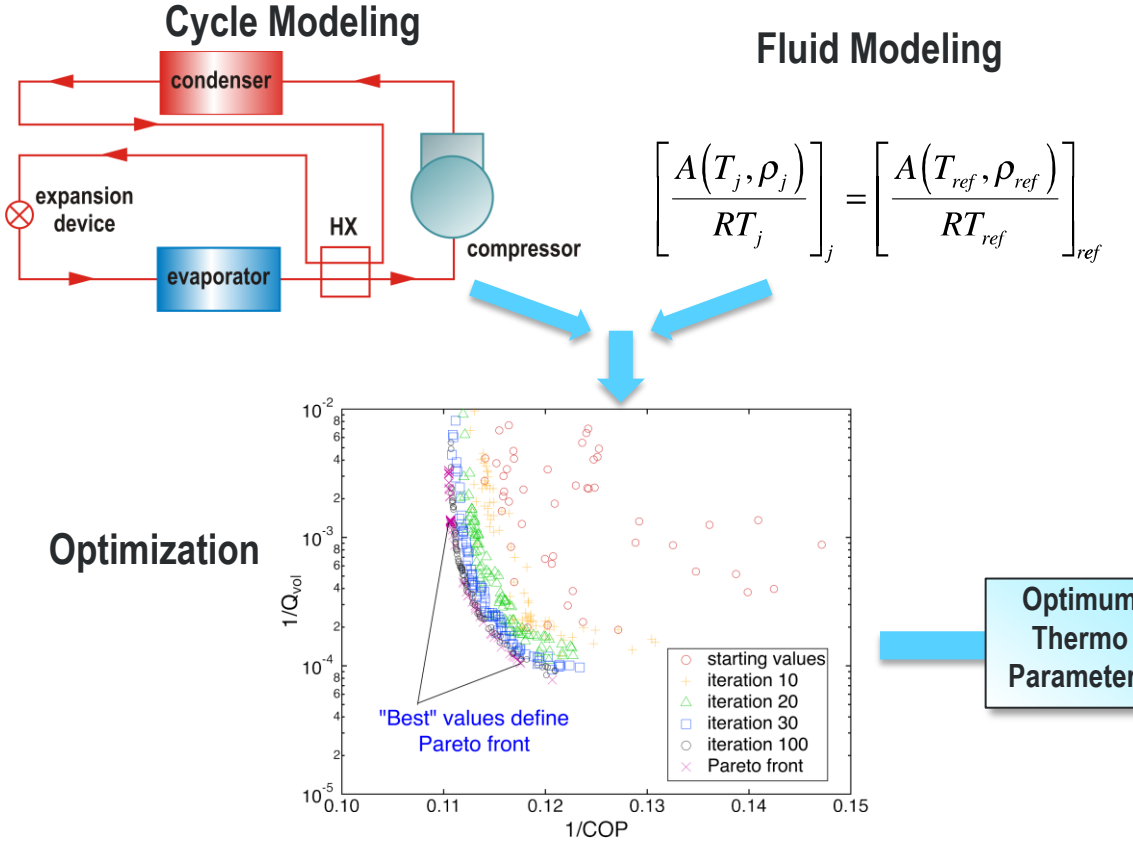

Thermodynamic Evaluation of Low-GWP Refrigerants

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April 3, 2013

Purpose & Objectives

Problem Statement: HFC refrigerants face restrictions:
U.S./Canada/Mexico proposal to Montreal Protocol (85 % cut)
EU regulations likely on all application areas (79 % cut)

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

Impact of Project:

- Identify best alternatives
- Identify cycle modifications needed to maximize efficiency

Project Focus:
Refrigerant choice affects equipment efficiency

Approach: Overall Project

Multi-Pronged Approach:

- Thermodynamic analysis:
  - What are the limits to performance?
  - What fluid parameters are needed to approach limits?
- Screening of candidate molecules:
  - What are the possibilities for low-GWP fluids?
- Combining the approaches:
  - Optimum parameters guide screening of candidates

To answer the fundamental question:

- Can we do better than current (and recently proposed) refrigerants?

Approach: Thermodynamic Cycle Analysis

Modify NIST CYCLE_D model

Investigate a variety of cycles:

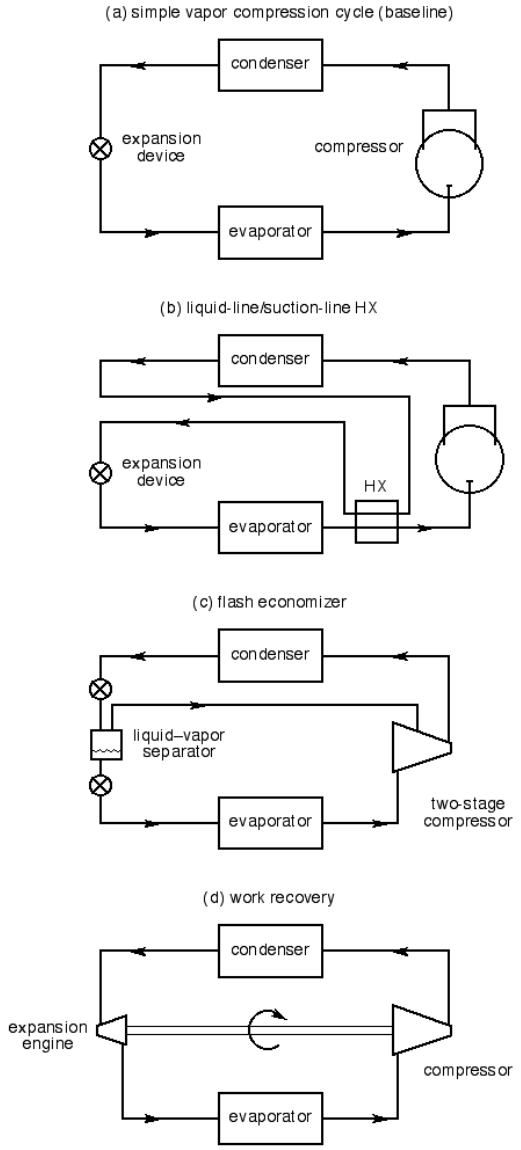
- ideal vapor compression cycle
- internal LL/SL heat exchanger
- single-stage flash economizer
- work recovery device

…and a variety of applications:

- cooling (T_{evap} = 10 ˚C, T_{cond} = 40 ˚C)
- heating (T_{evap} = –10 ˚C, T_{cond} = 30 ˚C)
- refrigeration (T_{evap} = –20 ˚C, T_{cond} = 30 ˚C)

Define what is possible:

- explore “Thermodynamic Space”
- define optimum refrigerant parameters



Approach: Thermo Properties by Extended Corresponding States

Concept: Thermo properties similar when scaled by critical parameters, T_{crit}, p_{crit}

Properties = *f*(9 parameters):

4 fluid parameters:

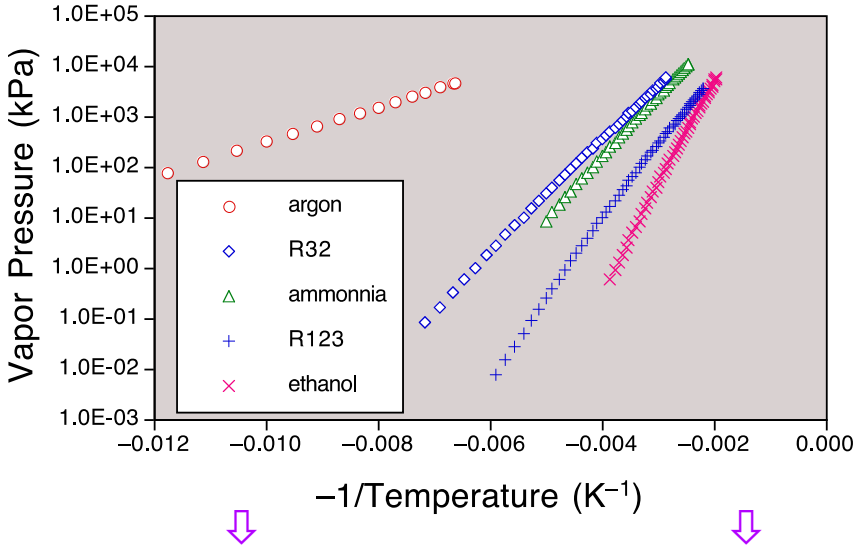
(T_{crit}, p_{crit}, C_p^o, ω)

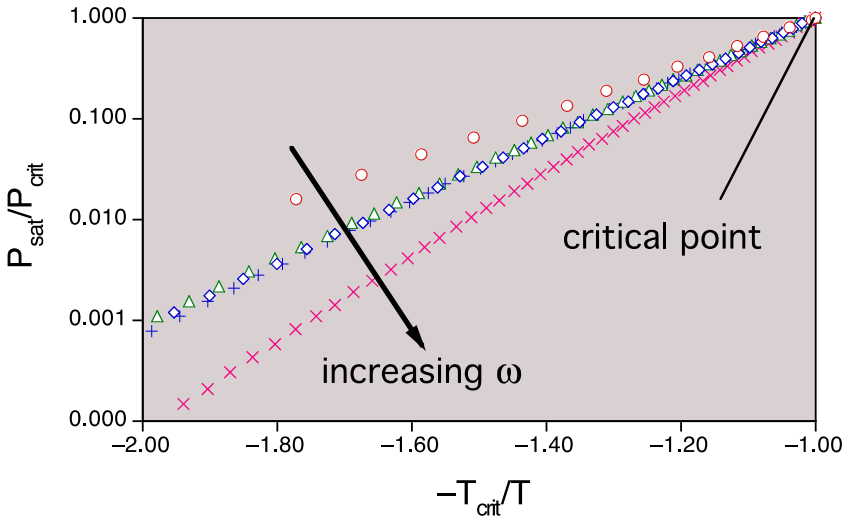
+ 5 model parameters

Amenable to optimization

Distinctive characteristics:

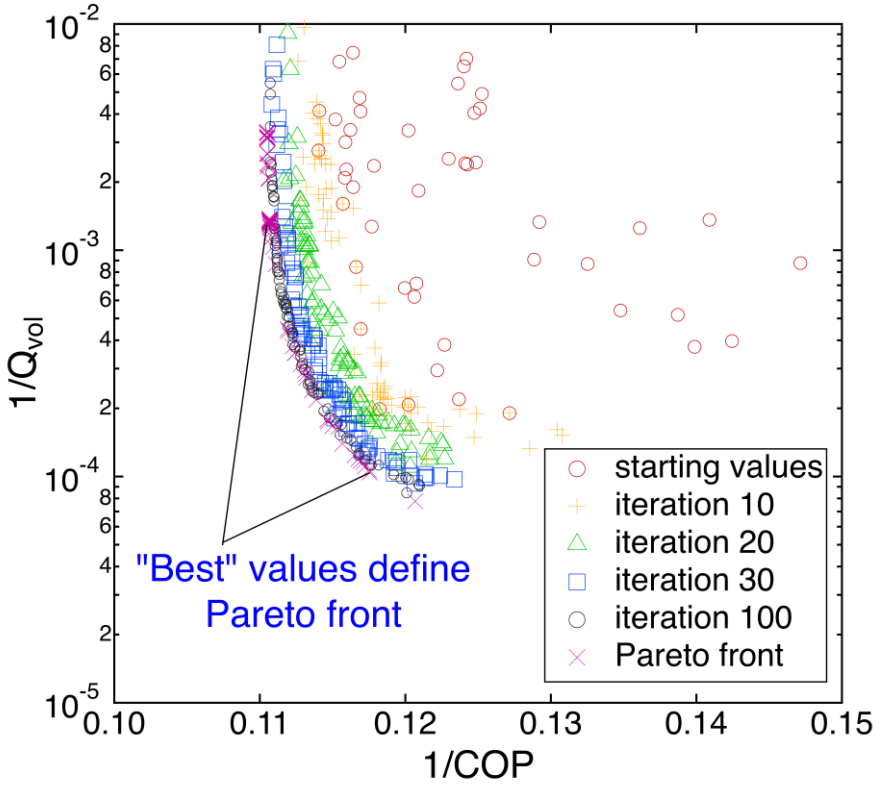
simulate hypothetical fluids (not constrained by real fluids)





Approach: Optimization by Evolutionary Algorithms

- Hypothetical fluids defined by sets of ECS parameters
- Starting "generation" is random
- Compute COP and Q_{vol}
- Evolutionary algorithm selects "children" for next iteration
- 100,000 hypothetical fluids for each cycle/application
- "Best" COP–Q_{vol} pairs define the Pareto Front



Accomplishments and Progress: Thermodynamic Limits to Performance

Simulations yield clear Pareto front

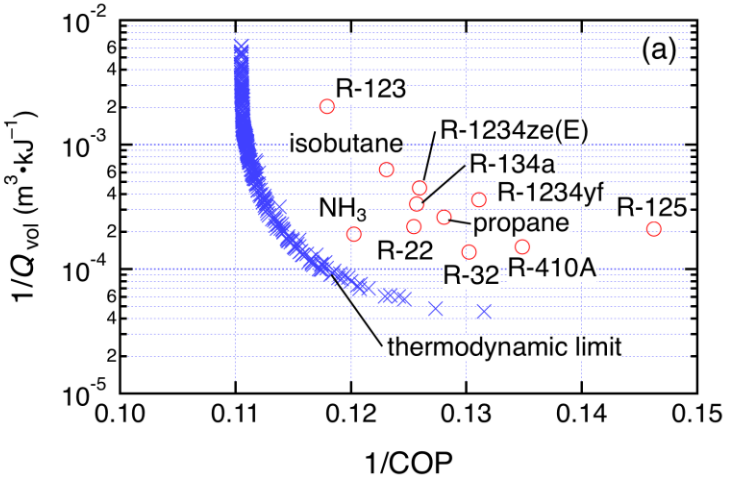
Current fluids well away from front:
- better fluids at least *allowed*

Cycle with internal HX:
- Pareto front (thermodynamic limit) shows better performance, effect for real fluids varies

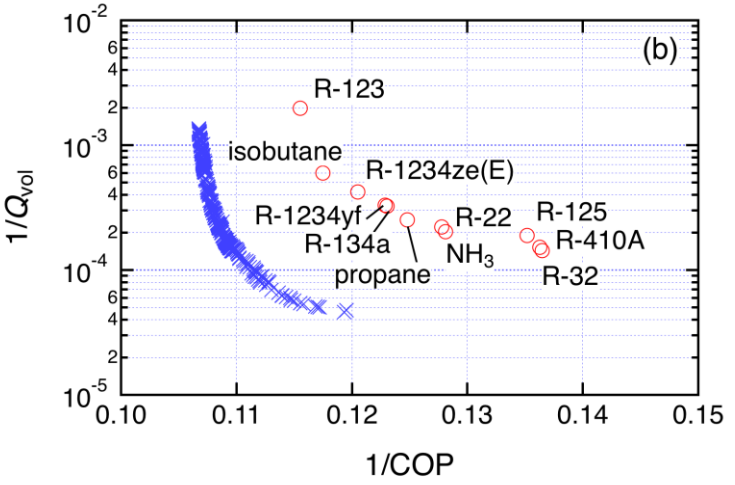
Cycle with work recovery:
- Approaches Carnot limit for some fluids

Distinctive characteristics:
- define efficiency/capacity limits considering fluid properties:
  - –not simply the Carnot limit
  - –not a tabulation of known fluids

Baseline cycle



Cycle with LL/SL heat exchange

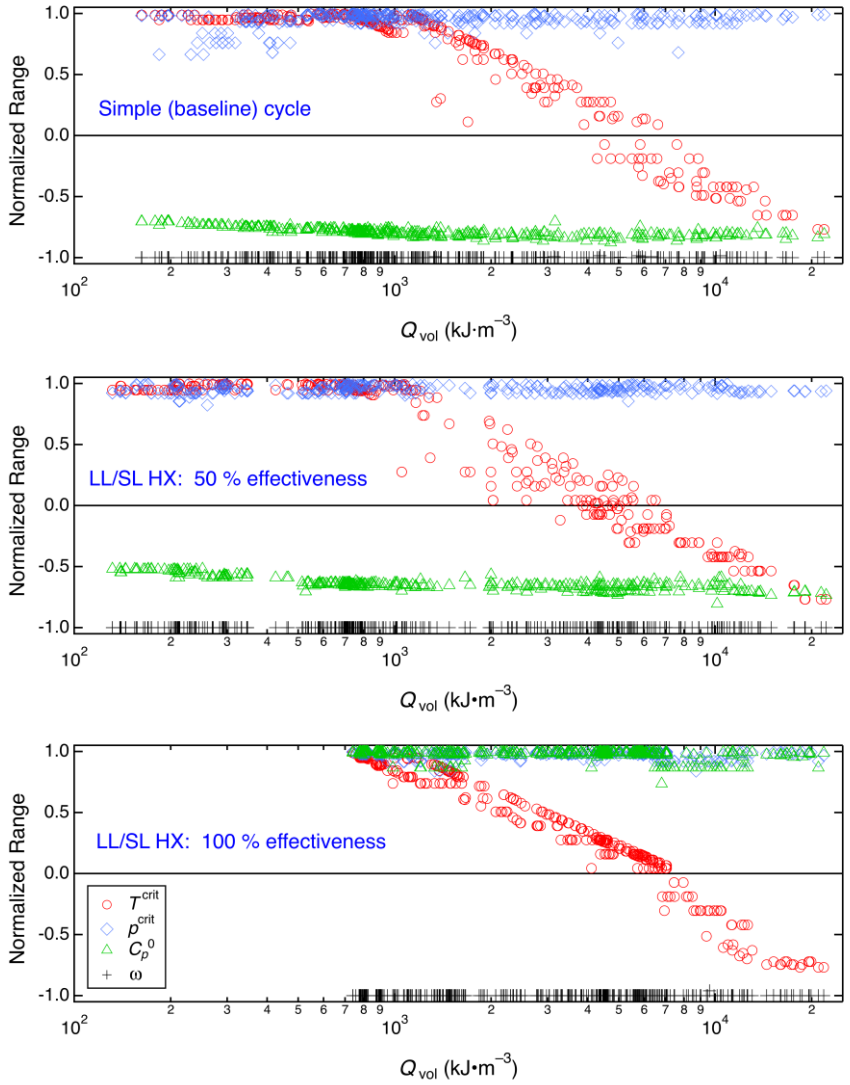


Accomplishments and Progress: Optimum Thermodynamic Parameters

Parameters along Pareto front:

- T_{crit}: COP vs. capacity tradeoff
- p_{crit}: high values optimal
- $\overline{7}$ (slope of vapor pressure): low values optimal
- C_p^o (vapor heat capacity): low values for simple cycle higher values for cycles w/ LL/SL HX or work recovery
- other parameters investigated: lesser effects

Adjust the cycle to fit the fluid

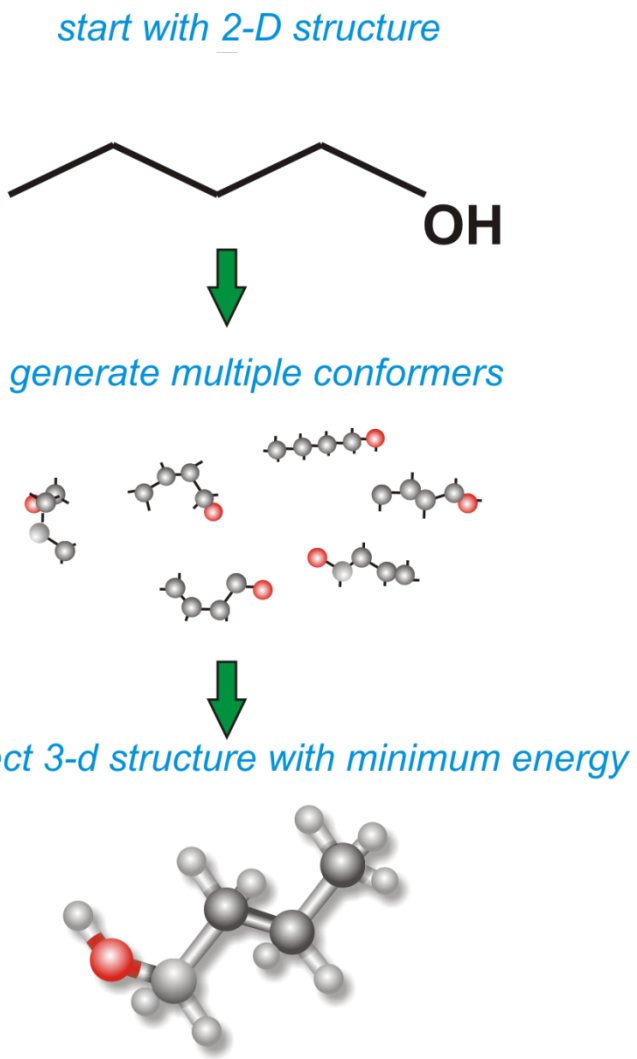


Approach: Properties from Molecular Structure

Fluids from PubChem database (NIH)
- listing of 100,000,000 molecules
- Select: 15 or fewer atoms in molecule
- only C, H, N, O, S, F, Cl, Br (Midgley, 1937)
- Yields: 56,203 candidate molecules
- (original goals were 1,000 then 20,000)

Optimize 3-D structure of each molecule
- by quantum mechanical methods

Estimate properties from 3-D structure:
- GWP—new method
- Toxicity screen—literature method
- Flammability—new method
- Critical *T, p*—recent NIST method



Accomplishments and Progress: Estimated GWP for 56000 Candidates

Most extensive set of GWP values
(literature values for 103 fluids)

RMS deviation = factor of 3
(adequate for screening)

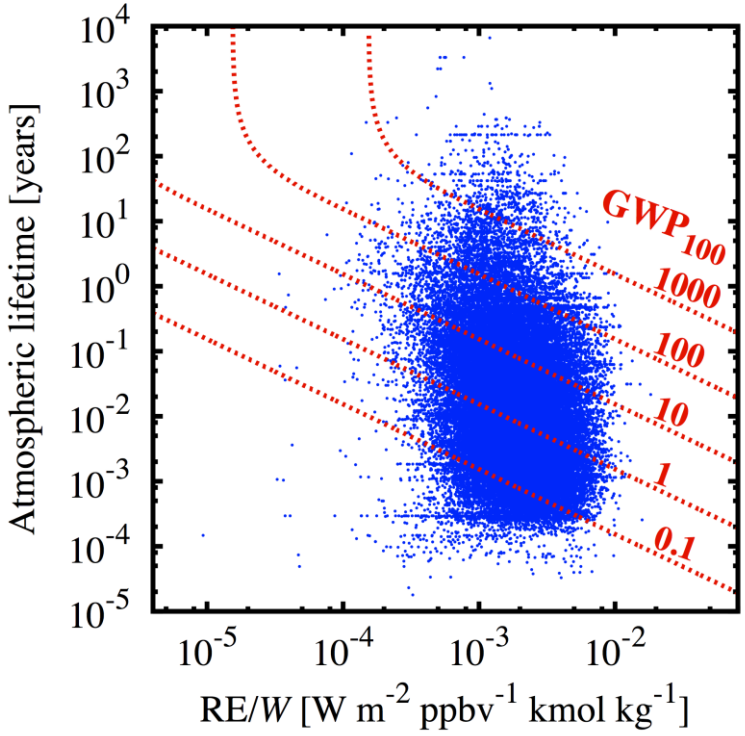
93 % have GWP_{100} < 200
GWP alone not sufficient filter

Toxicity screen: 30,125 remain

LFL > 0.10 kg/m^3: 20,277 remain

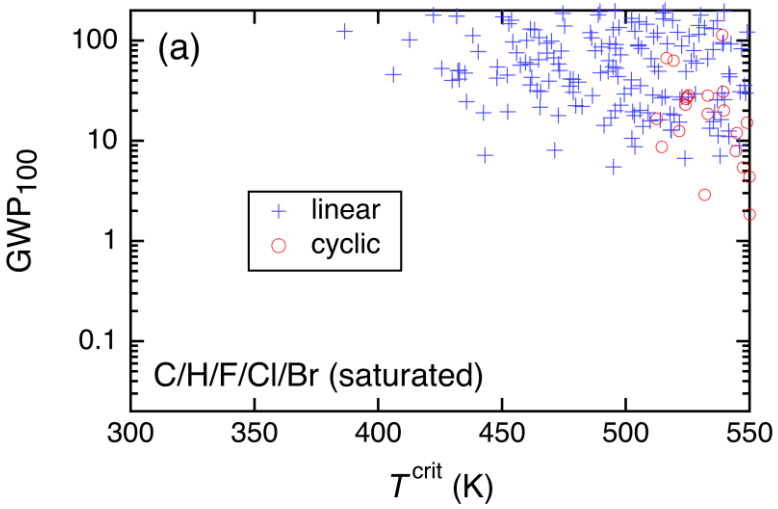
300 K < T^{crit} < 550 K: 1728 remain

Screen out unstable groups: (*e.g.*, peroxides)
1234 candidates to evaluate

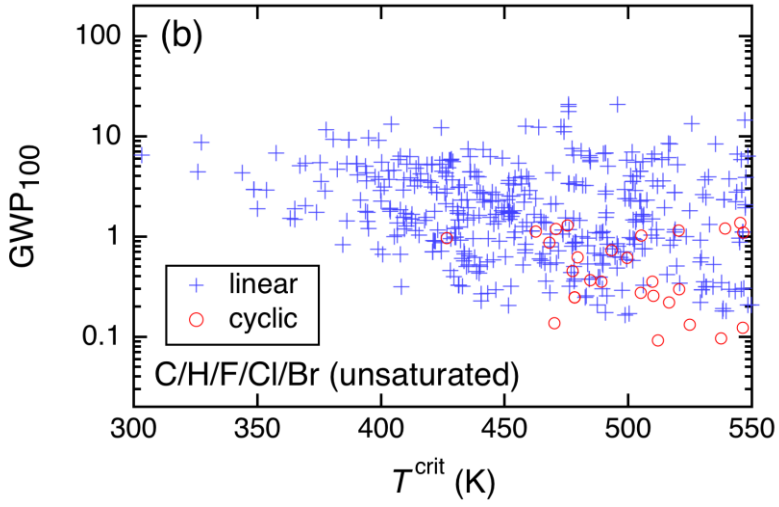


Accomplishments and Progress: 1200 Candidates Pass Screening

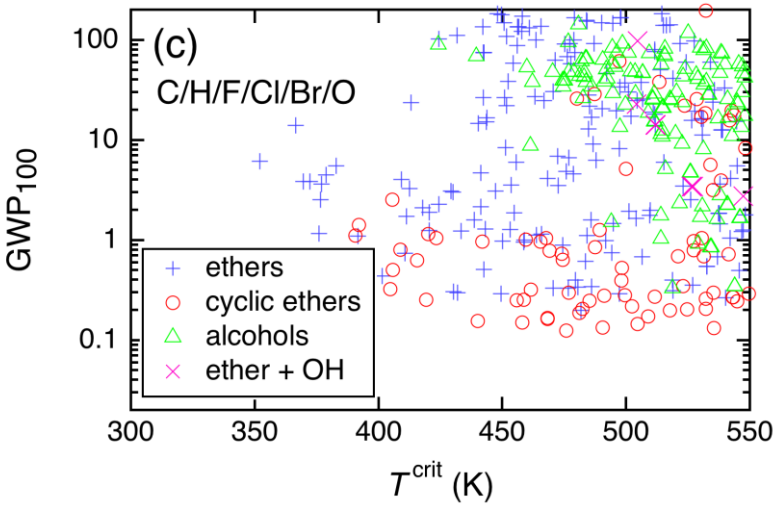
Halogenated alkanes (*e.g.*, HFCs)



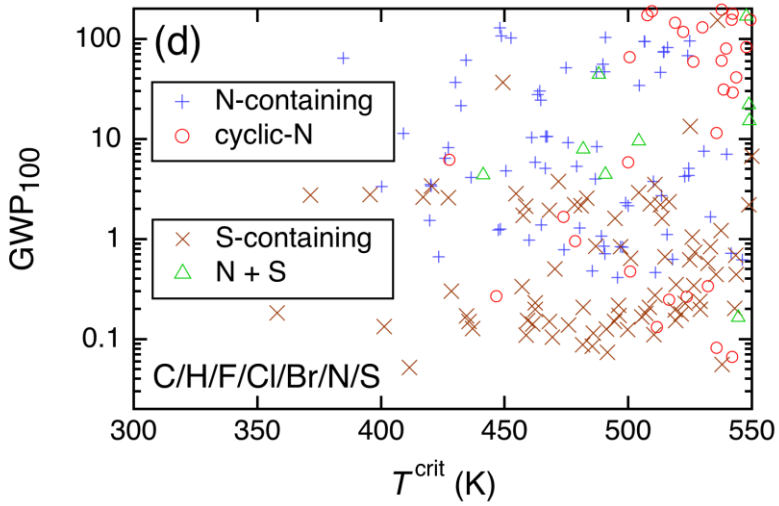
Halogenated alkenes (*e.g.*, HFOs)



Halogenated oxygenates (*e.g.*, ethers)



Nitrogen & sulfur compounds



Accomplishments and Progress: 62 Candidates for Further Evaluation

300 K < T^{crit} < 400 K

needed for common equipment types

62 candidates:

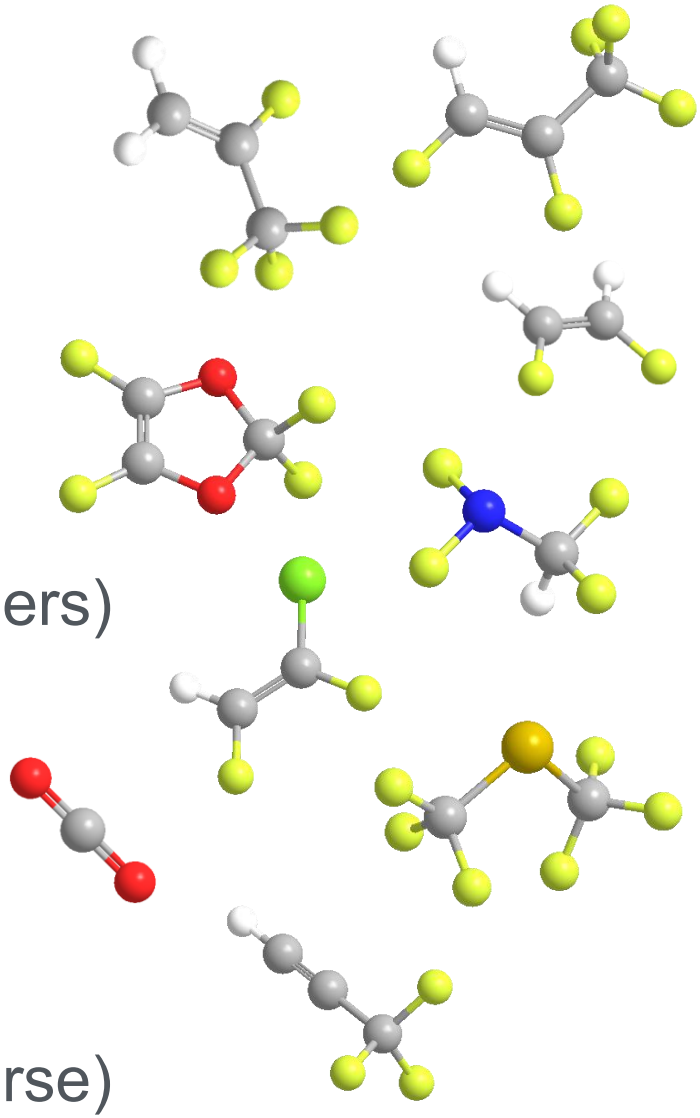
- 1 halogenated alkane (R-152a)
- 39 halogenated olefins (*e.g.*, HFOs)
- 11 halogenated ethers
- 4 halogenated amines
- 3 sulfur compounds (1 thiol, 2 thioethers)
- 1 inorganic (CO_2) (+ ammonia)
- 3 halogenated alkynes (triple bond)

Further evaluation (current effort):

thermo parameters *vis a vis* optimums

chemical stability

toxicity (initial tox screen was very coarse)



Project Plan, Schedule & Budget

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Project Dates: Feb 1, 2011 — Jan 31, 2014

Schedule slippage due to expanded scope & delay in FY'12 & '13funds:

- Fluids considered: 1000 (FY'11) ➔ 20,000 (FY'12) ➔ 56,000 (final)
- Range of fluids: only fluorocarbons (FY'11) ➔ also Cl, Br, N, S (final)

Budget: 4 years × $450k/year; no additional funding (NIST cannot cost-share)

- $740k (41 %) spent as of March 18, 2013

Summary	
WBS Number or Agreement Number	
Project Number	
Agreement Number	

Legend
Work completed
Active Task
Milestones & Deliverables (Original Plan)
Milestones & Deliverables (Actual)

	FY2011 (began Feb 1, 2011)				FY2012 (began Apr 27, 2012)				FY2013 (begins ~Apr 1, 2013)			
Task / Event	Feb–Apr	May–July	Aug–Oct	Nov–Jan	May–Jul	Aug–Oct	Nov–Jan	Feb–Apr	Apr–Jun	Jul–Sep	Oct–Dec	Jan–Mar
Task 1: Exploration of thermodynamic space												
1.1 Adapt cycle model to ECS fluid model												
1.2 Implement evolutionary algorithms into cycle model												
1.3 Determine optimum properties; present technical paper												
Task 2: Property predictions												
2.1 Identify 1000 fluids for study (expanded to 20,000 then to 56,000)												
2.2 Prediction of GWP; present technical paper												
2.3 Prediction of additional properties; present technical paper												
Task 3: Selection of most promising candidates & detailed cycle simulations												
3.1 Simulation of existing fluids												
Task 5: "Inverse" problem (construct fluids)												
5.1 Evaluate approaches												
Current and future research												
Task 2: Property predictions												
2.1 Develop simplified EOS for 1200 candidates												
2.2 Cycle simulation for 1200 candidates												
2.3 Develop detailed EOS for top 100 candidates (expanded from 20 candidates)												
Task 3: Selection of most promising candidates & detailed cycle simulations												
3.1 Selection of top 100 candidates (expanded from 20)												
3.2 Detailed cycle simulation of top 100 candidates (expanded from 20)												
Task 4: Development of new cycle model (including heat transfer)												
4.1 Implement heat source and heat sink (counter, parallel, and cross-flow)												
4.2 Implement HX/UA heat exchanger model												
4.3 Implement refrigerant circuitry optimization												
4.4 Test and debug program												

Project Integration, Collaboration & Market Impact

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Partners, Subcontractors, and Collaborators:

J. Steven Brown, Catholic University of America, Washington, DC
Janusz Wojtusiak, George Mason University, Fairfax, VA
Chemical manufacturers not participating because of I.P. concerns

Technology Transfer, Deployment, Market Impact:

We will not develop a new refrigerant, *but* we will identify the possibilities—if HFO-1234yf is the best you can do, so be it.
Our work will influence the choice of refrigerant and cycle modifications in next 3–5 years with impacts on efficiency.

Communications & Recognition:

A. Kazakov, et al., 2012. *Ind. Eng. Chem. Res*. **51**: 12537-12548
M. McLinden, et al., 2012 ASHRAE/NIST Refrigerants Conference (invited talk + paper)
M. McLinden, et al., 2013. 4th IIR Conf. on Thermophysical Properties and Transport Processes of Refrigerants (keynote talk + paper)
P. Domanski, et al., 2013. 4th IIR Conf. on Thermophysical Properties and Transport Processes of Refrigerants (talk + paper)

Significant media reporting of Kazakov paper

Chemical & Engineering News
September 24, 2012

NIST APPLIES COMPUTATIONAL METHODS TO REFRIGERANTS

By applying large-scale computational techniques used in drug discovery, NIST has identified more than 1,200 chemicals as candidates for development as refrigerants with low global warming potential (GWP). The compounds selected also have performance and safety characteristics appropriate for refrigerants, according to a report published this month in *Industrial & Engineering Chemistry Research* (DOI: 10.1021/ie3016126). NIST researchers began with more than 56,000 compounds, each with 15 or fewer atoms, and used a molecule's structure to estimate its GWP. After screening out those with high GWP, they filtered results to select for compounds estimated to have low toxicity and flammability and with a critical temperature suitable for refrigeration applications. NIST chemist Michael Frenkel says the effort is designed to help industry make the switch from today's refrigerants with high GWP to those with low GWP. In the next phase of the work, NIST researchers will narrow down the 1,200 compounds, which include fluorinated olefins, to 25 or so for detailed study, NIST says.—CH

Next Steps and Future Plans

Relax screening criteria
- compare moderate GWP & flammable with low-GWP

Evaluate cycle performance of 1200 candidates in effect,
- apply an efficiency screen to candidates
- select ~100 candidates for detailed study

New & expanded cycle model
- thermodynamic & transport properties
- heat transfer processes considered
- enhanced heat transfer *vs*. pressure drop penalty

Apply to 100 fluids identified in screening
- identify tradeoffs & best candidates

Possible follow-on work:
- Apply methodology to other applications (high-temperature heat pumps, organic Rankine power cycles, etc.)
- Investigate refrigerant blends
- Experimental property measurements for best candidates