Non-toxic, High-performance Ultra-Low Temperature Fluids for Use in a Single-Loop Control System

Andrew Wagner
Ted Amundsen
J. Michael Cutbirth, Ph.D
Mainstream Engineering Corp.

Presented By
(J. Michael Cutbirth)

Thermal & Fluids Analysis Workshop
TFAWS 2017
August 21-25, 2017
NASA Marshall Space Flight Center
Huntsville, AL

Agenda

- Design criteria
  - Baseline fluids
- Heat transfer fluid requirements
- Design/Selection Approach
  - Cheminformatics modeling
    - Thermal conductivity, viscosity, heat capacity, density boiling point, flash point, and melting point
    - Selection criteria
- Experimental Results
- Future Work

Design Criteria

- Assumptions:
  - Fully developed flow in radiator (hydraulic and thermal)
  - System temperature drop, heat load, and radiator geometry held constant
  - Fluid temperature range based on potential mission profiles
- Figures of Merit
  - Pumping ability:

$$\frac{\mu_{-90}}{\mu_{20}}$$

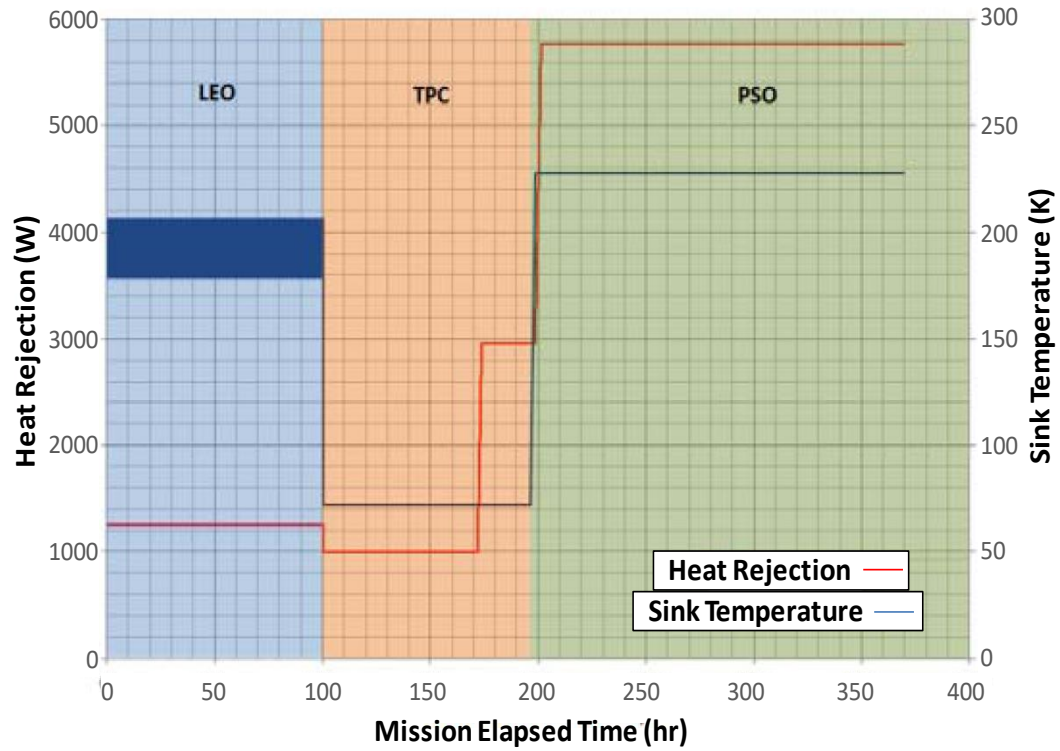
  - Heat transfer:

Laminar $$\frac{k_f}{k_{base}}$$

Turbulent $$\left(\frac{\mu_{base}}{\mu_f}\right)^{0.5}\left(\frac{\rho_f}{\rho_{base}}\right)^{0.33}\left(\frac{k_f}{k_{base}}\right)^{0.67}$$

  - Pump work:

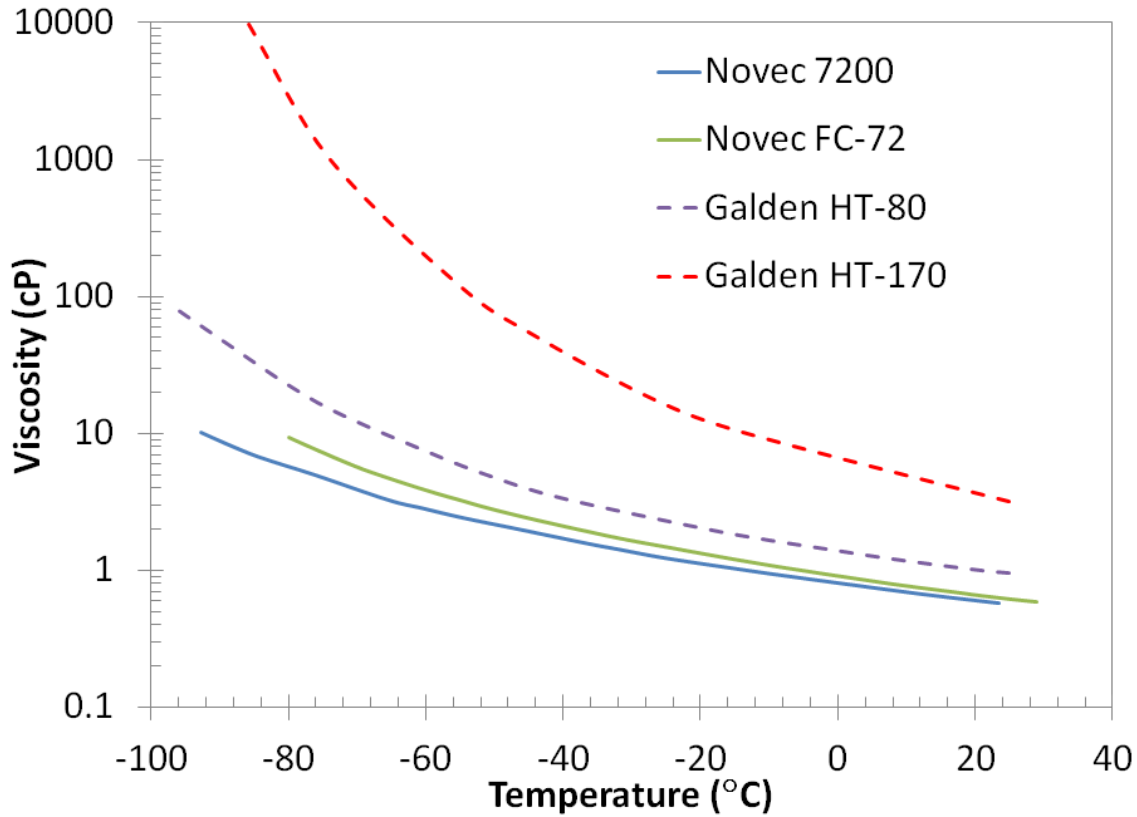
Laminar $$\left(\frac{(\rho c_p)_{base}}{(\rho c_p)_f}\right)^2\left(\frac{\mu_f}{\mu_{base}}\right)$$



Cognata, T.J., Hartl, D.J., Sheth, R., and C. Dinsmore. "A Morphing Radiator for High-Turndown Thermal Control of Crewed Space Exploration Vehicles", 23rd AIAA/AHS Adaptive Structures Conference, AIAA SciTech, (AIAA 2015-1509)

Baseline Fluids - Viscosity

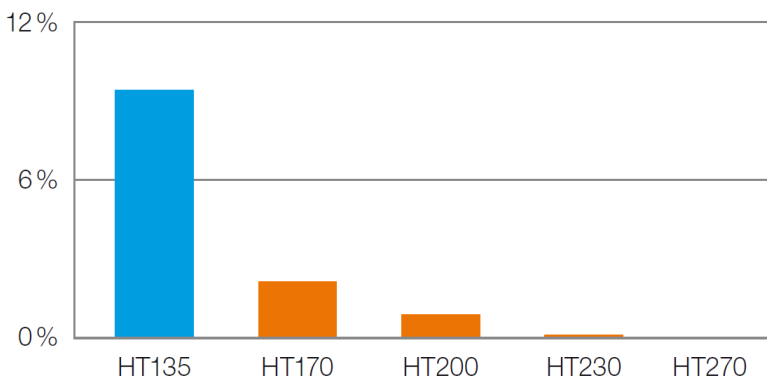
- Initial baseline
  - Galden HT-170
    - Perfluoropolyether
    - Molecular weight: 760
    - Temperature range: -97 to 170 °C
- Current baseline
  - Novec 7200
    - Ethoxy-nonafluorobutane
    - Molecular weight: 264
    - Temperature range: -138 to 76 °C
- Future baselines
  - Novec FC-72
    - Perfluorotri-n-butylamine
    - Molecular weight: 338
    - Temperature range: -90 to 56 °C
  - Galden HT-80
    - Perfluoropolyether
    - Molecular weight: 430
    - Temperature range: -110 to 80 °C



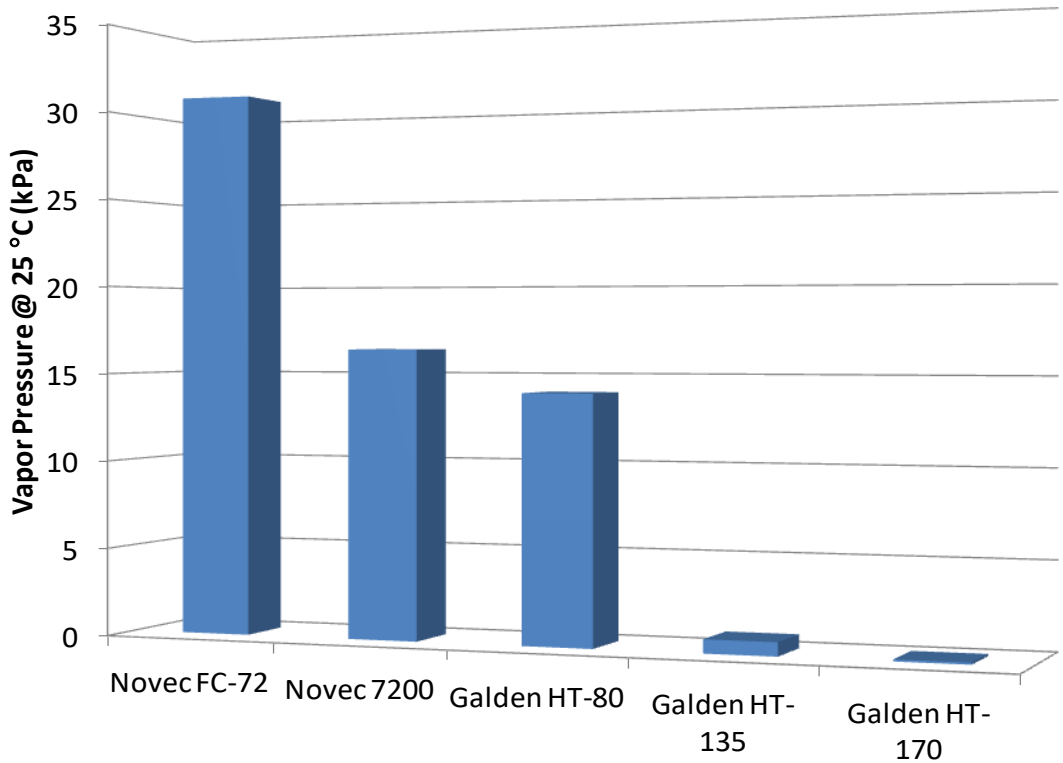
Baseline fluid viscosity as a function of temperature
[*from Manufacturer's specification sheets*]

Baseline Fluids – Vapor Pressure

- Evaporative Loss: Novec 7200
  - 5.7 kg leak into 13 m^3 crew cabin results in a vapor concentration of 43,000 ppm (4.3%)
  - Potential side affects at that concentration:
    - moderate respiratory irritation
    - moderate central nervous system depressant effects
    - moderately harmful effects to liver and kidneys
    - possible induction of cardiac arrhythmias



Evaporative loss comparison after 8 hrs @ 40 °C (JIS C2101)
[http://www.behlke.com/pdf/datasheets/galden_ht135.pdf]

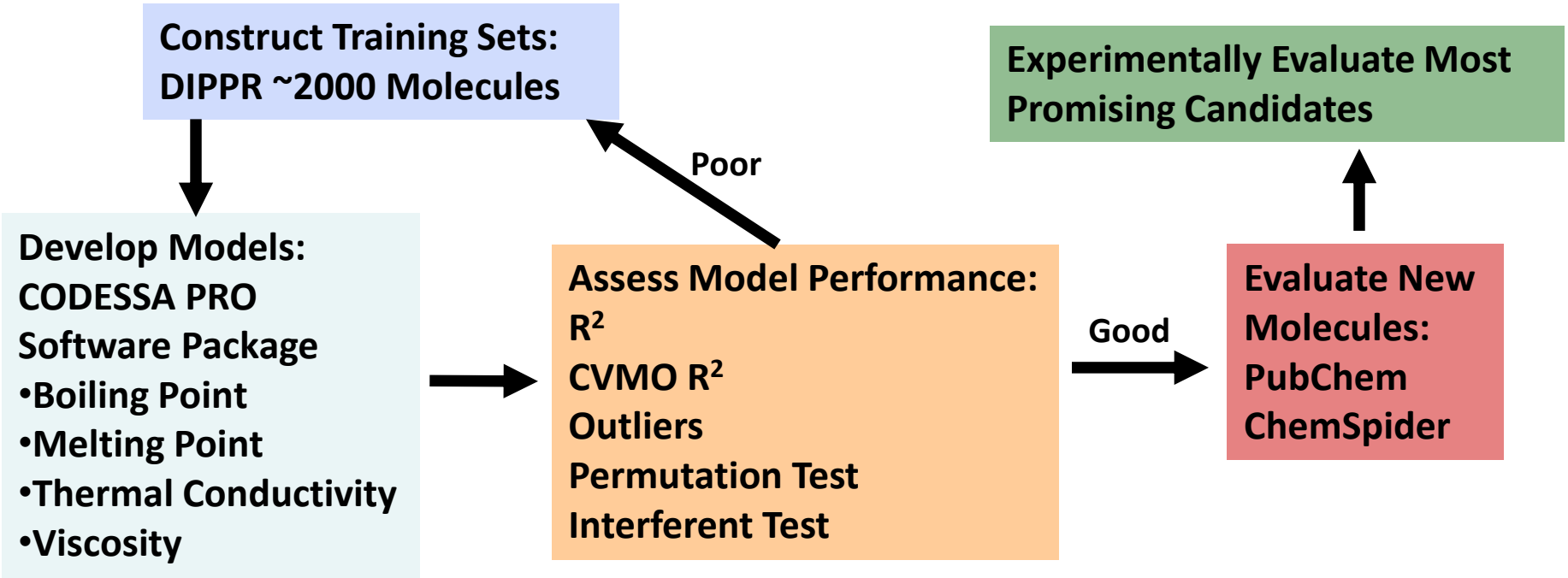


Vapor pressure comparison between baseline fluids
[from manufacturer's specification sheets]

Heat Transfer Fluid Requirements

- Goal: thermo-physical properties of H_2O with freezing point of N_2
  - Develop an improved Heat Transfer Fluid (HTF) for a single-loop TCS
    - Develop a low-freezing, non-toxic, non-corrosive, non-flammable HTF with favorable thermal properties to NASA's baseline.
- Specific Objectives Supporting Overall Goal
  - Develop HTF with pour point below –90 °C
  - Demonstrate pumpable fluid at –90 °C to avoid stagnation in radiator
    - $\mu_{-90^\circ C} / \mu_{20^\circ C}$ less than 25 (Novec 7200 = 12, Galden HT-170 = 212)
  - Demonstrate HTF with health and flammability ratings of 0 or 1
    - Demonstrate a flash point greater than 90 °C
    - Demonstrate fluid for use in cabin with advanced toxicity studies
    - Demonstrate boiling point above 150 °C to minimize inhalation hazard
  - Demonstrate HTF in thermal test loop with turbulent figure of merit relative to Novec 7200 greater than 0.9
  - Demonstrate HTF compatible with Al6061, Ni201, BNi-2, SS347, Ti6Al-4V, EPDM, PTFE, and FEP

Cheminformatics - Overview



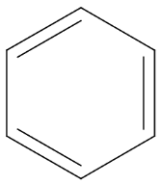
1. Identify properties of interest
   - Melting, boiling, and flash points, etc.
2. Develop data set(s)
   - 1200 compounds with known properties
     - 500 for calibration; 700 for prediction
3. Obtain SMILES representation of data
4. Test modeling properties individually or multiple at once
5. Update model with the entire 1,200 known set and predict remaining 9,000 compounds with unknown properties
6. Trim data set based on requirements and find the new fluid

Cheminformatics – Descriptors

- Quantitative Structure Property Relationship
  - Relates molecular descriptors to chemical property

$$y = a_1x_1 + a_2x_2 + \cdots + a_nx_n$$

- Molecular descriptors
  - Topological, geometrical, hybrid, constitutional, protein, electronic (289 descriptors total)
  - Examples:
    - Molecular weight
    - Bond count
    - Element count
    - Dipole moments
    - HOMO and LUMO energies
- CODESSA software used for descriptor calculation and selection (including quantum chemical descriptors)



Reference Data

SMILES

c1ccccc1

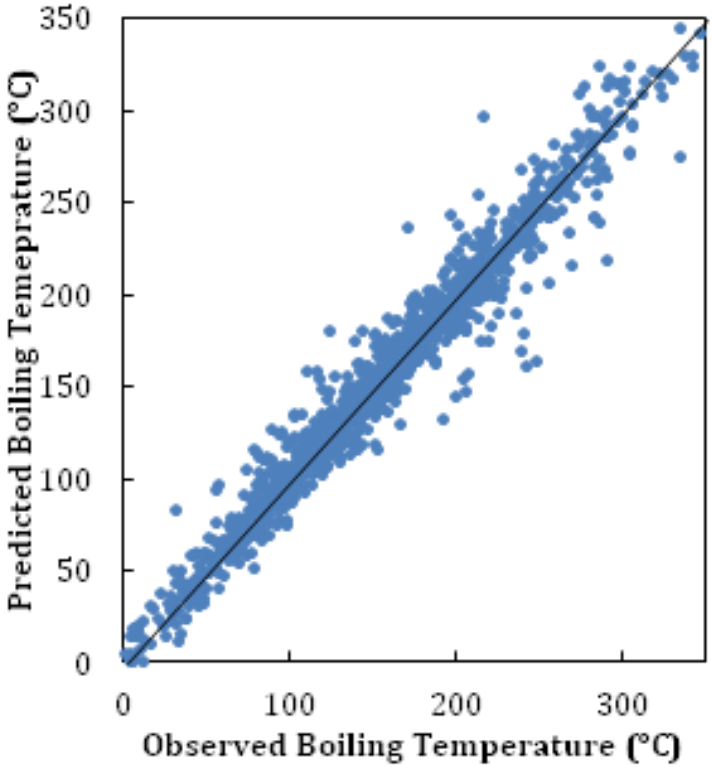
Boiling Point 80 °C

Atomic polarizability	14.56
OH e-state fragments	0
Intermolecular interaction index	12.15
Chain index	0.037
Number of bonds	6
Molecular shape index	2.22
CH e-state fragments	6
Molecular weight	78.05

etc…

Cheminformatics – Property Model

Boiling Point Model



Final QSPR model for boiling point based on the calibration made from 500 model compounds and prediction of700 known compounds

Model Parameters	Value
R^2	0.95
RMSEC	18
RMSEP	20
Range	350

Key Descriptors	Variance	Relative Weighting
Kier&Hall Index (order 2)	14	1
Polarity parameter / square distance (Zefirov)	33	0.8
HA dependent HDCA-2 (Zefirov PC)	18	0.3

Cheminformatics – Model Results

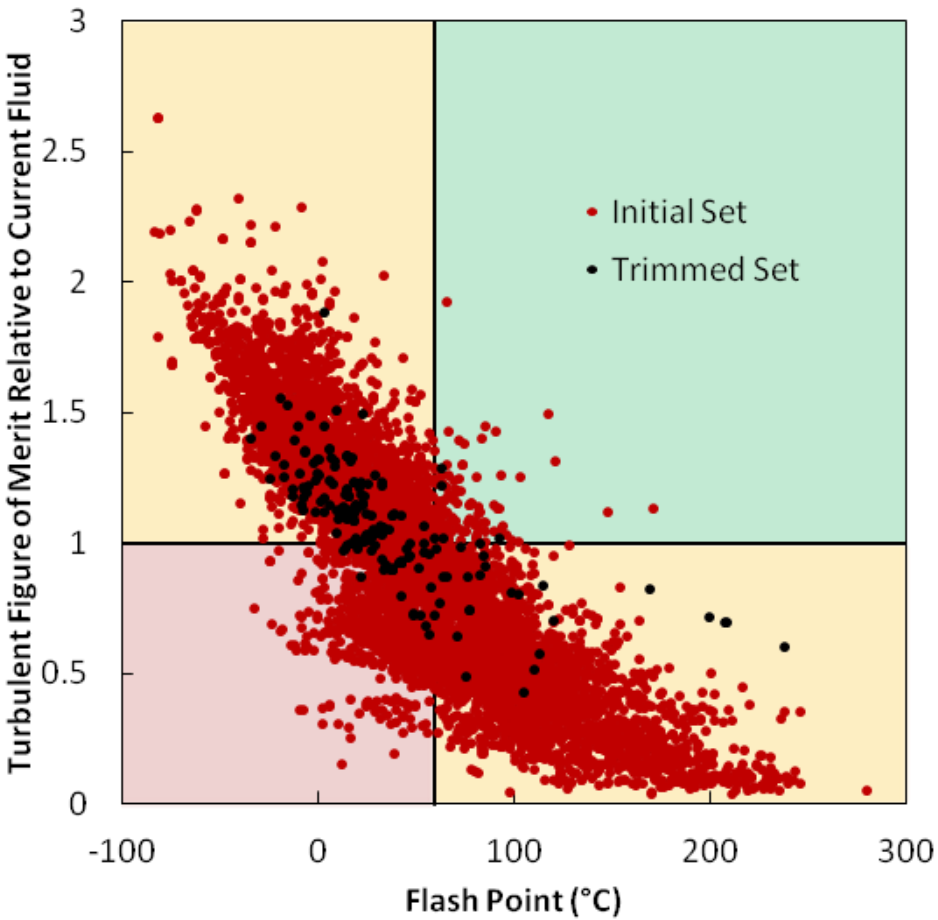
- Models made for all seven properties
  - Four were well predicted (green)
  - Three were adequately predicted (yellow)
- A few descriptors were heavily weighted in multiple models
  - HA dependent HDCA-1 (Zefirov PC)
  - Relative number of benzene rings

Model	R^2	Key Descriptor	σ (%)	Key Descriptor	σ (%)
Boiling Point (°C)	0.95	Kier&Hall index (order 2)	14	Polarity parameter / square distance (Zefirov)	33
Flash Point (°C)	0.84	Average Information Content (order 1)	19	HA dependent HDCA-1 (Zefirov PC)	17
Melting Point (°C)	0.70	HA dependent HDCA-1/TMSA (MOPAC PC)	17	HASA-1/TMSA (MOPAC PC)	15
Thermal Conductivity (W/[m·°C])	0.75	FPSA1 Fractional PPSA (PPSA-1/TMSA) (Zefirov PC)	20	HA dependent HDCA-1/TMSA (MOPAC PC)	13
Density (kg/m^3)	0.92	Relative number of benzene rings	19	DPSA1 Difference in CPSAs (PPSA1-PNSA1) (Zefirov PC)	14
Heat Capacity (J/[g·°C])	0.81	Relative number of benzene rings	19	HOMO-1 energy	14
Log Viscosity (Pa·s)	0.75	HA dependent HDCA-1 (Zefirov PC)	17	Relative number of triple bonds	25

Turbulent Metrics

- Turbulent flow regime
  - Primary metric: heat transfer
  - Used flash point as secondary metric
- Desired
  - Freezing point greater than -73 °C and boiling point above 100 °C (black points)
  - All compounds with turbulent figure of merit greater than Novec 7200 with a (green shading)

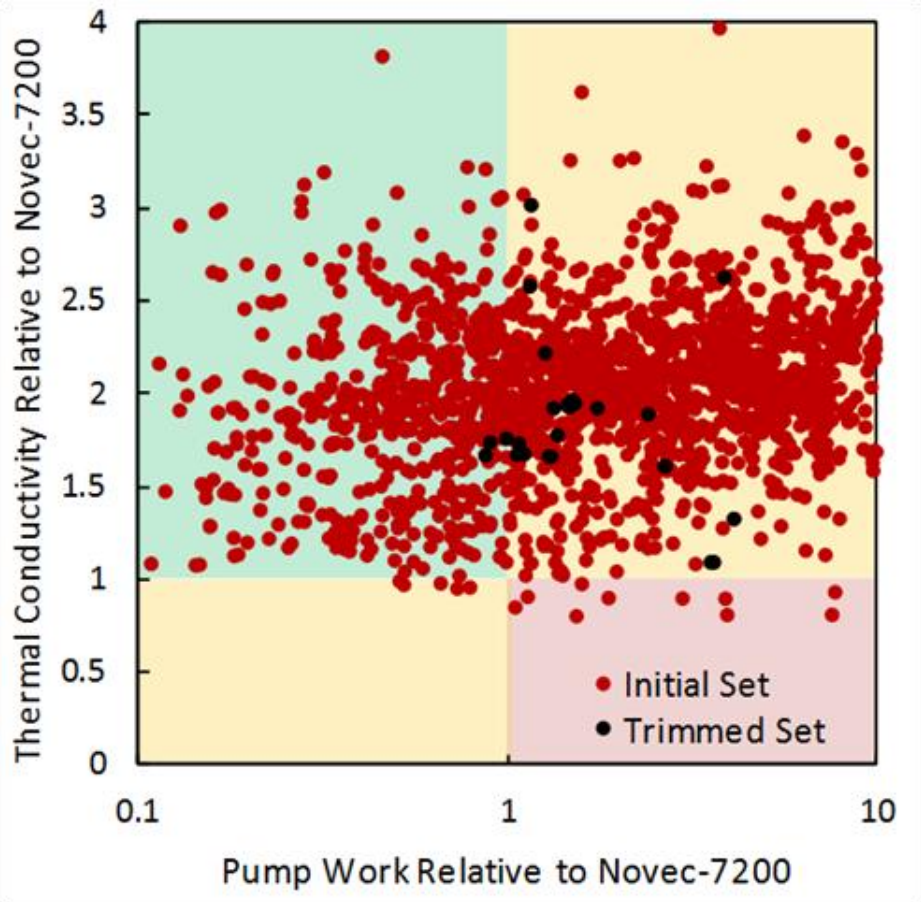
    No compounds identified
- Down-selection eliminated:
  - Stated freezing point, boiling point
  - Flash point below 20 °C
  - Flammability rating 2 or more
  - Toxicity rating 2 or more



Selection process starting from 8,000 compounds (red), to a trimmed set after the removal of compounds due to boiling points below 100 °C and freezing points higher than –73 °C (black)

Laminar Metrics

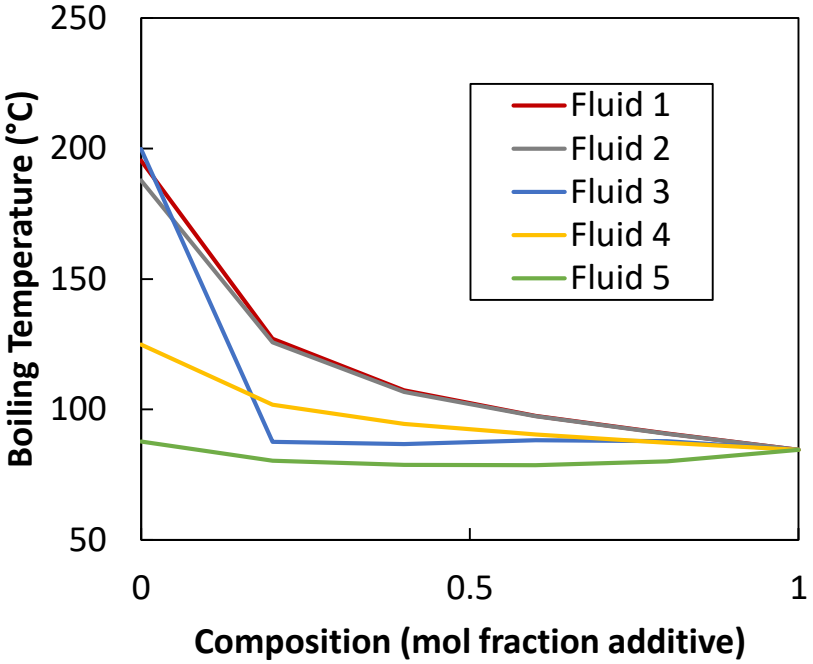
- Laminar flow regime
  - Metrics: thermal conductivity and pump work
- Down-selection eliminated:
  - All compounds with pump work greater and thermal conductivity less than Novec 7200 (red shading)
  - Boling point less than 77 °C
  - Freezing point greater than -73 °C
  - Flammability rating 2 or more
  - Toxicity rating 2 or more
- Fluids compared to turbulent flow results
  - Yielded 5 primary constituent compounds for experimental analysis



Selection process starting from 8,000 compounds (red), to a trimmed set after the removal of compounds due to boiling points below 77 °C, freezing points higher than –73 °C, high viscosity, high flammability, high toxicity, or other no-go conditions (black)

Computational Mixture Properties

- Down-selected primary constituents deficiency
  - All identified compounds had flash points ranging from 21 °C to 70 °C
- To mitigate deficiency, mixtures were examined
  - Used COSMOTherm to predict of mixture properties
  - Experimentally validated predictions
- Most thermophysical properties yielded no surprising results
  - For example, azeotropic behavior
  - Therefore, can fine-tune to desired properties based on concentration



Mol fraction of flash point suppressant added to the five selected fluids

Fluid Evaluation

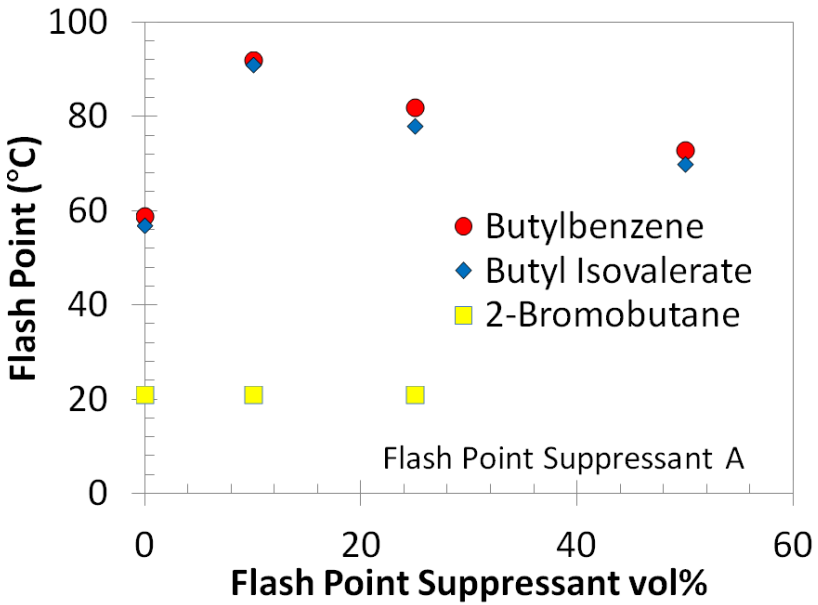
- Experimental Analysis
  - Melting Point: *ASTM 2386-15e1*
  - Congealing Point: *ASTM D1177-12*, *ASTM D97*-15
  - Boiling Point: *ASTM D1120-11e1*, *ASTM D2887-15e1*, *D2892-15*
  - Flammability (Flash Point): *ASTM D93*, *ASTM D92, ASTM E659*
  - Thermophysical Properties
    - Density: *ASTM D4052-09*, *ASTM D3505-12e1*
    - Viscosity: *ASTM D2983-09*, *ASTM D445-15*
    - Thermal Conductivity: *ASTM D2717-95*
    - Specific Heat: *ASTM D2766-95*

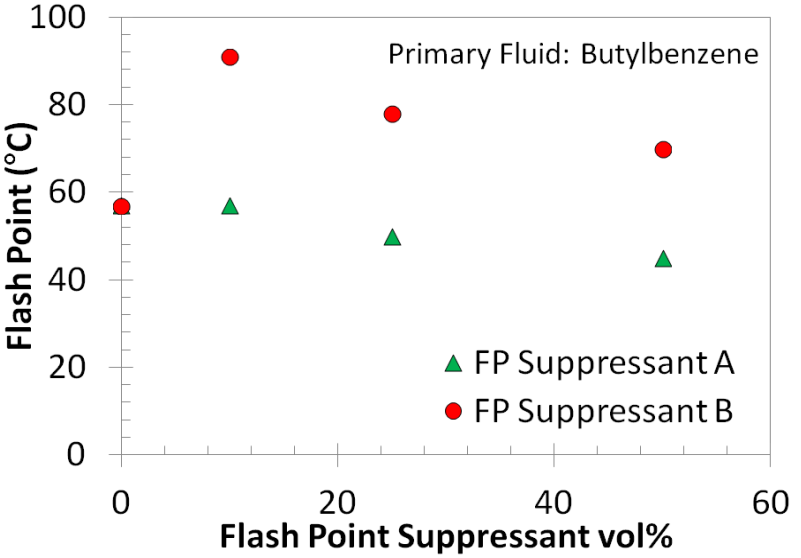
Full Temperature Range

  - Toxicology: *EPA OPPTS 870.1100*, *870.1300*, *870.2400*, *870.2500*
  - Thermal Stability: *ASTM D6743, Trace Contaminant*
  - Material Compatibility: *ASTM G-31*, *ASTM D-471*, *ASTM 1384*
  - Evaporative Rate: *JIS C2101*
- Experimental Demonstration
  - Simulated TCS cycling between -85 °C and 25 °C

Results – Flash Point

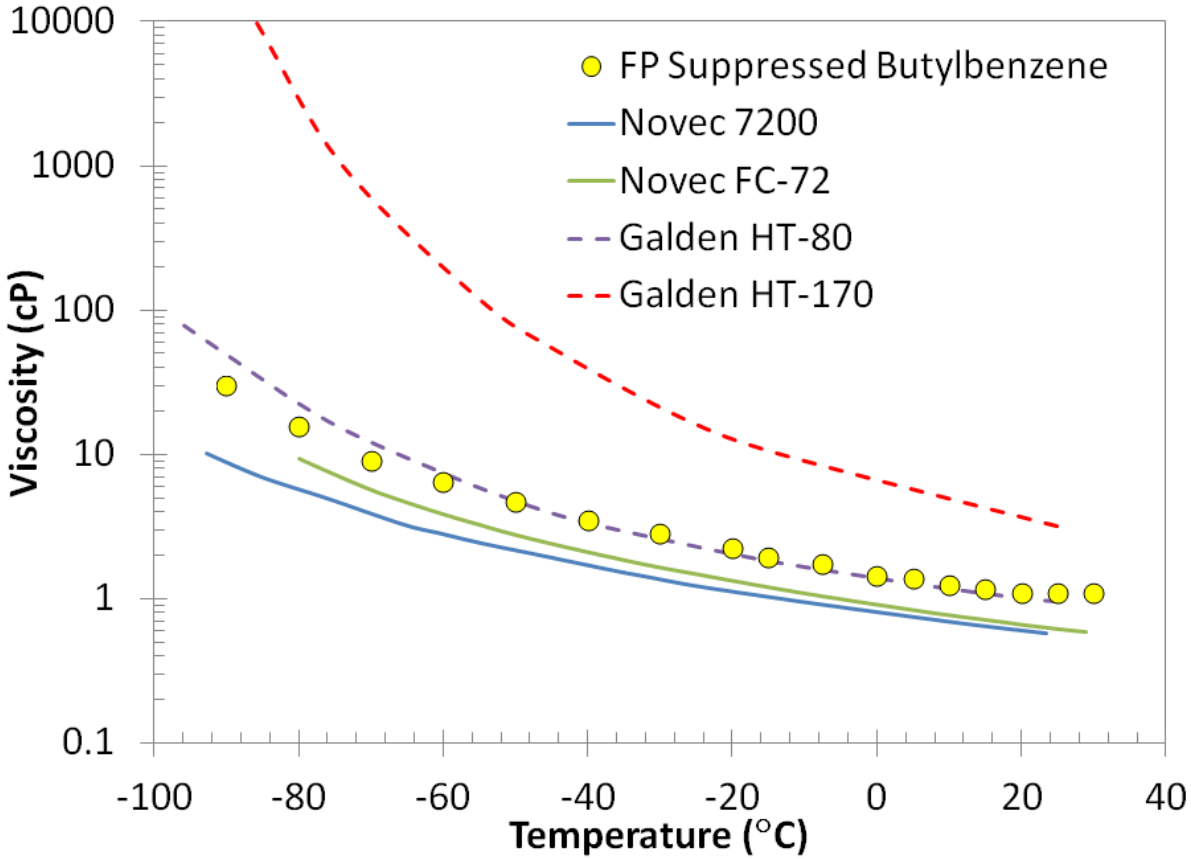
- Flash point Suppressants
  - High vapor pressure
  - Similar molecular structure to current non-aqueous flame suppression systems
- Evaluated using ASTM D56-05
  - Test fluid heated in sealed cup to 10°C below expected flash point
  - Flame introduced to headspace of the cup every 2°C
- Pure fluid flash point matched literature
- Flash point suppression dependent on:
  - Base fluid type
  - Suppressant fluid type
  - Concentration





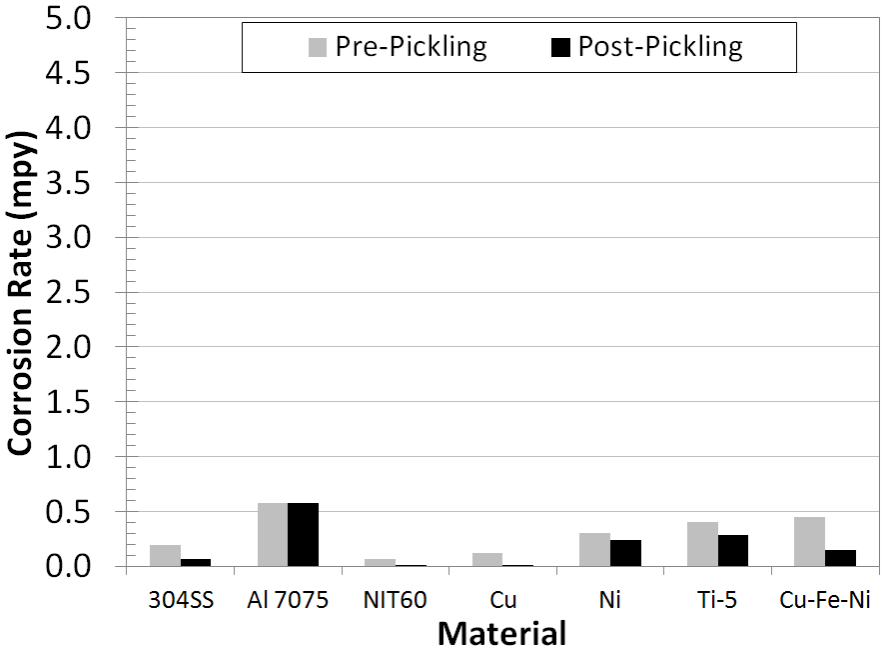
Results - Viscosity

- Goal: Minimize viscosity temperature dependence
  - Prevent stagnation and maintain turbulent flow regime in radiator
- Evaluated using ASTM D2983-08
  - UL spindle with cell cooled using ultra-low chiller
  - Lower bound for accuracy: 1 cP
- Method validated using known fluids:
  - Water, hexane, etc.



Results – Corrosion

- Validation using ASTM G-31
- Similar to Galden and Novec Fluids
  - Compatible with most metals
    - Stainless steel, copper, brass, iron, nickel, aluminum, titanium, etc.
  - Compatible with most plastics
    - FEP, PTFE, polypropylene, PMMA, etc.
  - Caution with elastomers
    - Viton (compatible)
    - EDPM, silicone rubber (not compatible)



Corrosion rate for 90:10 butylbenzene with FP suppressant

Elastomer and plastic compatibility with 90:10 butylbenzene with FP suppressant (% swell)

	Silicone Rubber	Buna N	EPDM 60	Viton B	Teflon	FEP
Novec 7200 baseline	17/14	-9/-5	-14/-6	26/18	1/1	5/0
Butylbenzene			59/76	-1/1	2/0	-8/0
90:10 Butylbenzene w/ FP Suppressant A	156/97	88/52	98/63	4/5	1/0	-2/0

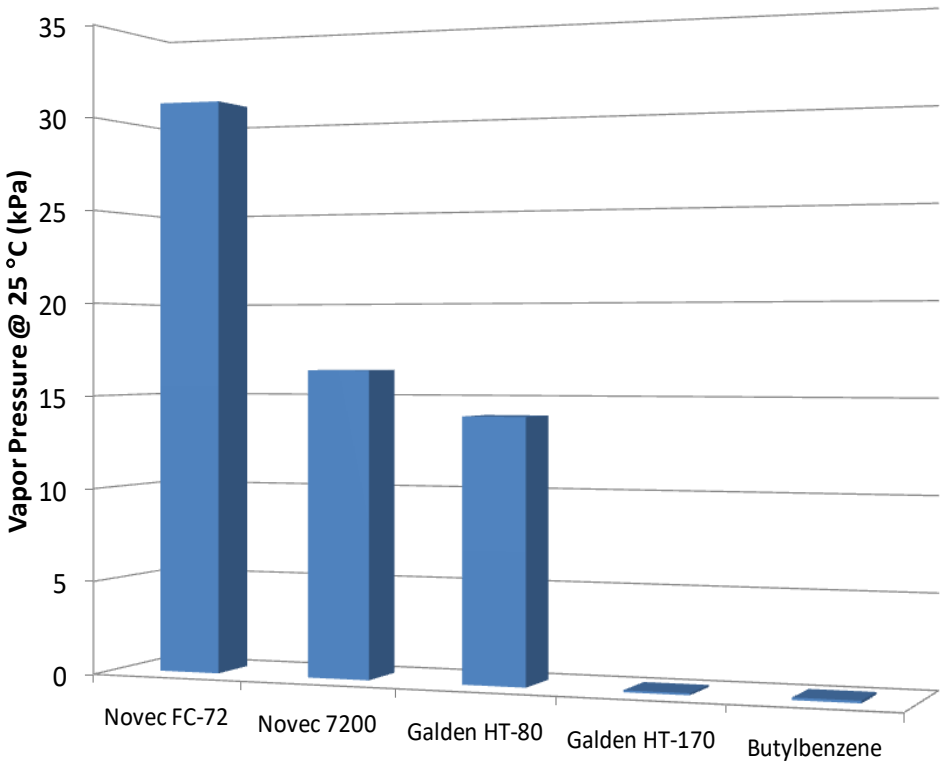
Fluid Comparison – Figures of Merit

HTF	Boiling Point °C	Flash Point °C	Flammability Rating	Health Rating	$\frac{\mu_{-90\,°C}}{\mu_{20\,°C}}$	Figure of Merit (Turbulent)	$\frac{W_f}{W_{7200}}$ (Laminar)	$\frac{k_f}{k_{7200}}$ (Laminar)
Novec 7200	76	-	1	1	12	1	1	1
Novec FC-72	56	-	1	1	25[1]	0.81	0.92	0.72
Galden HT-80	80	-	0	1	50	0.70	1.70	0.81
Galden HT-170	170	-	0	1	212	0.4	5.03	0.81
Paratherm CR	181	40	2	2	24	0.91	1.91	1.75
MultiTherm ULT170	176	53	2	1	25	0.88	1.98	1.64
Dynalene MV	176	53	2	1	20	0.88	2.05	1.65
Duratherm XLT-120		49	2	1	41[3]	0.91	1.62	1.70
Dowtherm J	181	57	2	1	11[2]	0.98	1.49	1.61
Therminol D12	192	59	2	1	249[3]	0.69	2.13	1.36
Syltherm XLT		47	2	1	24	0.67	2.86	1.39
Butylbenzene	183	59	2	0	31	0.91	1.95	1.63
FP Suppressed Butylbenzene	172	92	1	-	26	0.92	1.83	1.56

[1]Extrapolated viscosity to -90 °C (lowest viscosity value at -80 °C)
[2]Viscosity evaluated at -80 °C
[3]Viscosity evaluated at -85 °C

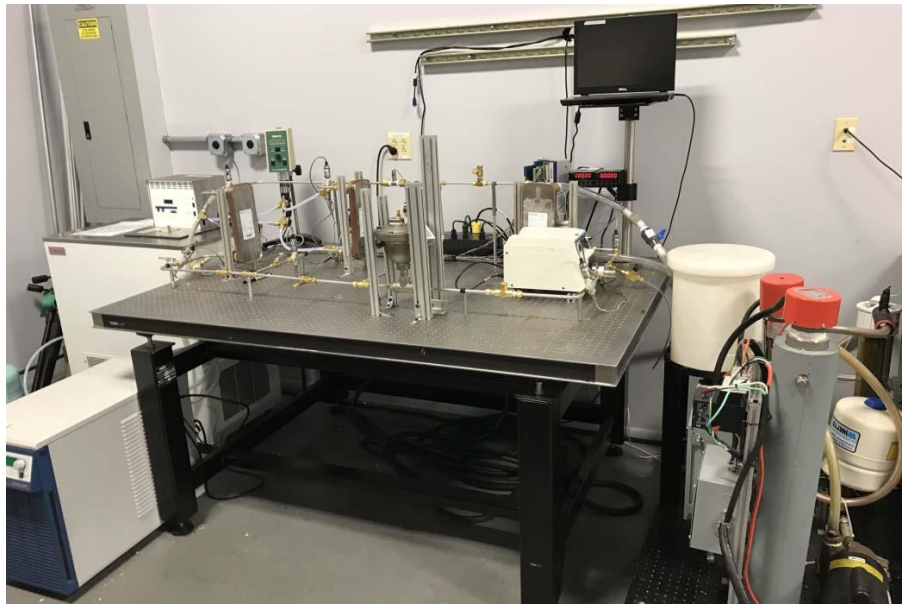
Conclusions

- Achieving ultra-low temperature HTFs based on a single constituent requires a compromise between the following properties:
  - Viscosity
  - Vapor pressure (i.e. inhalant danger)
  - Flammability
- Required parameters that can be readily met include:
  - Pour point
  - Corrosion
  - Ingested toxicity, handling danger
- Flash point suppressant inclusion offers alternative approach
  - Achieves >30% increase in flash point
  - Maintains low vapor pressure



Future Work

- Heat transfer fluid formulation
  - Additive package (anti-oxidant, inhibitor, etc.)
    - <1wt%
- Fluid evaluation
  - Thermal stability
  - Thermal decomposition
  - Toxicity
  - Evaporative rate
- Fluid demonstration
  - Thermal stability
  - Operating temperature range
- Update baseline comparison
  - Novec FC-72, Galden HT-80



Simulated TCS capable of -90 to 25 °C rejection temperature

SUPPORT SLIDES

Mainstream Engineering Corporation

- Small business incorporated in 1986
- 100+ employees
- Mechanical, chemical, electrical, materials and aerospace engineers
- 100,000 ft^2 facility in Rockledge, FL
- Laboratories: electric power, electronics, materials, nanotube, physical and analytical chemistry, thermal, fuels, internal combustion engine
- Manufacturing: 3- and 5- axis CNC and manual mills, CNC and manual lathes, grinders, sheet metal, plastic injection molding, welding and painting

1 - ENGINEERING OFFICES
2 - RESEARCH and DEVELOPMENT
3 - RESEARCH and DEVELOPMENT
4 - PRODUCTION FACILITY
5 - PRODUCT DEVELOPMENT
5a - MAINSTREAM EBEAM
6 - ADMINISTRATIVE OFFICES

- Basic Research, Applied Research & Product Development
- Transition from Research to Production (Systems Solution)
- Manufacture Advanced Products

Mission Statement

To research and develop emerging technologies.
To engineer these technologies into superior quality, military and private sector products that provide a technological advantage.

SBIR Successes and Awards

- 95% DOD Commercialization Index
- SBIR spinoffs – QwikProduct Line
- SBIR spinoffs – Military Product Line
- Honors
  - 2014 DOE's SBIR/STTR Small Business of the Year
  - 2013 Florida Excellence Award by the Small Business Institute for Excellence in Commerce
  - Winner Florida Companies to Watch
  - Blue Chip Enterprise Initiative Awards
  - Job Creation Awards
  - Two SBA's Tibbetts Awards for Commercialization
  - State of Florida Governor's New Product Award
  - SBA's Small Business Prime Contractor of the Year for the Southeastern U.S.
  - SBA's Administrator's Award for Excellence

Mainstream's Focus Areas

THERMAL CONTROL

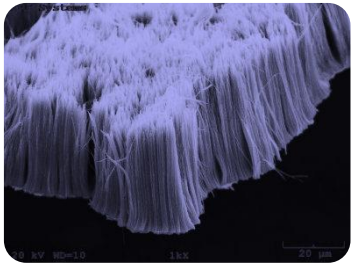
- High Heat Flux Cooling
- Thermal Energy Storage
- Directed Energy Weapons
- Rugged Military Systems

ENERGY CONVERSION

- Combustion
- Diesel/JP-8 Engines
- Biomass Conversion
- Alternative Fuels
- Fuel Cells

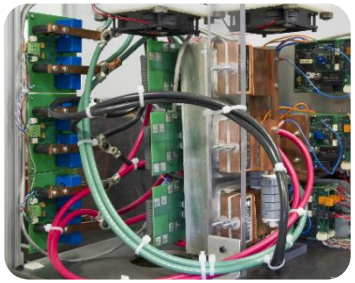
TURBOMACHINERY

- Compressors
- Turbines
- Bearings/Seals
- Airborne Power Systems



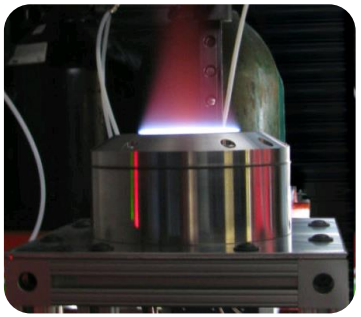
MATERIALS SCIENCE

- Thermoelectrics
- Batteries/Ultracapacitors
- Hydrogen Storage
- E-Beam Processing
- Nanostructured Materials



POWER ELECTRONICS

- High Speed Motor Drives
- Hybrid Power Systems
- Solar/Wind Electronics
- Pulse Power Supplies
- Battery Chargers



CHEMICAL TECHNOLOGIES

- Heat Transfer Fluids
- Catalysis
- Chemical Replacements
- Water Purification
- Chemical Sensors