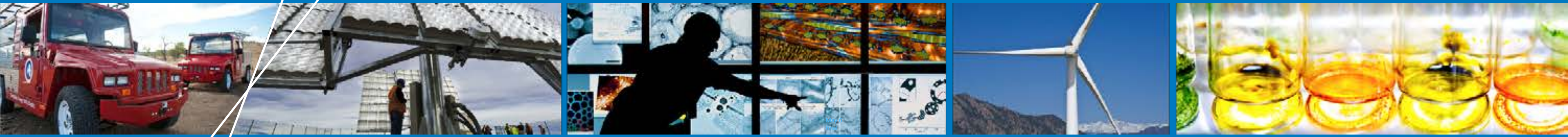
Improved Hydrogen Liquefaction through Heisenberg Vortex Separation of para and ortho-hydrogen



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National Renewable Energy Laboratory
June 8, 2016

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*: $175k

* As of 3/31/16

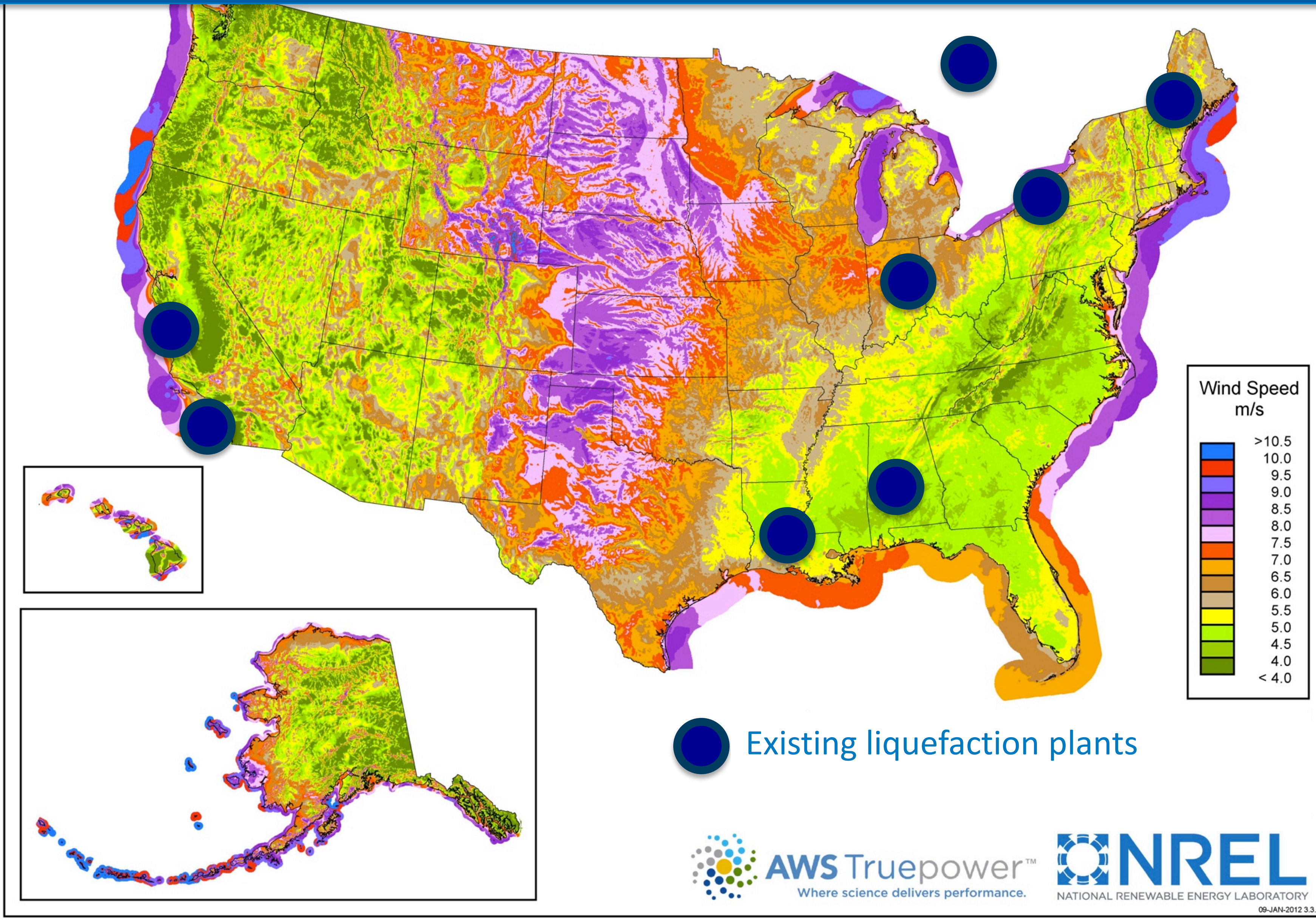
Barriers

- 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.



Relevance: Liquefaction plants aren't very efficient.

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

FOM = ratio of ideal to real specific work

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.**

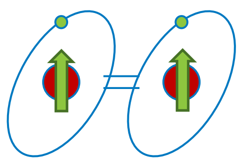
- **Scientific Merit: Improve efficiency of liquefaction by > 40% (from 0.35 to >0.5 FOM) by minimizing use of refrigerant.**
  - Exothermic ortho/para conversion results in significant refrigerant use. Vortex concept leverages catalysts for reverse endothermic reaction
  - Vortex motion cools para hydrogen 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]

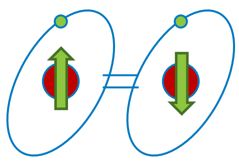
[1]Nobelprize.org accessed 2010



Orthohydrogen (higher energy state)

Normal Hydrogen 3:1

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

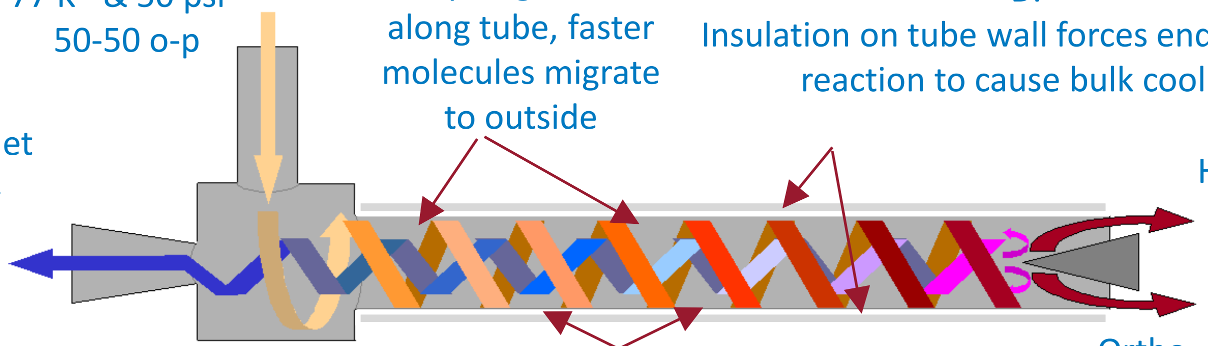


Parahydrogen (lower energy state)

"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.

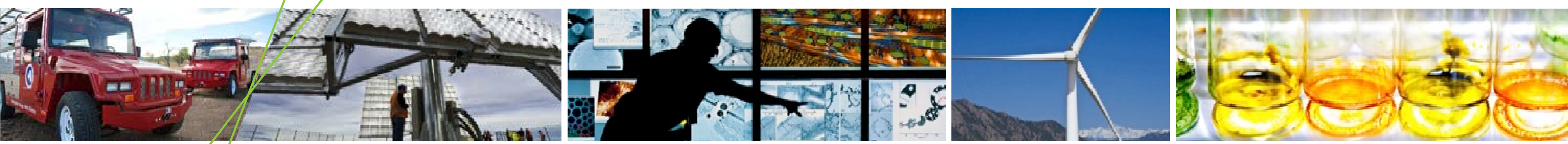


Ortho/para separation and conversion drives cooling.

Milestones & Accomplishments

Customer-centric development approach.

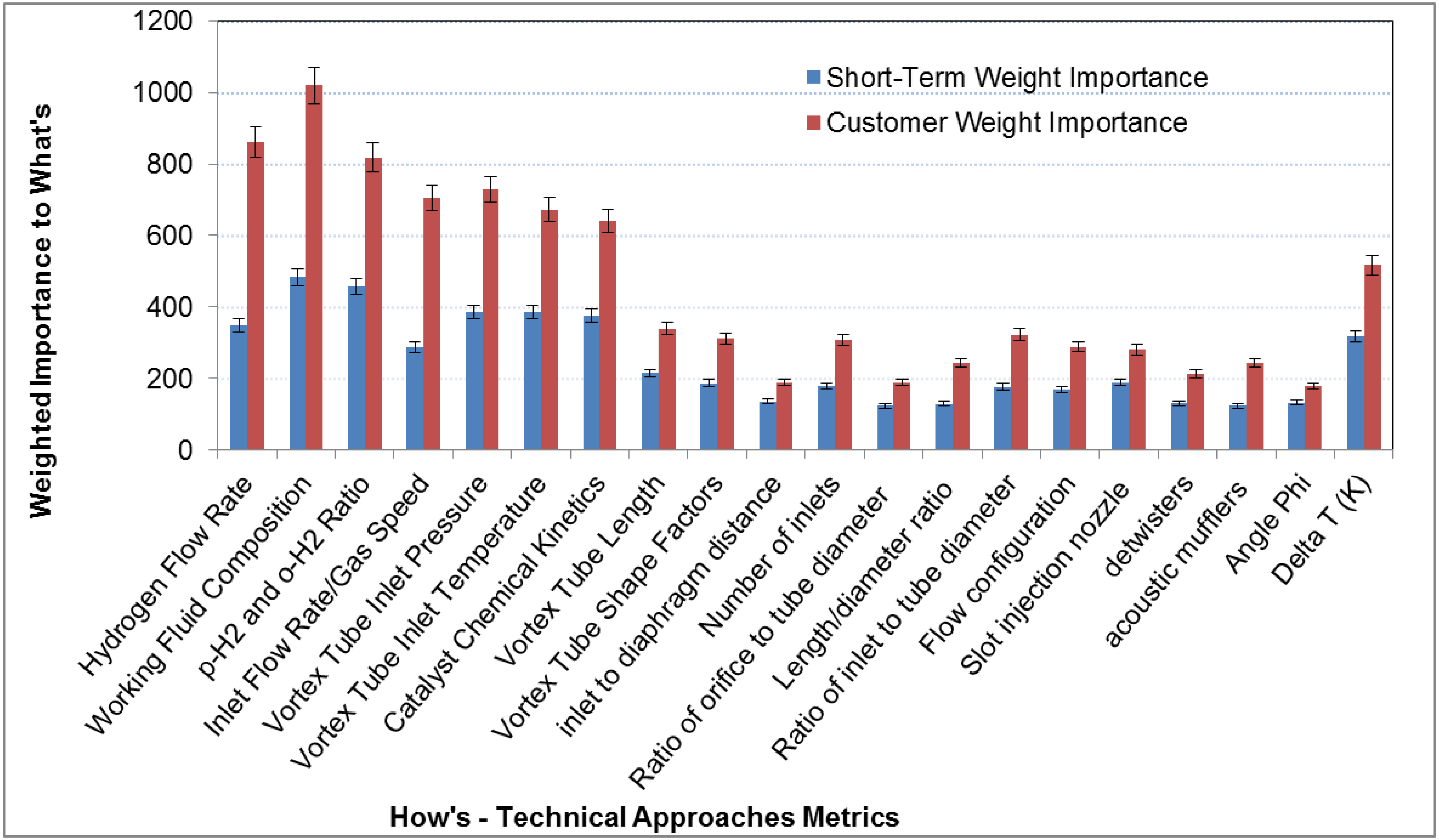
1. Completed a House of Quality (HOQ) analysis to align project with stakeholder needs.
2. Developed predictive 1st order and CFD models of vortex tubes at cryogenic temperatures with hydrogen.
   a. Modified an existing experiment to measure cryogenic hydrogen vortex tube performance.
3. Completed 1st helium-hydrogen-neon liquid phase density measurements for refrigerant mixtures.
4. Developed a steady state model of cycle performance and conducted exergy analysis.



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

Task 1.3) Vortex Tube HoQ

Key variables: Refrigerant composition, para-ortho conversion rate



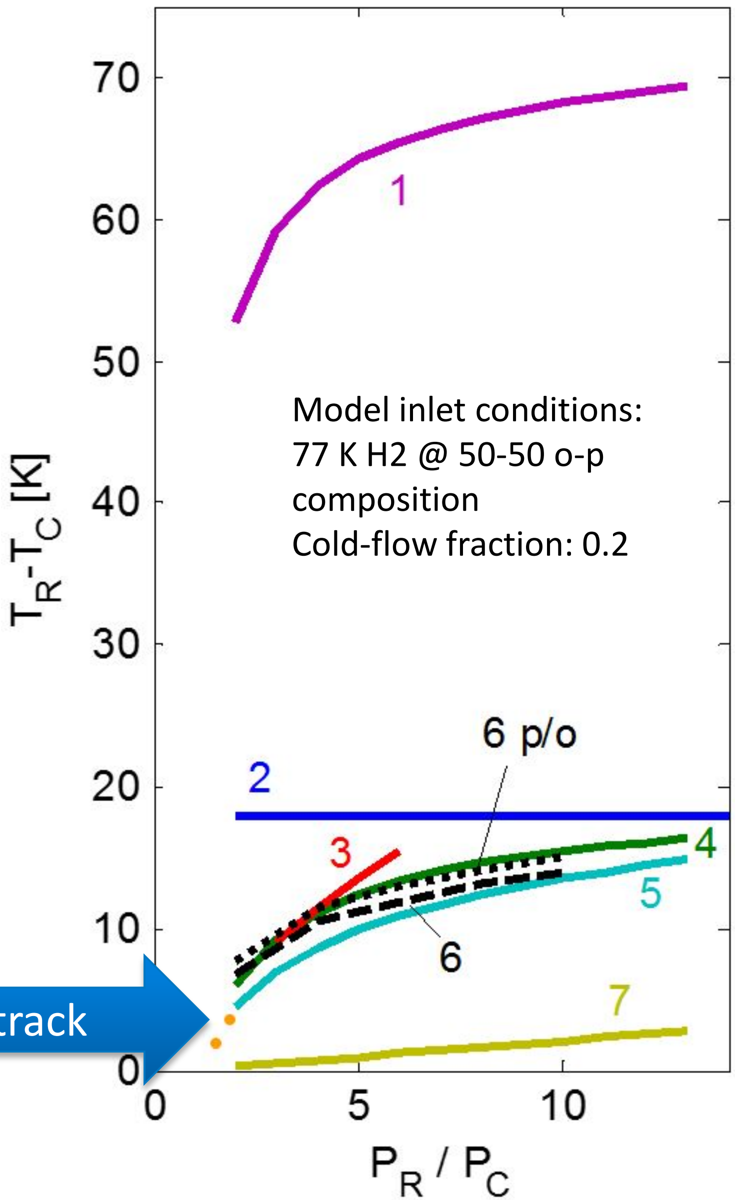
Task 1.2) 1st Order Vortex Tube Model

Vortex tube offer much more potential than incumbent J-T valve

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

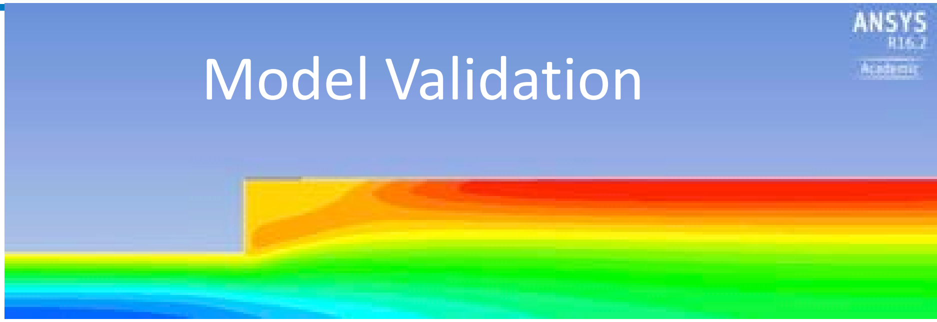
Preliminary experimental data (orange) is on track



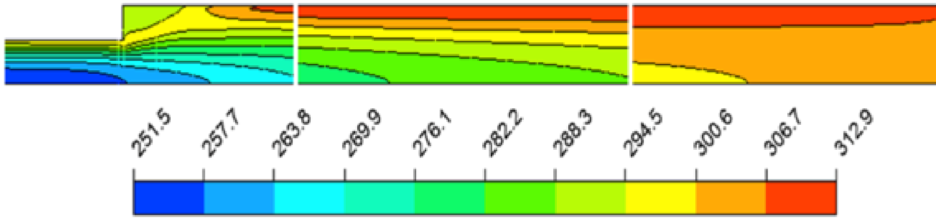
Task 1.2) CFD Vortex Tube Modeling

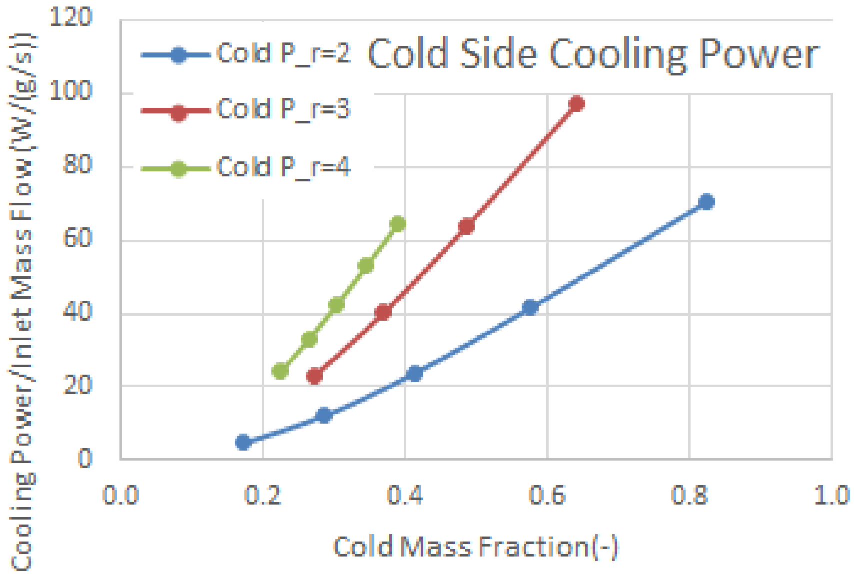
- **ANSYS Fluent was selected as a Computational Fluid Dynamics (CFD) tool for detailed modeling of processes in a vortex tube**
- **Mesh-independence studies and model validated with previous numerical simulations.**
- **Parametric model optimization underway.**

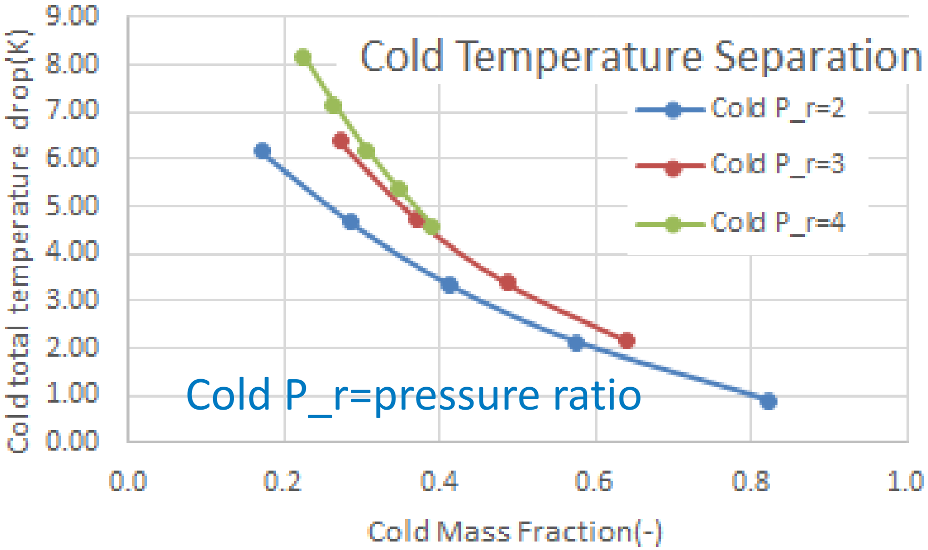
Have a predictive CFD model validated against literature.



Literature results (Bej 2015)

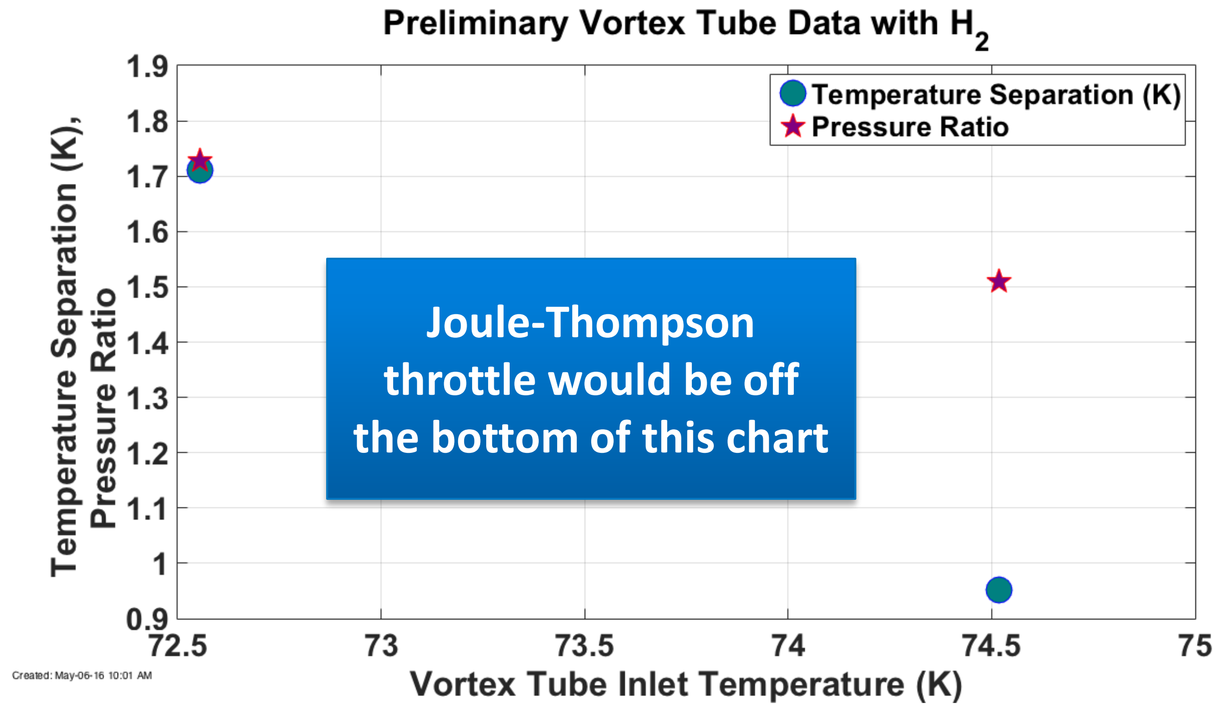






Task 1.3) Vortex Tube Experiment

- Cryocatalysis Hydrogen Experiment Facility (CHEF) has previously completed para-ortho conversion studies.
- Liquefies hydrogen and converts to pure para, utilizes hot-wire anemometers to measure outlet composition.
- Test plan varies cold-fraction, pressure ratio, temp, catalysis.



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

Task 2.1) Refrigerant Mixture Review

- **He-Ne-H2 (a.k.a. helium) mixtures considered for use as refrigerant**
- **No liquid P-ρ-T-x for any binary He-Ne-H2, required by EOS**

Helium-Neon System Summary of Property Data

Author	Year	#	Temperature range (K)	Pressure range (MPa)
	P-ρ-T			
Holborn & Otto	1924	39	233.16-313.14	0.109-3.705
Vogl & Hall	1972	51	273.10-673.47	2.361-10.057
	VLE			
Heck & Barrick	1974	76	26.95-41.91	0.284-20.336
Knorn	1967	22	24.71-27.03	0.608-5.168
	Second Virial Coefficient			
Brewer & Vaughn	1969	8	148.16-323.13	
Knobler et al.	1959	1	90.02	
Holborn & Otto	1924	5	273.10-673.13	

Hydrogen-Neon System Summary of Property Data

Author	Year	#	Temperature range (K)	Pressure range (MPa)
	VLE			
Heck & Barrick	1966	92	26.00 - 42.50	0.710 – 2.513
Streett & Jones	1965	94	24.59 – 33.73	0.045 – 1.389
	Second Virial Coefficient			
Brewer & Vaughn	1969	8	148.15 - 323.13	
Knobler et al.	1959	1	90.02	
	SND			
Güsewell et al.	1970	76	25.00 – 31.00	

Extensive literature review. We think we have everything worldwide, since the beginning of time.

Task 2.2) Refrigerant PvT-x Measurements

Modified single sinker densimeter for cryogenics to enable PvT-x measurements of He-Ne-H2 mixtures.

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

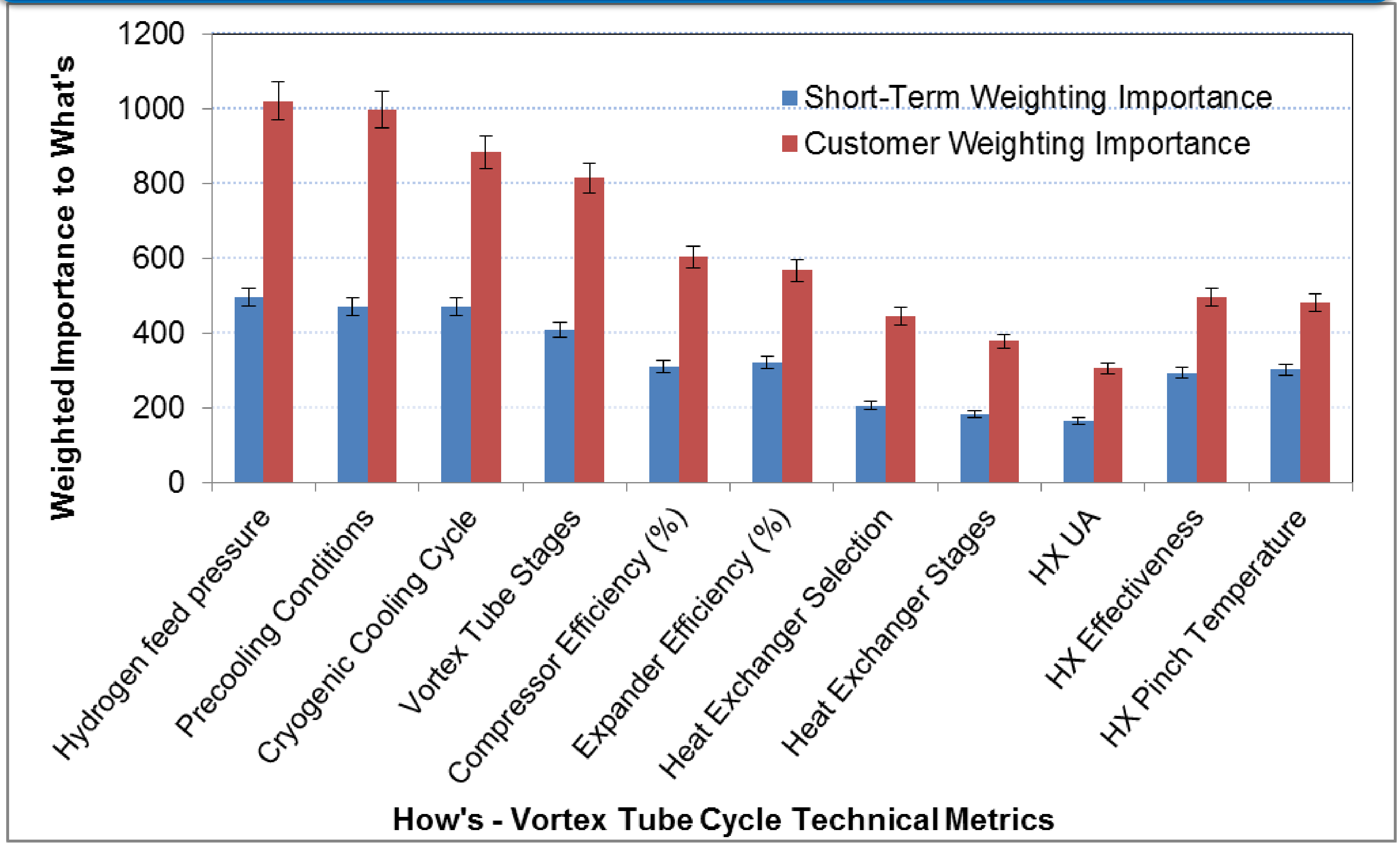
Ne and Para-H2 measurements within 0.15% of standards!

Single Sinker Densimeter

Task 3 - Design and assess vortex liquefaction cycle performance

Task 3.3) Cycle House of Quality

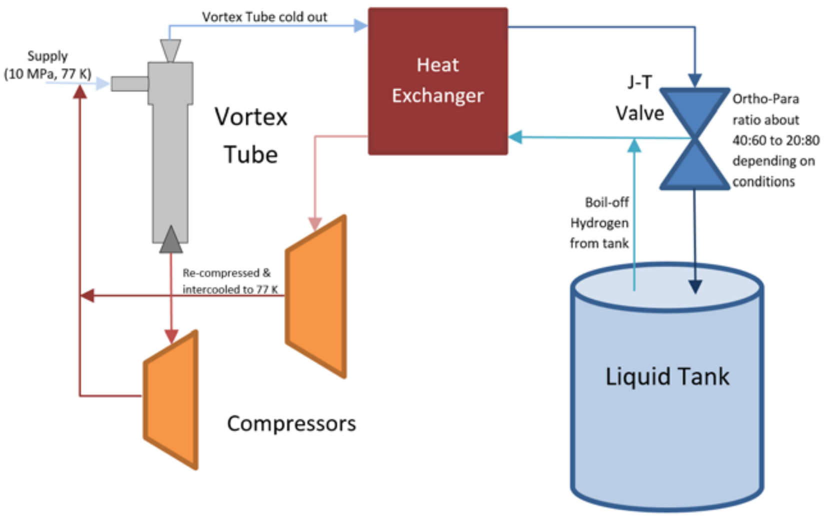
Vortex tube performance and precooling method are key

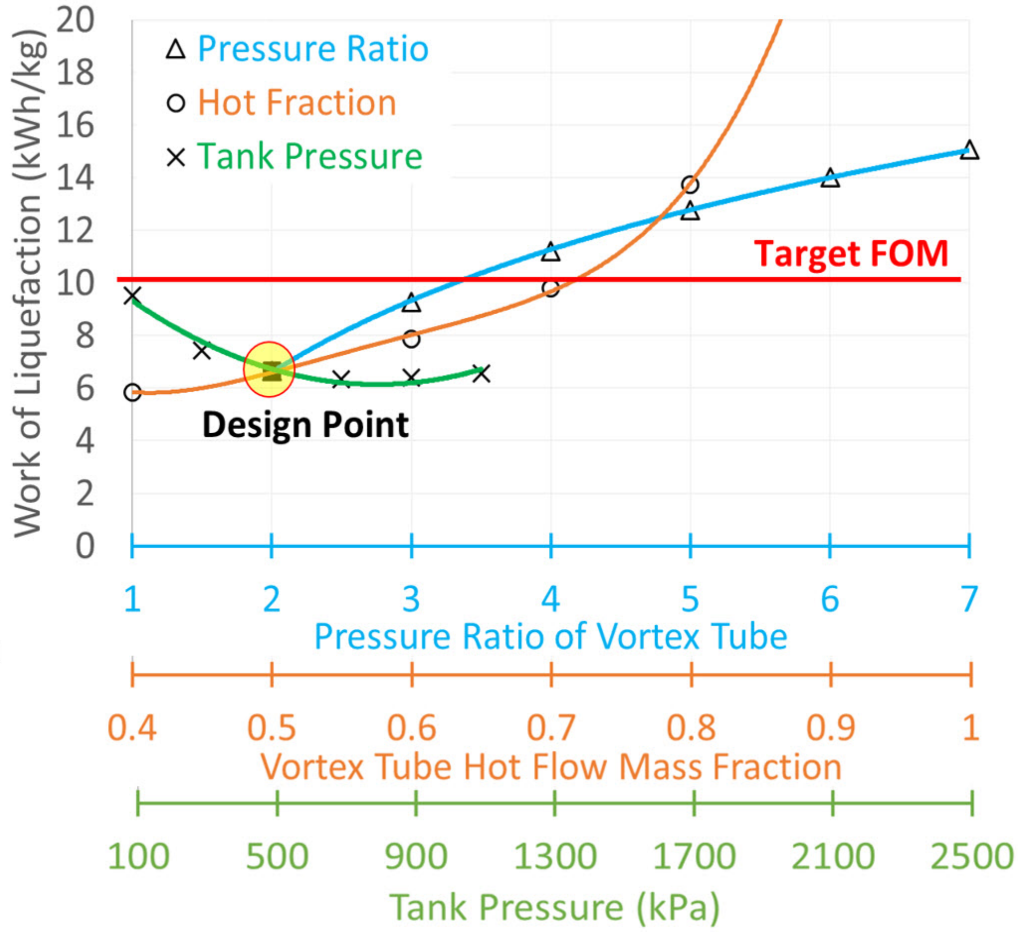


Task 3.3) Steady State Cycle Analysis

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

FOM 0.5 goal is achievable!



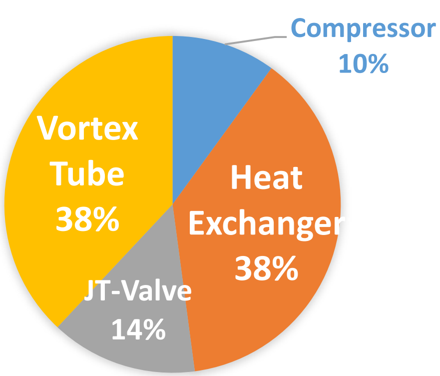


Task 3.3) Steady State Exergy Analysis

All effort focused on the no. 1 exergy destroyer in the system

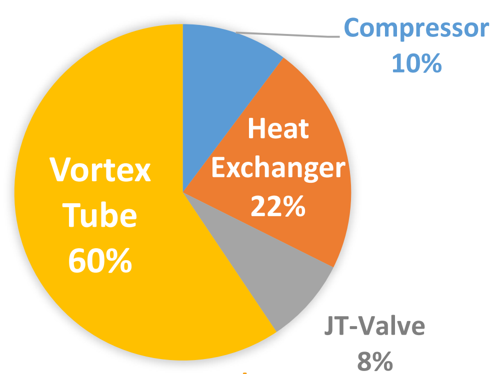
- The majority of the exergy destruction is in the vortex tube and heat exchanger
- Raising the pressure ratio across the vortex tube increases its contribution to exergy losses
- Increasing the hot flow fraction indirectly increases exergy losses, as the hydrogen has to flow through the vortex tube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

DESIGN CONDITION



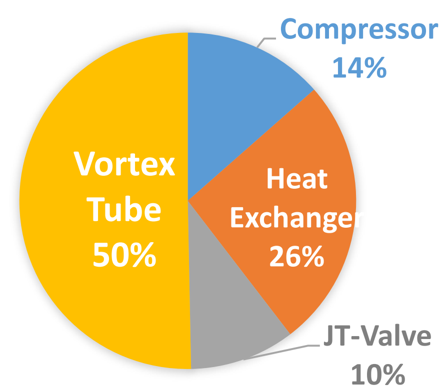
33.4% ‡

HIGHER VORTEX PRESSURE RATIO



47.2% ‡

HIGHER VORTEX TUBE HOT FLOW



27.7% ‡

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

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This is the first review for this project.

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

- Prove the performance of the vortex tube at the bench scale
- 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 go/no-go for end of June.**
  - 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.

	Major Tasks	QT1	QT2	QT3	QT4	QT5	QT6	QT7	QT8	QT9	QT10	QT11	QT12
1	Optimize vortex device for para-ortho conversion & separation			◆				◆					
2	Develop fundamental property models for ternary refrigerants		◆			◆							
3	Design and assess vortex liquefaction cycle performance					◆	◆						
4	Perform nationwide tecnoeconomic trade study for optimal placement				◆				◆				
5	Validate vortex liquefaction test bed in HITRF at NREL						◆	◆	◆	◆	◆	◆	◆ ◆

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, initial bench testing, refrigerant mix properties
- Collaborations – Active industry participation and oversight
- Future Work – SMART go/nogo and annual milestones.