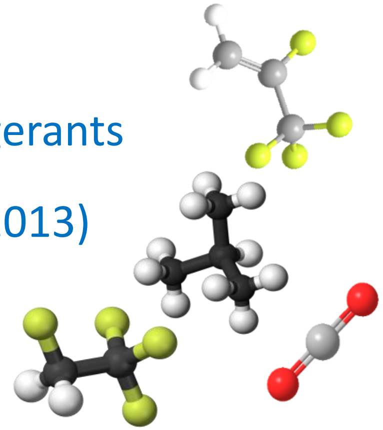
Concern: some fluids may have been passed over due to overly restrictive screens

Decision: repeat the screening with modified screens

Progress and Accomplishments

Accomplishments:

- Equation of State (EOS) parameters and cycle simulations for 62 refrigerants
- New estimation method of the acentric factor (NIST, Kazakov, *et al.*, 2013)
- New estimation method of T^{crit}, p^{crit}, C_p^0 (NIST, Kazakov, *et al.*, 2013)
- Second filtering through PubChem with modified screens using improved estimation methods



	Compound Count
• PubChem Compound Database	100 000 000
• Component atoms; only C, H, N, O, S, F, Cl, Br • Max. number of atoms in the molecule: 18	281 000
• Global Warming Potential: GWP < 1000	??
• Critical temperature: 300 K < T^{crit} < 400 K (80 °F - 260 °F) *(improved estimation)*	??
• Stability	

Trade-offs

- Toxicity ← EPA T.E.S.T. (toxicity estimation software tool)
- Flammability  ← (current estimation method of Kazakov)

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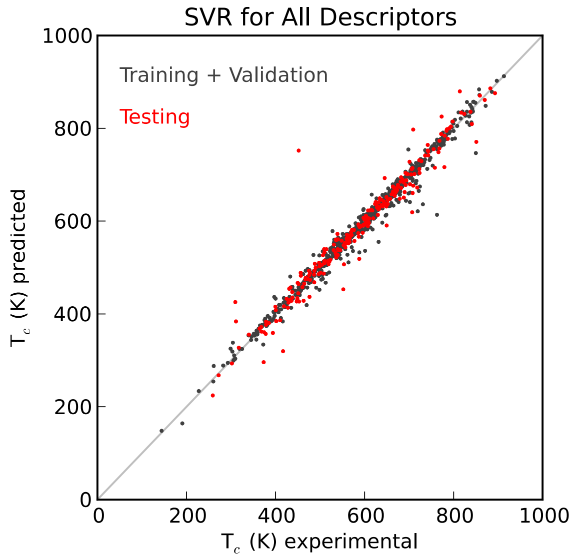
Development of New Correlations for Compound Screening and EOS Parameter Estimation

- **targeted properties**: T_c, p_c, and acentric factor
- **training data**: evaluated by the TRC ThermoDataEngine from all available raw experimental data; 900+ compounds total
- **3D molecular structures**: PM6 optimization (conformer with the lowest free energy)
- **descriptors (correlation parameters)**: computed from 3D structures with the open source chemoinformatics packages (OpenBabel, RDKit, CDK) and derived from QC calculations in-house; ~250 per compound
- **machine learning method**: Support Vector Regression (SVR)
- **feature (correlation variables) selection**: multi-objective (performance vs number of variables) genetic algorithm
- **result**: better coverage (includes acentric factor), faster evaluations (critical for screening)



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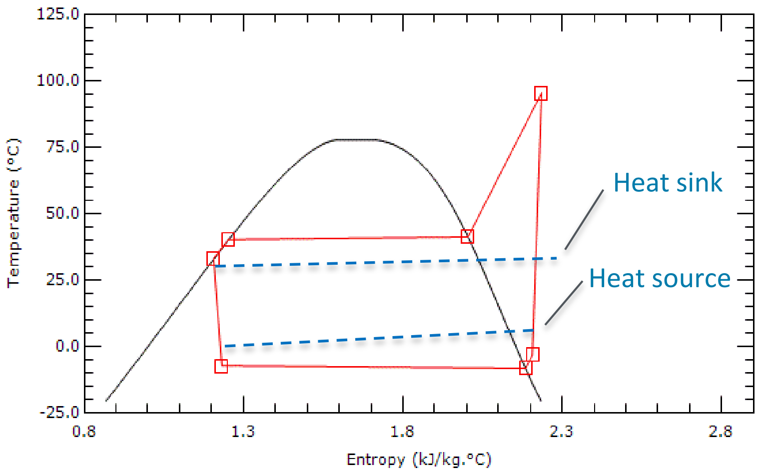
Progress and Accomplishments

Accomplishments:

- CYCLE_D-HX simulation model
  - Accounts for irreversibilities in heat exchangers
  - Compares refrigerants' performance at the same heat flux in the evaporator
    (Domanski and McLinden, 1992; Brown *at al*., 2004)



Model inputs:

- Inlet and outlet temperatures of heat sink and heat source
- ΔT or UA (overall conductance; generic HXs)

Model features:

- Accounts for heat transfer & pressure drop in heat exchangers in relation to a selected reference fluid
- Searches for optimum number of parallel refrigerant circuits in HX to maximize system COP (trade-off between improved refrigerant heat transfer and pressure drop penalty)
- Counter-flow, parallel-flow and cross-flow heat exchangers
- Refrigerant properties by REFPROP

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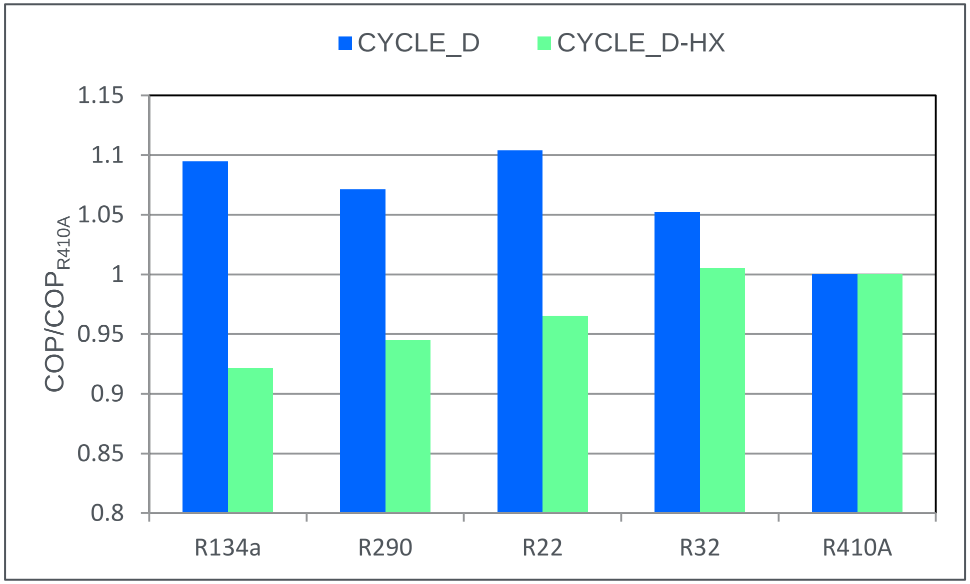
Progress and Accomplishments

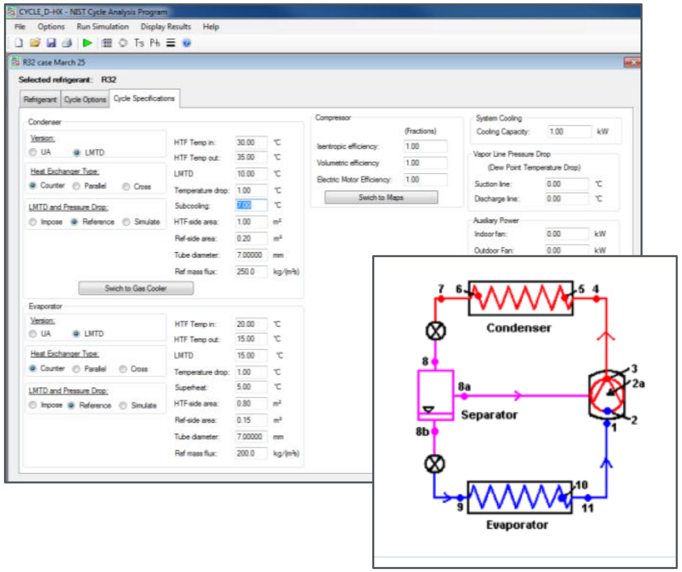
Accomplishments:

High pressure fluids show improved COP when evaluated in systems with optimized forced-convection evaporators and condenser (vs. pool-boiling and space-condensation heat exchangers).

Simulation methods:

- CYCLE_D: thermodynamic properties only
- CYCLE_D-HX: thermodynamic and transport properties with optimized refrigerant mass flux in the heat exchangers.





The preliminary CYCLE_D-HX results are consistent with a previous study involving CYCLE_D and a detailed NIST heat pump model (Domanski and Yashar, 2006).

Progress and Accomplishments

Market Impact:

- The published data helps industry in selecting next generation low-GWP refrigerants; (very significant interest in the study).

  The intermediate results have been broadly disseminated.

- CYCLE_D_HX model (product of this project) will be used to assess merits of low-GWP fluids currently considered by industry.

- The study will ‘close the book’ on refrigerants possibilities.

Awards/Recognition:

Four invited/keynote presentations of this work were given from 2012 through 2014.

Two additional keynote invitations have been accepted for 2014 and 2015.

Project Integration and Collaboration

Project Integration:

NIST/Boulder, CO: refrigerant properties and screening

NIST/Gaithersburg, MD: modeling and cycle analysis

Contacts with industry: Internet-based conferences with two equipment manufacturers (09/2013)

Meeting at ASHRAE Winter Conference with AHRI Low-GWP AREP participants (01/2014)

Partners, Subcontractors, and Collaborators:

J. S. Brown, Catholic Univ. of America, Washington, DC; cycle modeling

J. Wojtusiak, George Mason Univ., Fairfax, VA; evolutionary optimization

Communications:

A. Kazakow, et al. 2012. Ind. Eng. Chem. Res. 51:12537-12548

M. McLinden, et al. 2012. ASHRAE/NIST Refrigerant Conference (invited talk and paper)

M. McLinden, et al. 2013. 4th IIR Conference on Thermophysical Properties and Transport Processes of Refrigerants (keynote talk and paper)

P. Domanski, et al., 2013. 4th IIR Conference on Thermophysical Properties and Transport Processes of Refrigerants (talk and paper)

P. Domanski, et al. 2013. China Sustainable Refrigeration Summit (invited talk)

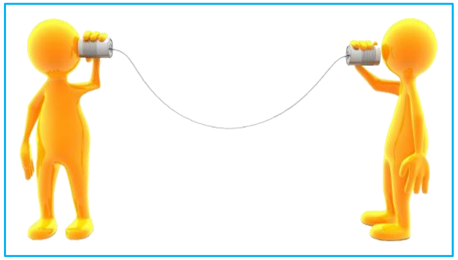
M. McLinden, et al., 2014. ASHRAE Winter Meeting (seminar talk)

P. Domanski, et al. 2014. ASHRAE Winter Meeting (seminar talk)

P. Domanski, et al., 2014. Int. J. Refrig. 38: 71-79

M. McLinden, et al. 2014. Int. J. Refrig. 38: 80-92

P. Domanski, et al. 2014. Univ. of Illinois/ACRC Meeting (keynote lecture)



Next Steps and Future Plans

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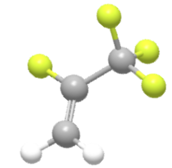
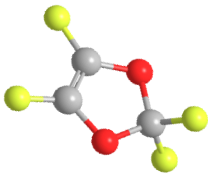


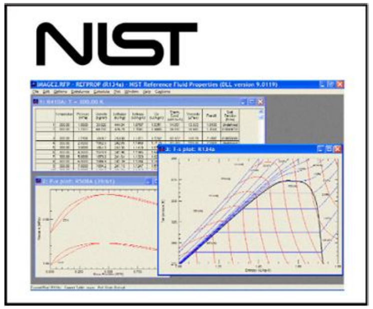
FY2014 tasks completing this projects

- Additional (second) filtering through PubChem with new screens and upgraded estimation methods (on going)
- Selection and complete simulations for 20 best refrigerants (including heat transfer)
- Technical paper with conclusions and recommendations of the project



Possible future work

- Experimental data to derive mixing parameters for AREP binary pairs
- Estimation scheme for mixing parameters for REFPROP (other binary pairs)
- Analysis of relative merits of low-GWP fluids considered in Low-GWP AREP accounting for both thermodynamic and transport properties.
- Measurements of two-phase heat transfer coefficient (evaporation, condensation)
- Performance of low-GWP refrigerants in optimized heat exchangers and systems



Project Budget

Project Budget: Starting date: February 1, 2011
Variances: Projects years run from February to January (following year)
Cost to Date: 72 % been expended as of March 31, 2014.
Additional Funding: NIST cannot cost share but the project builds on NIST expertise and existing refrigerant property and cycle models.

Budget History					
FY2011 – FY2013 (past)		FY2014 (current)		FY2015 (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
$1350k	0	$400k	0	0	0

References

Brown, J. S., Yana-Motta, S. F., Domanski, P.A., 2002. Comparative analysis of an automotive air conditioning system operating with CO_2 and R134a”, *Int. J. Refrig.*, 25(1), 19-32

Domanski, P.A., McLinden, M.O., 1992. A Simplified Cycle Simulation Model for the Performance Rating of Refrigerants and Refrigerant Mixtures, *Int. J. Refrig.*, 15(2), 81-88.

Domanski, P.A., Yashar, D., 2006. Comparable Evaluation of HC and HFC Refrigerants in an Optimized System. 7th IIR G. Lorentzen Conference on Natural Working Fluids, Int. Institute of Refrigeration, www.iifiir.org

Lagorce, D.; Sperandio, O.; Galons, H.; Miteva, M. A.; Villoutreix, B. D., 2008. FAF-Drugs2: Free ADME/tox filtering tool to assist drug discovery and chemical biology projects. *BMC Bioinformatics*, *9*, 396.

Midgley, T., 1937.From the periodic table to production. *Industrial and Engineering Chemistry, 29* (1), 241-244

Kazakov, A.; Muzny, C. D.; Diky, V.; Chirico, R. D.; Frenkel, M., 2010. Predictive correlations based on large experimental datasets: Critical constants for pure compounds. *Fluid Phase Equilib., 298*, 131-142.

Project Plan and Schedule

Project Schedule

Project Start: February 1, 2011

Projected End: April 2015

Legend: Completed Work; Active Task (in progress work); Milestone/Deliverable (Originally Planned); Milestone/Deliverable (Actual)

FY2011 (Start Feb 1, 2011): Feb - Apr | May - July | Aug - Oct | Nov - Jan
FY2012 (Start Apr 27, 2012): May - Jul | Aug - Oct | Nov - Jan | Feb - Apr
FY2013 (Start Apr 1, 2013): Apr - Jun | July - Sep | Oct - Dec | Jan - Mar
FY2014 (Start Apr 1, 2014): Apr - Jun | July - Sep | Oct - Dec | Jan - Mar

Task
Past Work
Task 1: Exploration of thermodynamic space
1.1 Adapt cycle model to ECS fluid model
1.2 Implement evolutionary algorithm into the cycle
1.3 Determine optimum properties; technical paper
Task 2: Property predictions
2.1 Identify 1000 fluids for the study (expanded to 56 000)
2.2 Prediction of GWP; technical paper
2.3 Predictions of additional properties; technical paper
2.4 Develop simplified EOS for 1200 candidates
2.5 Cycle simulations for 1200 candidates (limited EOS)
2.6 Develop detailed EOS for top 100 candidates
Task 3. Selection of most promising candidates & complete cycle simulations
3.1 Simulations of existing fluids
3.2 Selection of 100 most promising candidates (expanded from 20)
3.3 Detailed cycle simulations of top 100 candidates (expanded from 20)
Task 4. Development of new cycle model (including heat transfer)
4.1 Implement heat source & heat sink (counter, parallel, cross-flow)
4.2 Implement HX/UA heat exchager model
4.3 Implement refrigerant circuitry optimization
Task 5. "Inverse" problem (construct fluids)
5.1 Evaluate approaches
Current/Future Work
Task 2: Property predictions
2.1 (Expanded) Additional screening with upgraded property screens
2.7 Thermodynamic and transport properties for top 20 fluids
Task 3. Selection of most promising candidates & complete cycle simulations
3.4 Selection of final 20 candidates
3.5 Complete simulations of final 20 candidates (include heat transfer)
3.6 Technical paper (conclusions and recommendation of the project)
Task 4. Development of new cycle model (including heat transfer)
4.4 Test and debug program
4.5 Demonstrate utility/validate CYCLE_D_HX