NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Improved Hydrogen Liquefaction through Heisenberg Vortex Separation of para and ortho-hydrogen

Chris Ainscough (NREL), Jacob Leachman (WSU)
presenting

Annual Merit Review June 7, 2017

PROJECT ID: PD130

Overview

Timeline and Budget

- **Project start date: 11/1/2015**
- **Project end date: 9/30/2018**
- **Total project budget: $2,094k**
  - Total recipient share: $0
  - Total federal share: $2,094k
  - Total DOE funds spent*: $506k

* As of 3/31/16

Barriers

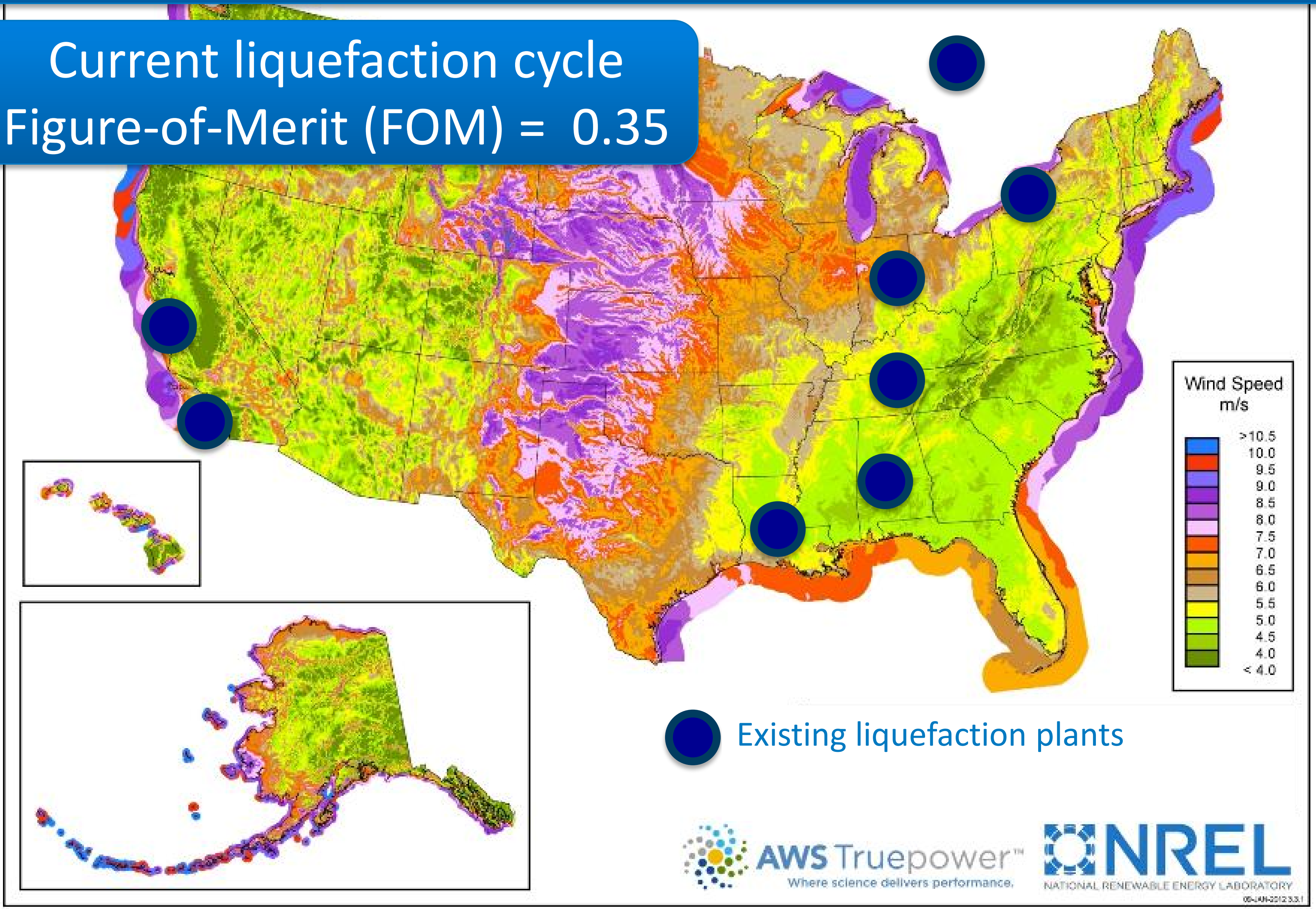
- H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction
- Increase liquefaction cycle efficiency from FOM 0.35 → >0.5
- Lower liquefier installed capital cost (~$2.5M/MTPD) / unit capacity (30 MTPD)
- Lower liquid delivery cost ($4-15/kg depending on range)

Partners

- **Washington State University**
- **Praxair**

Relevance: Good renewable resources aren't generally where the liquefaction plants are.

Current liquefaction cycle
Figure-of-Merit (FOM) = 0.35



Relevance

First concept in history that directly uses ortho/para conversion to aid in cooling.

- Goal: Develop vortex tubes for hydrogen liquefaction from TRL 2 to TRL of 4 in three years, such that technology can be commercialized to units 5-30 MTPD in size.

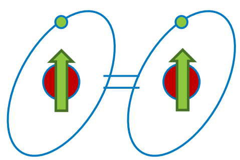
- Scientific Merit: Improve efficiency of liquefaction by minimizing use of refrigerant.
  - Exothermic ortho/para conversion results in significant refrigerant use. Vortex concept leverages catalysts for reverse endothermic reaction
  - Vortex motion cools para hydrogen for subsequent liquefaction

Approach: Para-orthohydrogen manipulation

In 1932, Werner Heisenberg won the Nobel Prize:

"for the creation of quantum mechanics, the application of which has, *inter alia*, led to the discovery of the allotropic forms of hydrogen."[1]

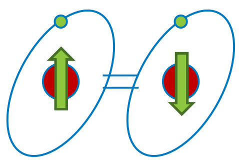
[1]Nobelprize.org accessed 2010



Orthohydrogen (higher energy state)

Normal Hydrogen 3:1

Ortho to Para heat = 700 kJ/kg exothermic (vs. latent heat of vap. 420 kJ/kg)



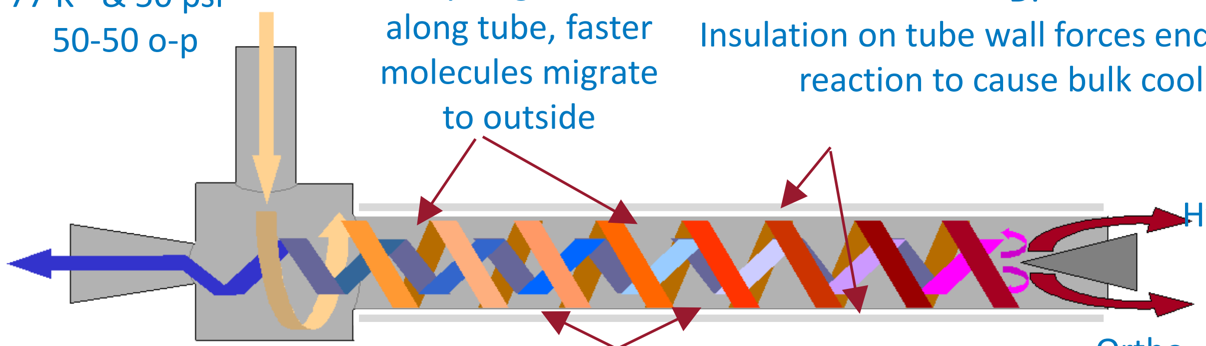
Parahydrogen (lower energy state)

"Partial ortho-para conversion . . . offers the greatest opportunity for reduced liquefaction power consumption."
C. Baker, Union Carbide 1979

Approach: Para-ortho hydrogen manipulation

Fluid Mechanics of Vortex Tube:

- Compressed gas forms a vortex, with outer fluid flowing right and core left.
- Radial ΔP promotes ΔT drop in core.
- Heat pumping from the cold core to the hot due to viscous work streaming
- More complications from frictional heating, turbulence, recirculation, etc.



* Subject to measured performance

Ortho/para separation and conversion drives cooling.

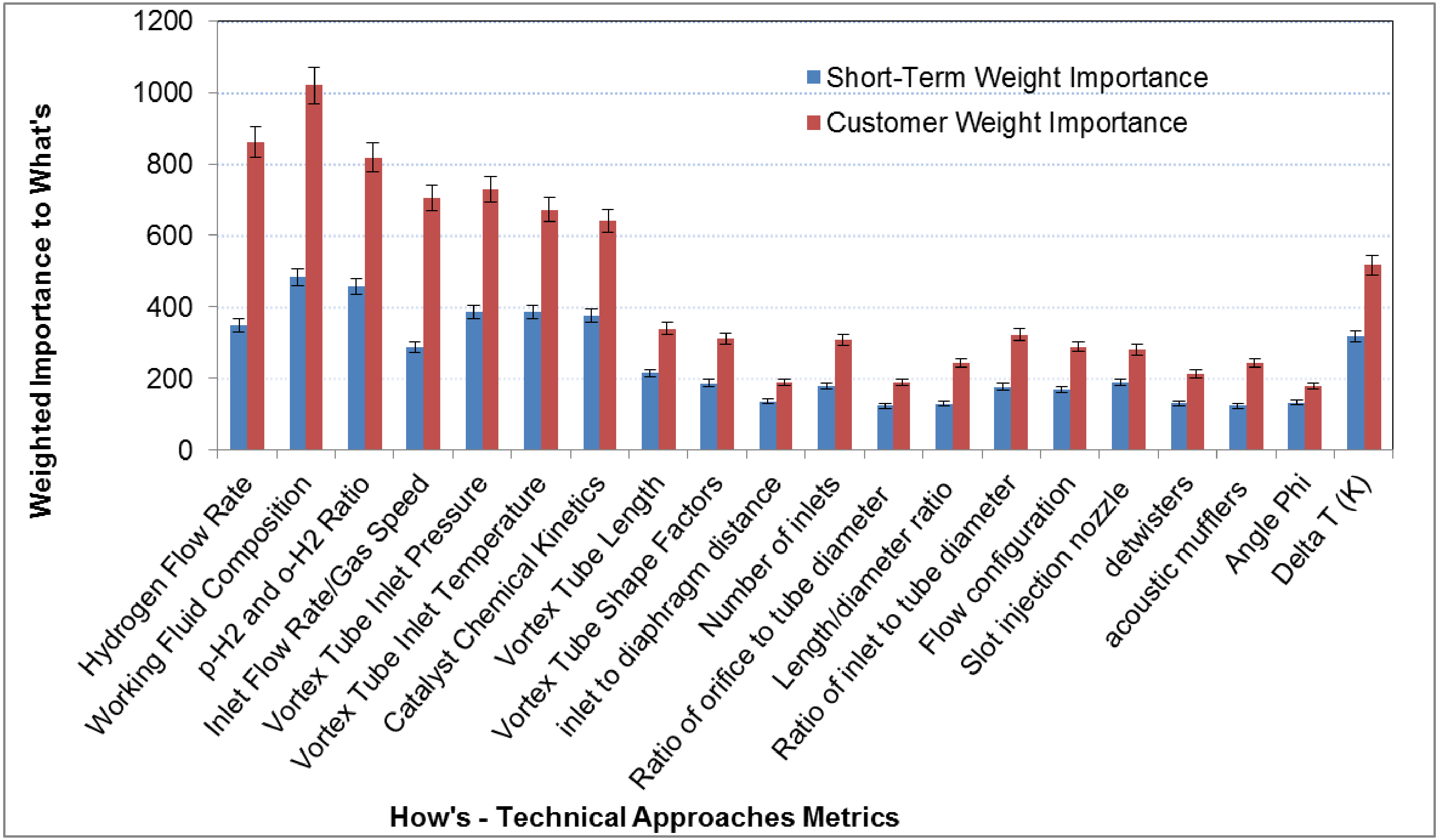
Customer-centric development approach.

1. Retrofitted an existing experiment to safely measure para-ortho conversion and cryogenic hydrogen vortex tube performance.
    a. Validated numerical and CFD model predictions.
2. Developed 1st helium-hydrogen, neon-hydrogen mixture Equations of State.
3. Refined steady-state cycle analysis, completed detailed exergy analysis.
4. Technoeconomic analysis of 5-30 TPD liquefaction plant complete.

Task 1 - Optimize vortex device for para-ortho conversion & separation

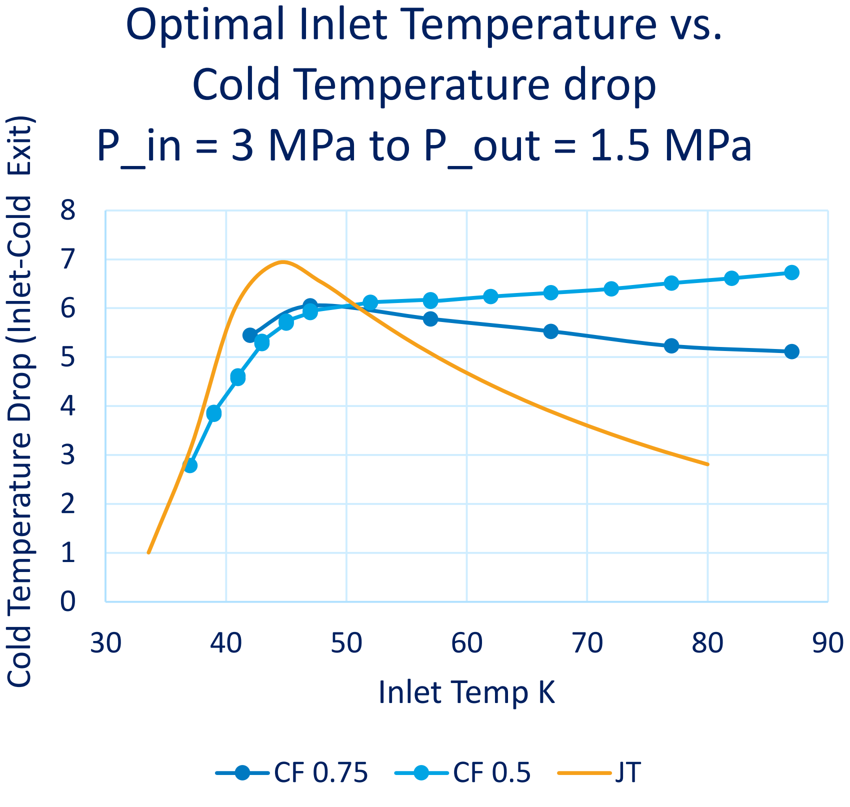
Task 1.3) Vortex Tube HoQ

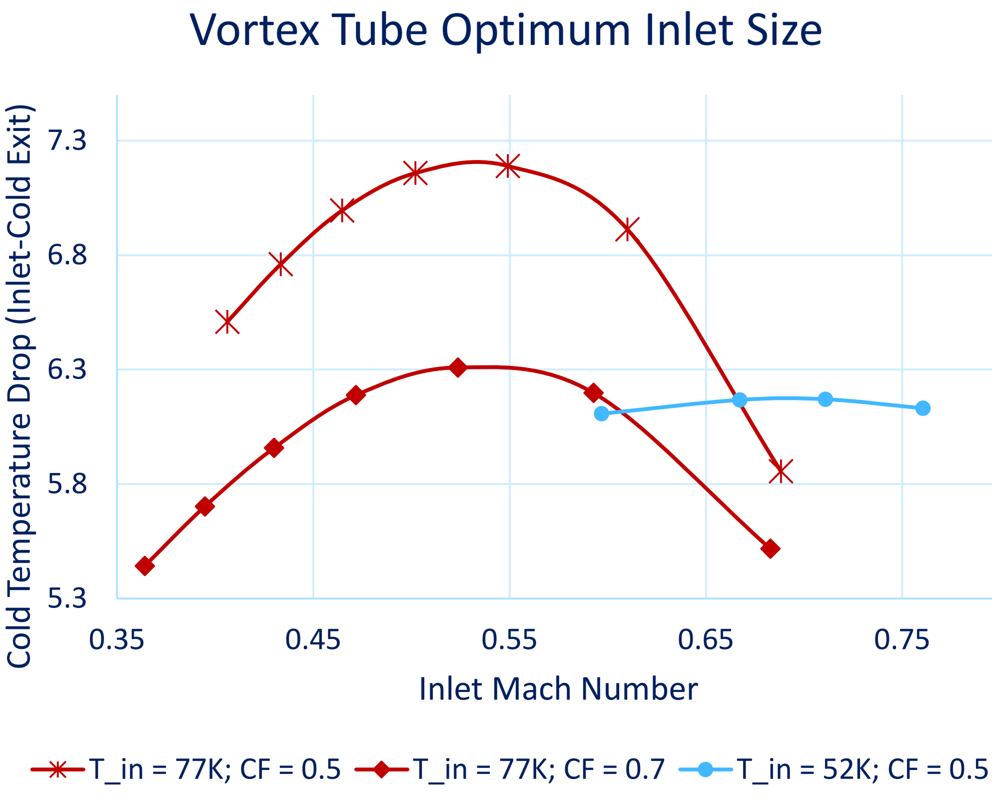
Key variables: Refrigerant composition, para-ortho conversion rate



Used CFD to calculate performance and size geometry in supercritical region.

1st order models based on ideal-gas assumptions were insufficient, we used ANSYS/FLUENT to optimize vortex tube geometries.





Task 1.1) Experimental Safety Upgrades

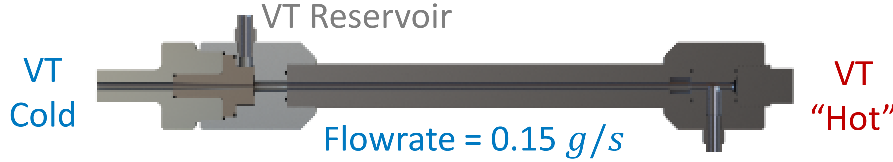
August 16th, 2017– A power outage caused a near-miss vent, the DOE Hydrogen Safety Panel (DOE HSP) identified areas of improvement to experimental safety.

DOE HSP recommendations:

- Increased redundancy with higher quality valves and storage cylinders.
- Backup power now allows for intermediate (<20 minute outages).
- A new dedicated vent line was installed by the university.
- Safety and experiment designs were collated and updated into a single 69 page living document to be kept digitally and near the experiment.

Near-miss caused four month delay.

Task 1.1) Vortex Tube Experimental Data

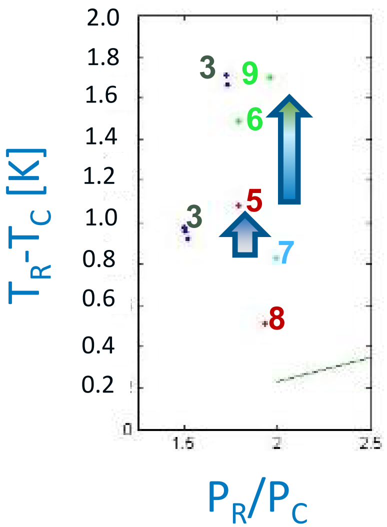


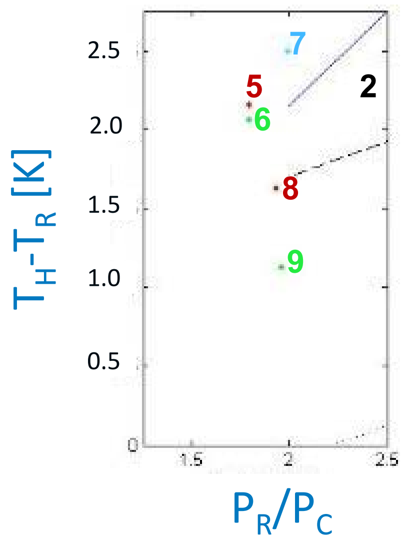
Subscripts:

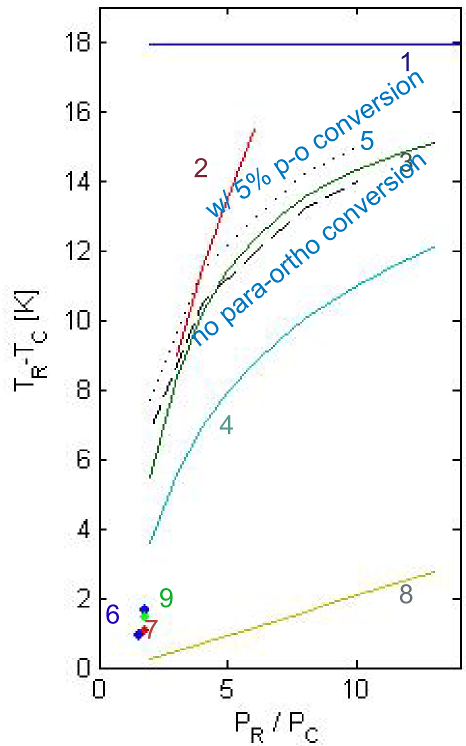
R=reservoir; C=Cold End; H=Hot End

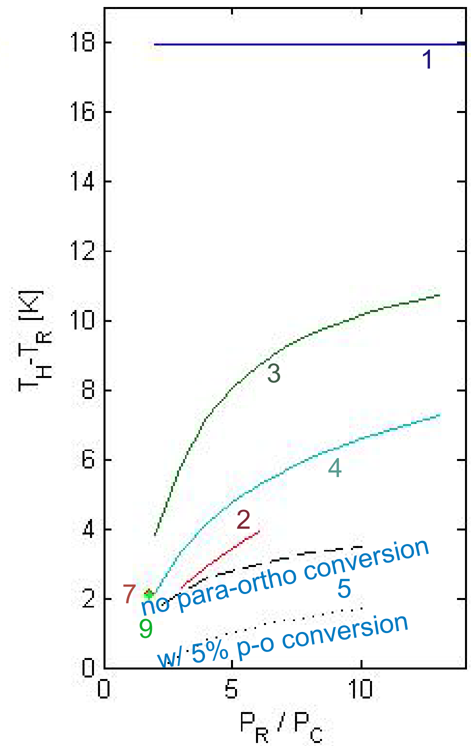
Theoretical – Experimental Comparison

1. "Empirical model" Merkulov (1969)
2. "Thermodynamic estimate" Polihronov and Straatman (2012)
3. "Semi-empirical" Ahlborn and Gordon (2000)
4. "Maxwell demon" Liew et al. (2012)
5. "Extended HEX-model" Matveev and Bunge (2016)
6. Commercial Vortex Tube (smooth, no catalyst)
7. **Custom Cryogenic Vortex Tube (rifled, no catalyst)**
8. Joule-Thomson Valve
9. **Custom Cryogenic Vortex Tube (rifled, catalyst)**
10. **Custom Cryogenic Vortex Tube (smooth, no catalyst)**
11. **Custom Cryogenic Vortex Tube (rifled, no catalyst)**





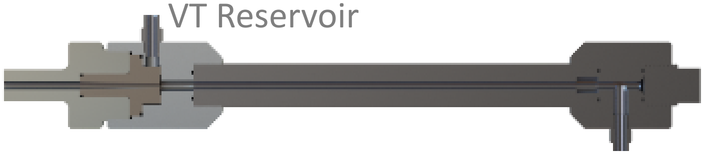




Task 1.1) Vortex Tube Experimental Data

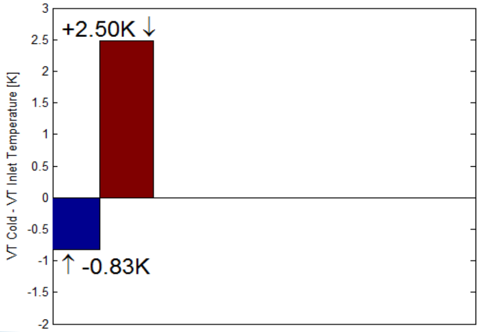
Flowrate = 0.15 g/s

VT Cold



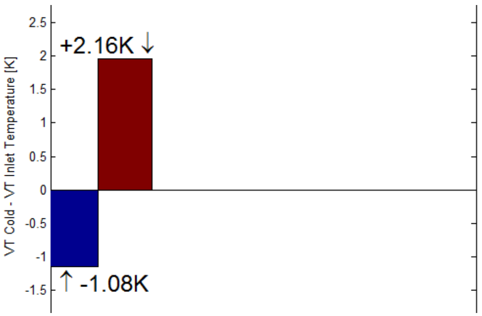
VT Reservoir

VT "Hot"



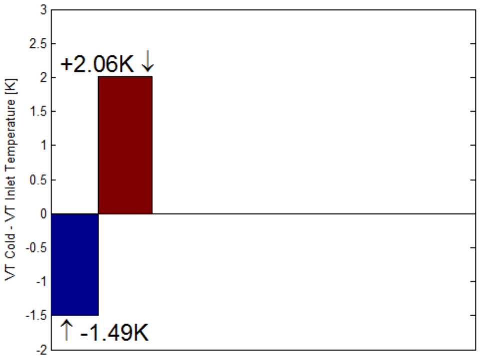
Smooth main tube, non-catalyzed

PR = 1.99 ± 0.09
CF = 0.37
$T_{in} - T_c$ = 0.83 K ± 0.35 K
$T_h - T_{in}$ = 2.50 K ± 0.35 K



Rifled main tube, non-catalyzed

PR = 1.8 ± 0.09
CF = 0.38
$T_{in} - T_c$ = 1.08 K ± 0.35 K
$T_h - T_{in}$ = 2.16 K ± 0.35 K



Rifled main tube, catalyzed

PR = 1.79 ± 0.09
CF = 0.38
$T_{in} - T_c$ = 1.49 K ± 0.35 K
$T_h - T_{in}$ = 2.06 K ± 0.35 K

38-57% improvement with catalyzed tube. We are probably getting p-o conversion along the wall.

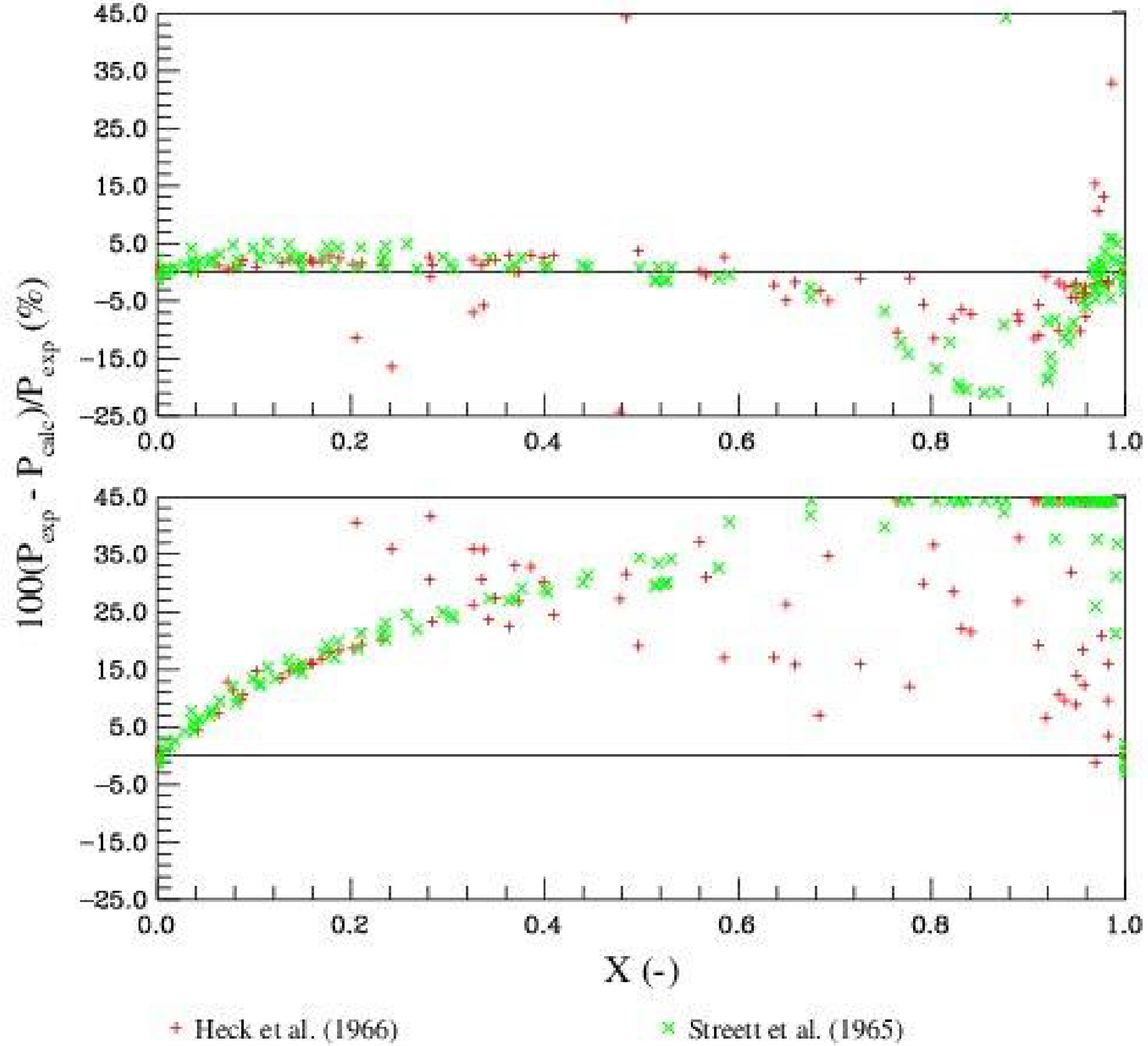
Task 2 - Develop fundamental property models for He-H_2-Ne refrigerant mixtures

Task 2.3) Refrigerant EOS Development

- Two new mixture EOS developed for He-H2, Ne-H2 & implemented in NIST's standard property program REFPROP. Currently in NIST review.
- Ne-He mixture EOS is preliminary.

Developed three new mixed refrigerant property models.

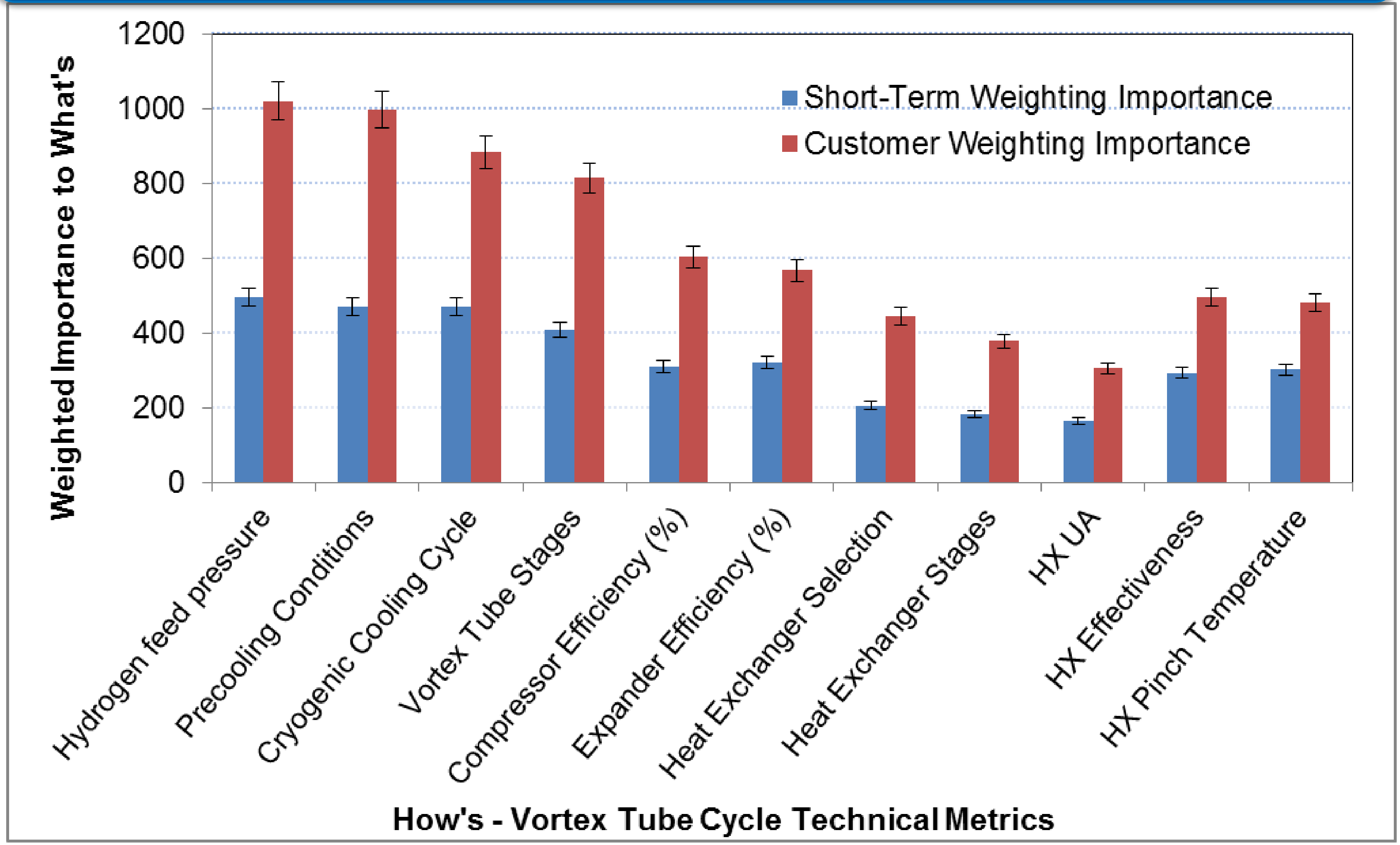
Percent deviations in calculated pressures vs. composition for the new Ne-H2 EOS (top) and prior model (bottom)



Task 3 - Design and assess vortex liquefaction cycle performance

Task 3.3) Cycle House of Quality

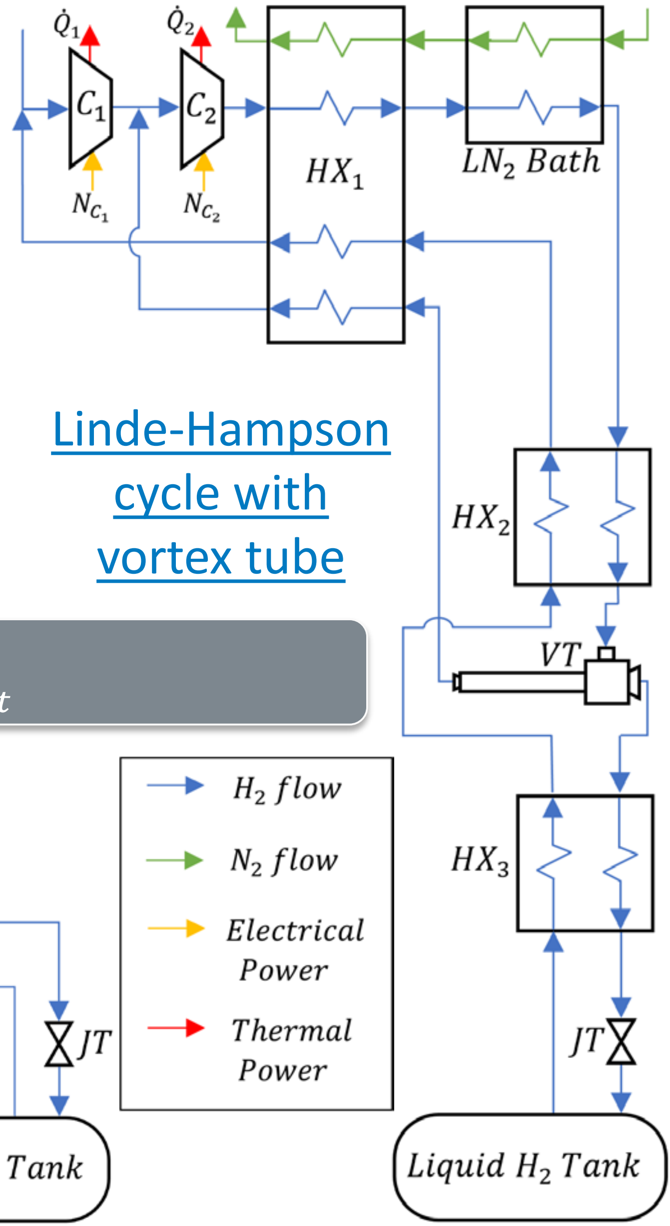
Vortex tube performance and precooling method are key



Task 3.3) Steady State Cycle Analysis

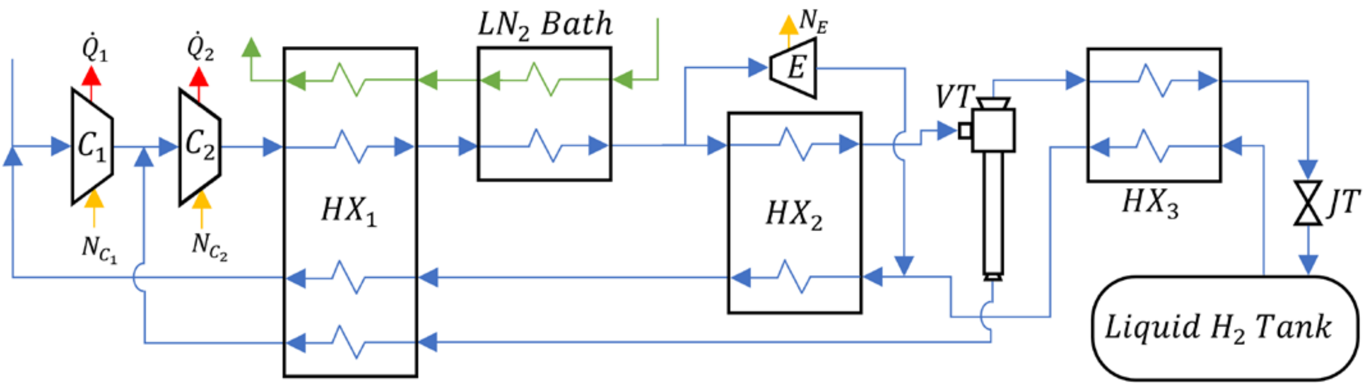
- Liquefaction cycles with vortex tube
  - Linde-Hampson (right) and Precooled Claude (below)
- Can re-optimize cycle performance for vortex tube integration
- Improvement from standard cycles depends on the achievable cooling effectiveness of vortex tube
- Non-dimensional "effectiveness" translates experiment operating conditions to cycle operating conditions

Effectiveness: $\varepsilon_{VT} = {}^{\Delta H_{inlet} - \Delta H_{cold}}/_{\Delta X_{Dest}}$

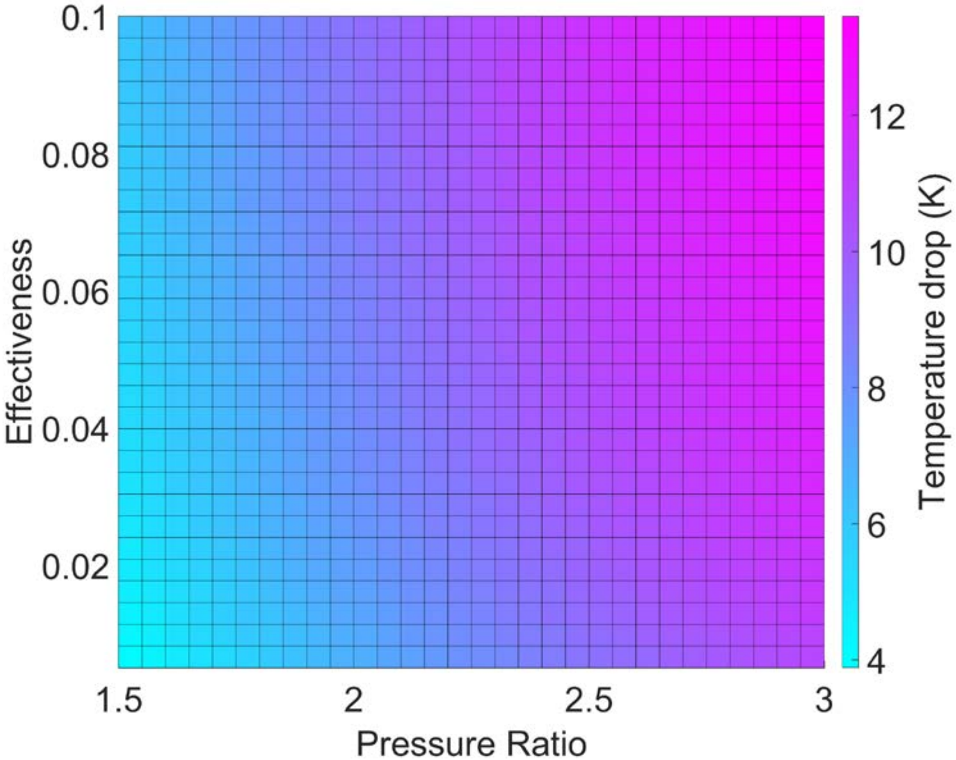


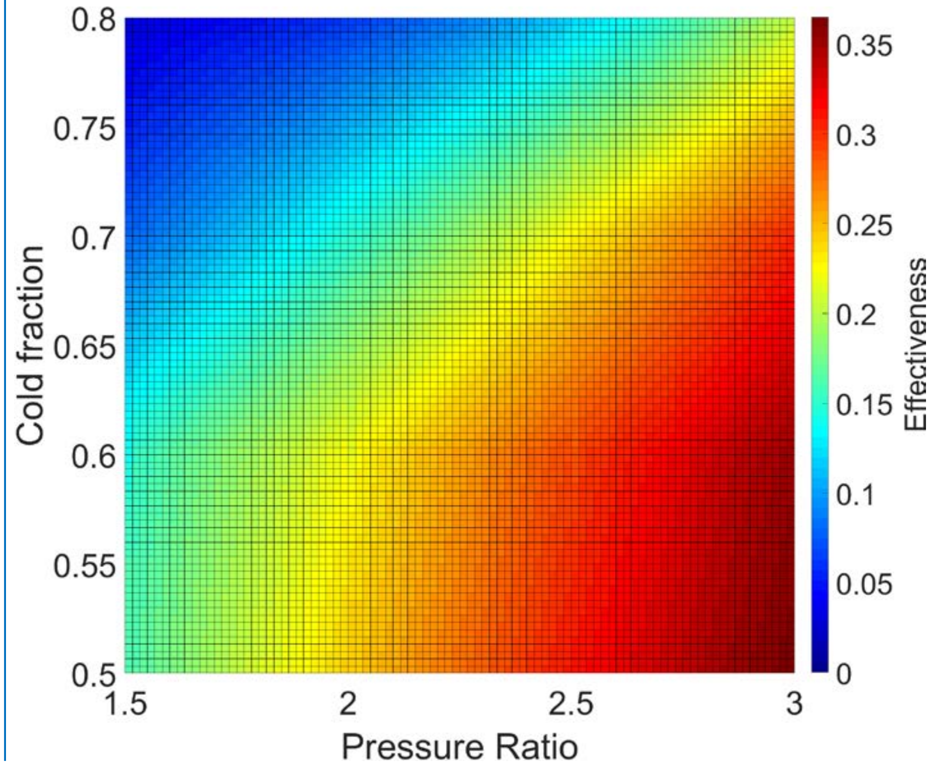
Linde-Hampson cycle with vortex tube

Precooled Claude cycle with vortex tube



Task 3.3) Vortex Tube and Cycle Analysis



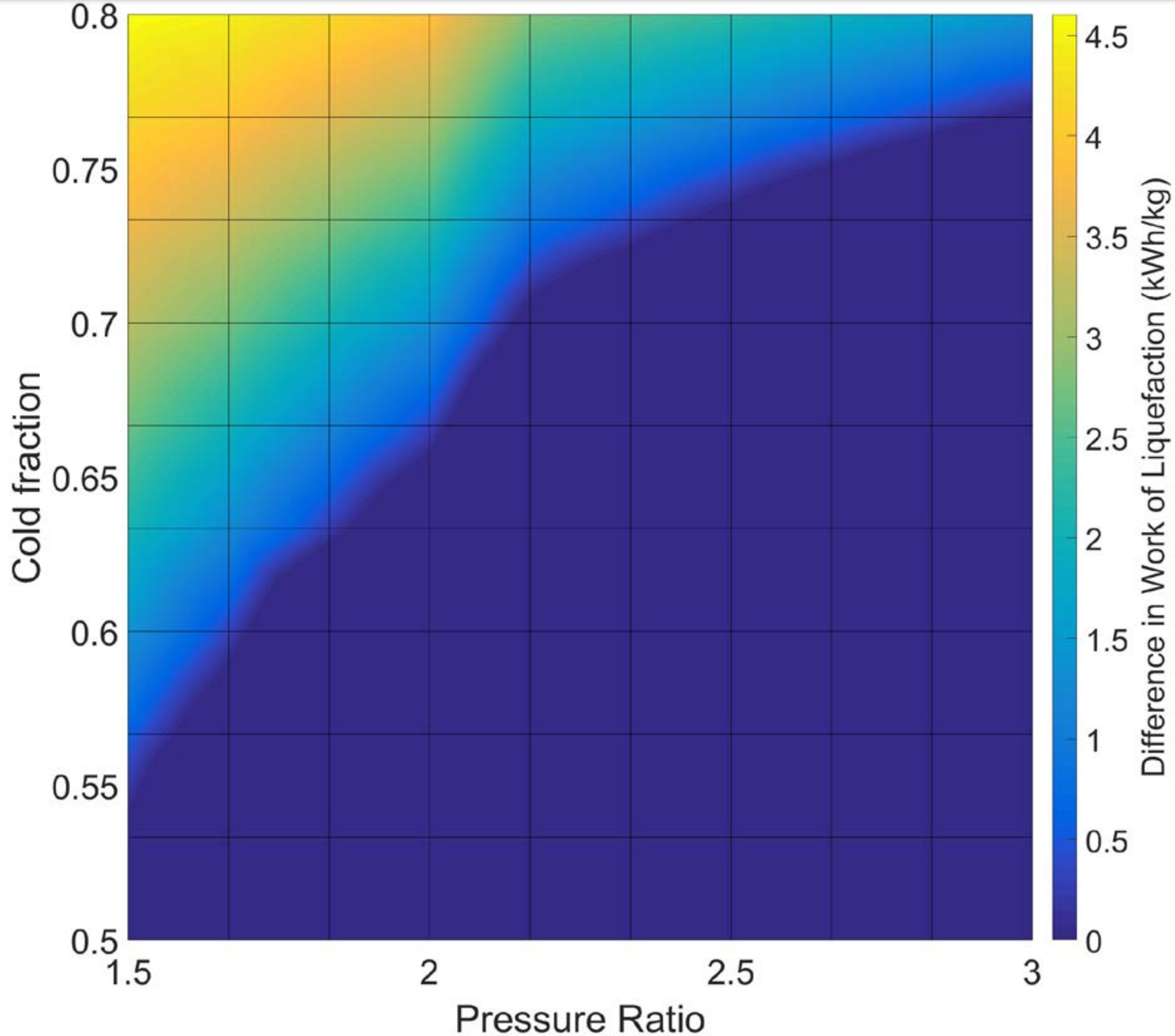


- Actual cooling is function of operating condition and "effectiveness"
- Higher pressure ratios require more "effective" vortex tube

Better liquefaction performance requires improvement over standard vortex tube, i.e. para-ortho catalysis.

Task 3.3) Cycle Analysis with Vortex Tube

Liquefaction work can be decreased by >15% in a standard Linde-Hampson cycle assuming a vortex tube "effectiveness" of 20%.



Task 3.5) TEA and Thermal Analysis

Simulated L-H with VT performance

Work of Liquefaction	Ideal Linde Hampson (L-H)	Ideal L-H (RefProp)	Ideal L-H w/ VT* (RefProp)	Realistic L-H	Realistic L-H w/ VT*
H_2 Total	16.3 kWh/kg	20.4 kWh/kg	15.4 kWh/kg	30.8 kWh/kg	23.7 kWh/kg
N_2 Contribution	3.13 kWh/kg	2.67 kWh/kg	2.40 kWh/kg	5.71 kWh/kg	5.30 kW/kg
Differences in Ideal Assumptions	Uses constant H_2 properties measured at 300K	Utilizes state-of-art RefProp para-H_2 and ortho-H_2 EOS	**Vortex Tube Parameters:** Pressure Ratio = 2 Cold fraction = 0.5	**Realistic Parameters:** Compressor Efficiency = 85% LN_2 Figure of Merit = 0.5 Heat Exchanger pinch point ΔT = 2 K	
	Only accounts for Ortho-Para conversion at 80K and 20K	Accounts for Ortho-Para conversion at local HX conditions			

* Assumes 5% para→ortho conversion of the hot stream.

Vortex tube adding to L-H cycle decreased the work of liquefaction by ~25%.

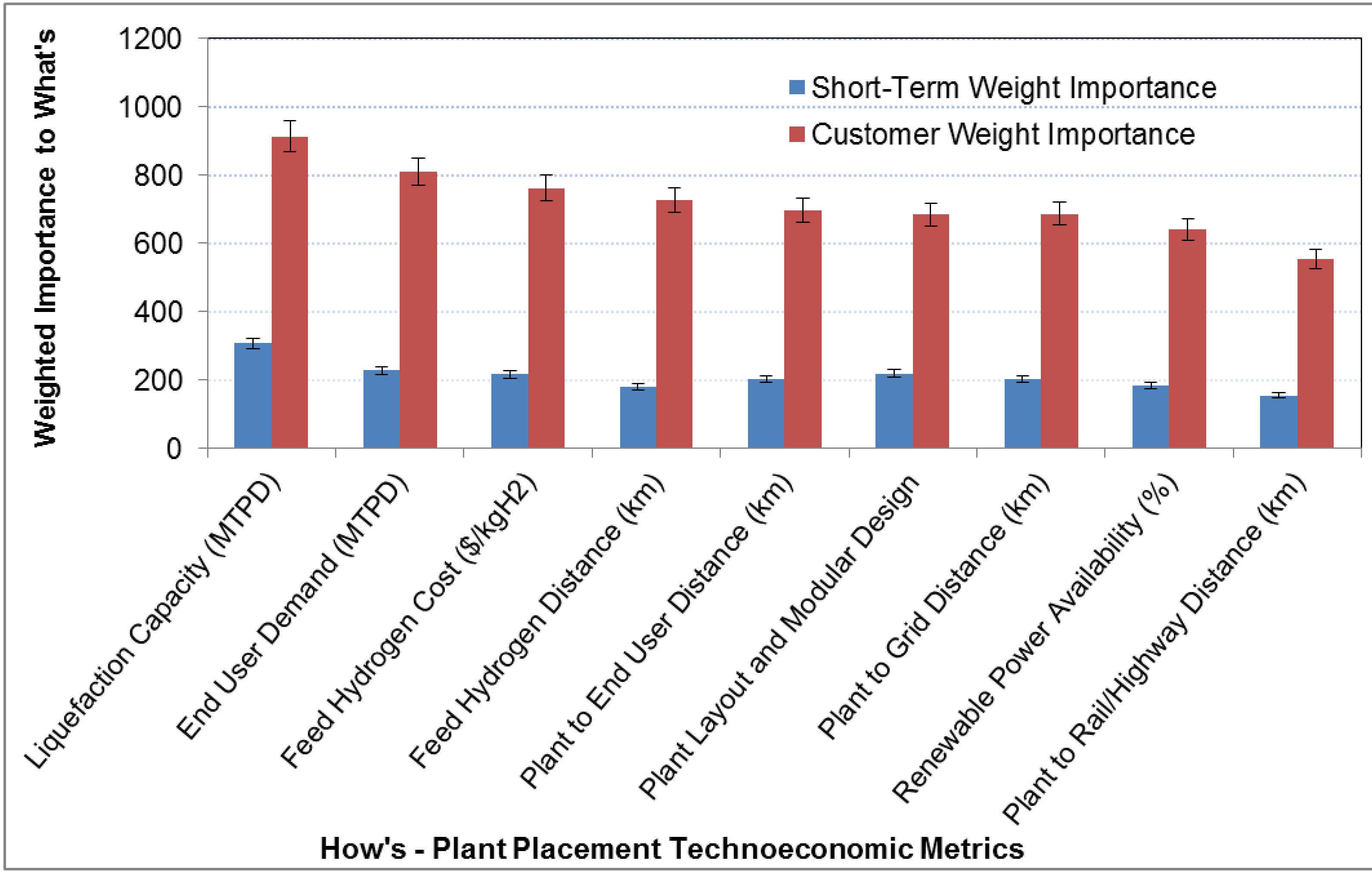
Task 3.5) Cost and performance comparison

30 Ton/day liquefaction plant cost summary	Vortex Tube Cycle	Advanced Plant (Shimko)	DOE Target in proposal
Liquefaction Plant Size (TPD)	1-30	50	5-30
Liquefier Capital Cost (million$)	~18 for 30 TPD	39.1 for 50 TPD	70
Liquefier Unit Cost: $1000 per kg/day	0.6	0.782	2.046
Energy Required (kWh/kgLH$_2$)	16.7	7.4-12	15

- VT cycle liquefaction plant capital cost is about 1/3 of the DOE cost target and also lower than the plant developed by Shimko.
- VT cycle liquefaction plant has excellent scalability.

Task 4 – Nationwide Technoeconomic Analysis

Task 4.1) Identify Drivers of Plant Placement



Liquefaction plant capacity and end user demand are the two most important factors in determining the plant location.

Task 4.3) Installed Capital Cost of 30 MTPD

Item	System Bill of Material	Shimko 50 TPD	Shimko Plant with Vortex Tube (5 TPD)	Shimko Plant with Vortex Tube (30 TPD)	
#	Description	Cost ($)	Cost ($)	Cost ($)	Reference
1	Vertex Tube	N/A	~100,000	~200,000	
2	Compressor 1 H2	5,700,000	2,500,000	10,800,000	
3	Compressor 2 He	24,000,000	1,000,000	1,200,000	
4	Heat Exchanger	4,084,000,000 (HX 1-2-3)	427,000 (I)	2,496,000 (I)	Shimko[9]
5	Heat Exchanger	2,062,000 (HX 3A-8)	138,900(II)	622,133 (II)	
6	Heat Exchanger	1,220,000 (TBX 1-4)	72,600 (III)	216,018 (III)	
6	H2 Expander	125,000	~75,000	125,000	Shimko[9]
7	Piping and Valves	455,000	~200,000	~400,000	Shimko[9]
8	Electric Control	100,000	~200,000	~400,000	Shimko[9]
9	Insulation	150,000	~100,000	~130,000	Shimko[9]
10	Structures	200,000	~120, 000	~180,000	Shimko[9]
11	Miscellaneous	500,000	~200,000	~400,000	Shimko[9]
12	Electric Switchgear	500,000	~200,000	~400,000	Shimko[9]
	Total	39,106,000	5,333,000	~17,569,000	

- Cost of 5 TPD and 30 TPD is derived from component list.
- VT cycle simplifies system and reduces heat exchanger use.

- **Cost is significantly lower than DOE target ($70 million [$2007] for a 30-TPD plant).**
- **VT-liquefaction plant can be modular design for scaling up.**

Required Slides

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- "Express more clearly how the proposed innovation would enable a FOM increase from 0.3 to 0.5, for example in a similar way to what is done in Peschka's "Liquid Hydrogen" book (table 13)."
  - This table states the irreversibilities of each component. Of which the expander and o-p conversion account for % of the overall cycle. Although the compressor is the primary contributor, and could be removed using just an electrolyzer for compression, which would substantially increase performance, the overall vortex tube performance is not at a level capable to achieve FOM 0.5.

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- "Clear discussion of liquefier capital (+O&M with energy input separated out) cost vs. efficiency gains, and impact of variable power inputs (renewable energy integration) should be addressed simultaneously in the reporting."
- In the early stage of the project last year, we did not have good energy consumption estimates. Those are now included on slides 21-22.

Collaborations

- Washington State University (sub)
  - Development of o/p conversion and separation technology
  - Bench scale testing
  - Static thermodynamic modeling

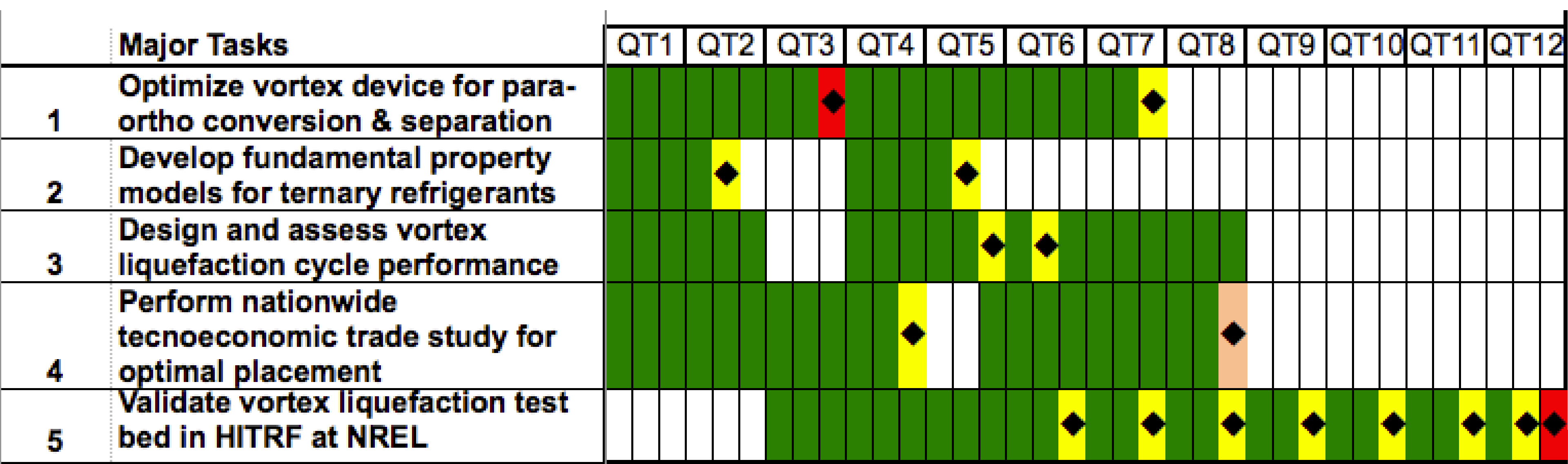
- Praxair
  - Industry input and oversight
  - Makes sure the project will result in relevant technology

Remaining Challenges and Barriers

- Increase vortex tube performance
- Scale up the technology and demonstrate performance at NREL
- Optimize the locations for small scale plants with respect to hydrogen markets and renewable resources

Proposed Future Work

- All efforts focused on vent-delayed go/no-go.
  - While flowing < 500 gm/hr of hydrogen to a vortex tube, obtain thermal conductivity measurements and calculations showing endothermic para/ortho conversion of 5% of a stream.
- Once successful, we will proceed with tasks 4 and 5 for techno - economic analysis and design of the scale up test bed. Milestone for end of FY.
  - Complete techno-economic and thermodynamic analysis based on models and data developed in the project to date of a 5,000-30,000 kg/day liquefier. Compare to DOE goals of FOM 0.5, 12 kWh/kg H2, and incumbent technologies.



Technology Transfer Activities

- J.W. Leachman, "Device to separate and convert ortho & parahydrogen using a vortex tube with catalyst," Provisional Patent Application Number 62101593, 01/09/2015.

Summary

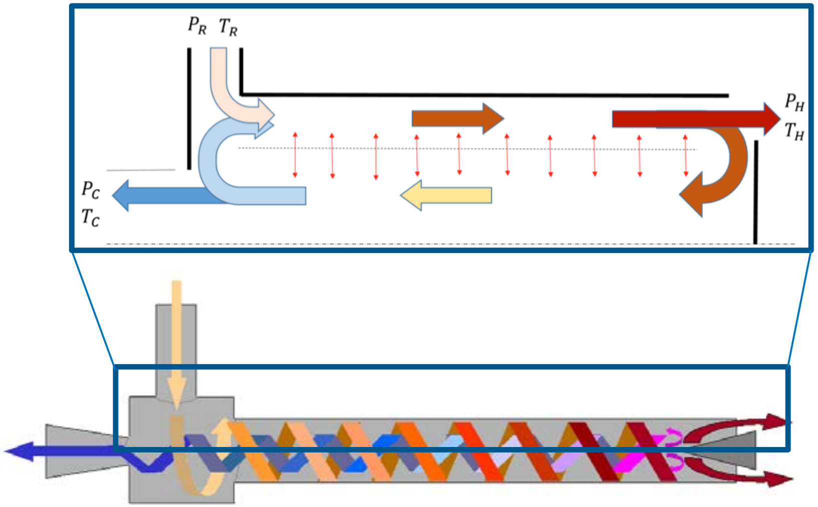
- Relevance – Increase Efficiency, reduce cost
- Approach – Exhaustive incorporation of earlier work, world's leading researchers
- Accomplishments – CFD model, HoQ, proven concept, refrigerant mixture models
- Collaborations – Active industry participation and oversight
- Future Work – SMART go/nogo and annual milestones.

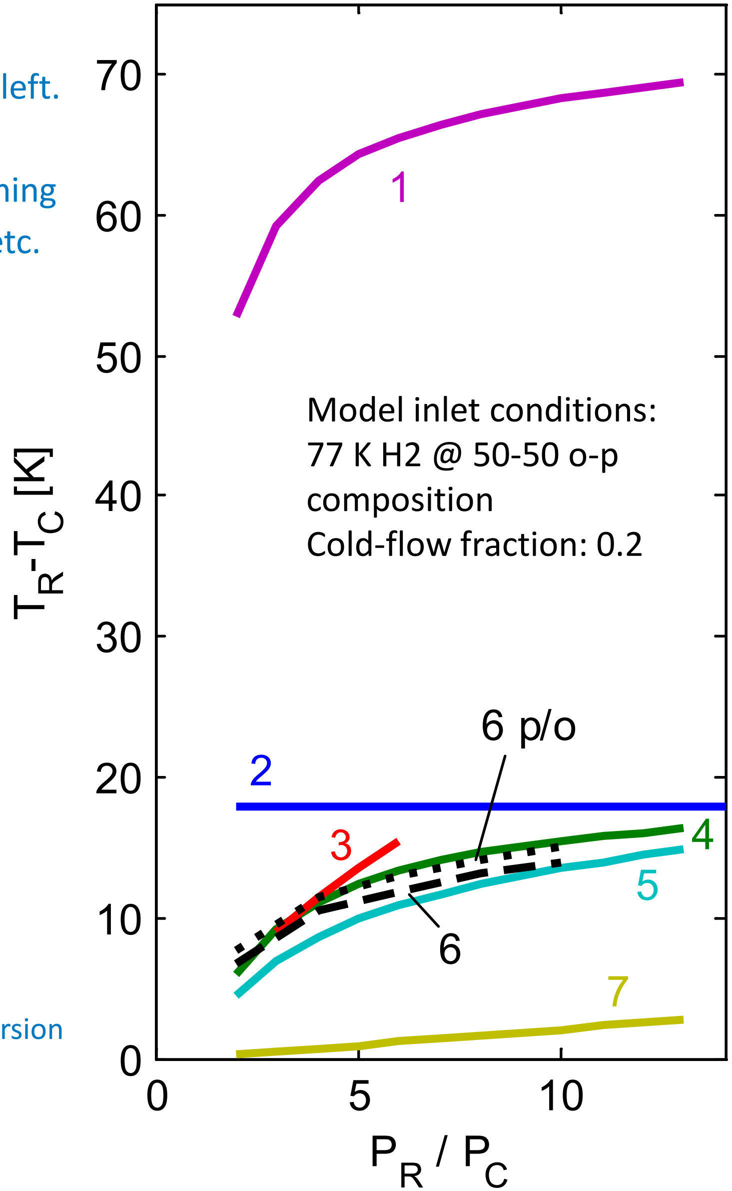
Technical Back-Up Slides

(Include this “separator” slide if you are including back-up technical slides **[maximum of five]**. These back-up technical slides will be available for your presentation and will be included in the electronic media and Web PDF files released to the public.)

Task 1.2) 1st Order Vortex Tube Model

- How the vortex tube works is complex:
  - Compressed gas forms a vortex, with outer fluid flowing right and core left.
  - Radial ΔP promotes ΔT drop in core.
  - Heat pumping from the cold core to the hot due to viscous work streaming
  - More complications from frictional heating, turbulence, recirculation, etc.





Model predictions for T drop:
1. "2nd law estimate" Eiamsa-ard and Promvonge (2008)
2. "Empirical model" Merkulov (1969)
3. "Thermo estimate" Polihronov and Straatman (2012)
4. "Semi-empirical" Ahlborn and Gordon (2000)
5. "Maxwell demon" Liew et al. (2012)
6. "Extended HEX-model" Matveev and Bunge (2016) with and without 5% p/o conversion
7. Joule-Thomson process

Task 2.2) Refrigerant PvT-x Measurements

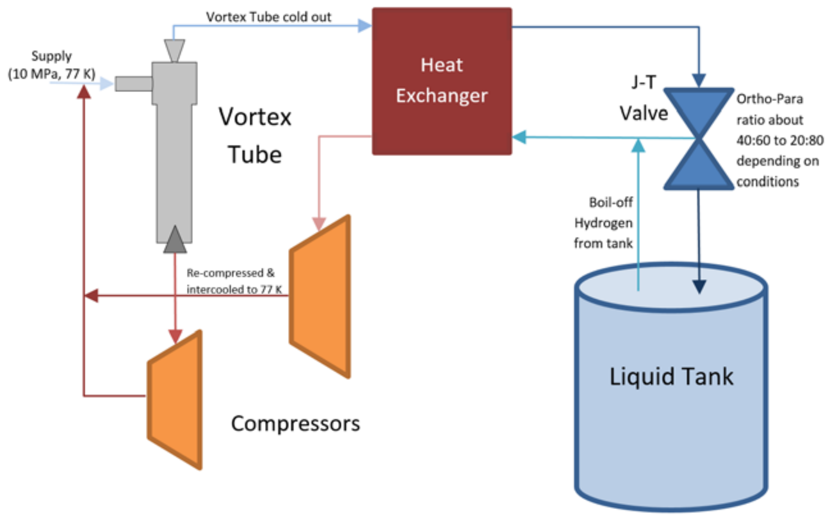
- Rubotherm Isosorp 2000 single sinker densimeter modified for cryogenics
  - Uses Archimedes principle with calibrated quartz sinker
  - Neon and parahydrogen measurements within 0.15% of current standards
- He-H2 model completed, Ne-He measurements completed, Ne-H2 measurements underway.
- Enables mixture equation of state development.

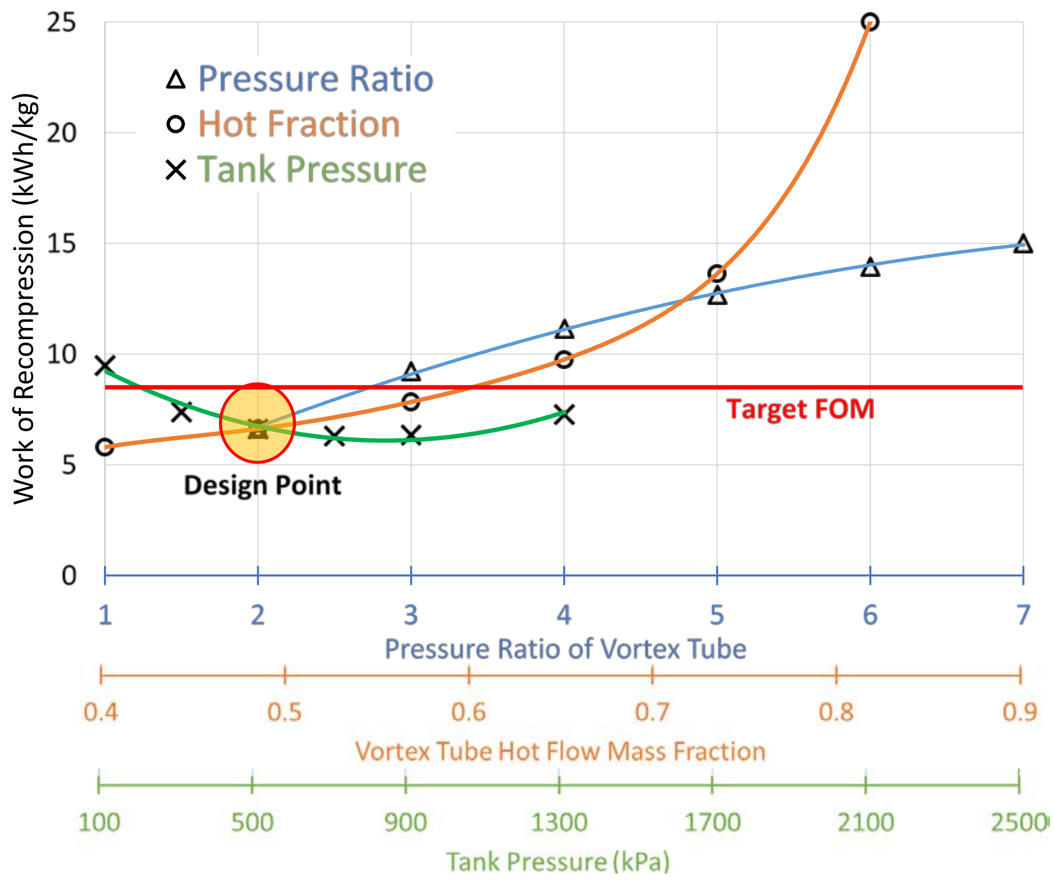
PURE NEON			
Temperature	Pressure	Density	Ref. Density
[K]	[PSI]	[kg/m^3]	[kg/m^3]
31.2	50.4	1133.0	1130.4
34.0	174.6	1076	1076.3
38.0	238.8	976.4	975.92
42.0	281.3	809.2	807.97

Neon-Helium Mixtures				
Temperature	Pressure	Density	Neon	Helium
[K]	[PSI]	[kg/m^3]	(% Mole)	(% Mole)
32.0	69.1	1112	98.4	1.6
36.0	134.5	1012	97.8	2.2
33.0	285.0	1095	98.7	1.3
38.0	298.3	939.9	98.2	1.8

Task 3.3) Steady State Cycle Analysis

- Fully integrated REFPROP hydrogen ortho/para equations of state
- Modular platform enables rapid layout re-configuration

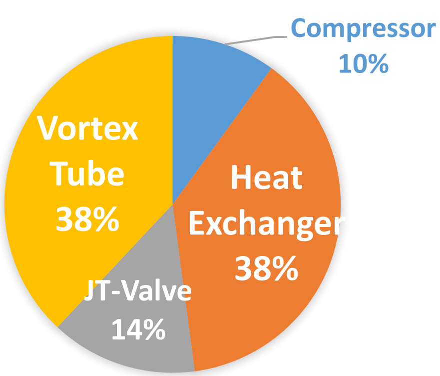




Task 3.3) Steady State Exergy Analysis

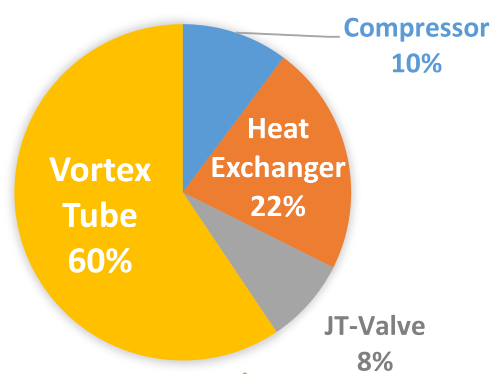
- The majority of the exergy destruction is in the vortex tube and heat exchanger
- Raising the pressure ratio across the vortex tube increases its contribution to exergy loses
- Increasing the hot flow fraction indirectly increases exergy loses, as the hydrogen has to flow through the vortex tube multiple times on its path to liquefaction

DESIGN CONDITION



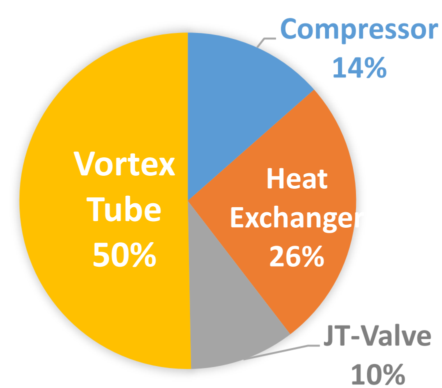
33.4% ‡

HIGHER VORTEX PRESSURE RATIO



47.2% ‡

HIGHER VORTEX TUBE HOT FLOW



27.7% ‡

‡ Total Exergy Destroyed as % of exergy @ Vortex Tube Inlet