III.9 Improved Hydrogen Liquefaction through Heisenberg Vortex Separation of Para- and Orthohydrogen

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Project Start Date: November 11, 2015
Project End Date: September 30, 2018

Overall Objectives

- Increase liquefaction cycle efficiency from figure of merit (FOM) 0.35 to > 0.5.
- Lower liquefier installed capital cost (~$2.5M/metric tonne per day [MTPD])/unit capacity (30 MTPD).
- Lower cost of liquid hydrogen delivery toward the DOE target of $2/gge.

Fiscal Year (FY) 2016 Objectives

- Complete the first house of quality in a quality function deployment analysis of the vortex tube and the liquefaction cycle which will contain it. Identify three critical-to-quality metrics.
- Determine pressure–volume–temperature–x measurements of cryogenic helium–hydrogen–neon mixtures focusing on gas dissolved in liquid and at high pressure (<200 bar). Prepare a review of available measurements and needs for cycle design.
- Analysis of vortex performance through experiments and numerical (first order and computational fluid dynamics [CFD]) analysis. Develop device and cycle design house of quality matrices.
- Go/No-Go: While flowing <500 gm/h of hydrogen to a vortex tube, obtain thermal conductivity measurements and calculations showing endothermic para/ortho conversion of 5% of a stream.
- Complete technoeconomic and thermodynamic analysis based on models and data developed in the project to date of a 5,000–30,000 kg/d liquefier. Compare to DOE goals of FOM 0.5, 12 kWh/kg H_2, and incumbent technologies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(H) High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

Technical Targets

TABLE 1. DOE Targets for Small Scale (30 MTPD) Liquefaction

Characteristic	Units	DOE 2020 Targets	Project Status
Installed Capital Cost	$MM	70	TBD
Figure of Merit	Unitless	0.5	Modeling shows 0.5 is achievable

TBD – To be determined

FY 2016 Accomplishments

- Completed first house of quality, determining critical to quality metrics.
- Developed predictive first order and CFD models of vortex tubes at cryogenic temperatures with hydrogen.
- Completed first helium–hydrogen–neon liquid phase density measurements for refrigerant mixtures.
- Developed a steady state model of cycle performance and conducted energy analysis.

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INTRODUCTION

This project has dual aims: (1) improve the efficiency of hydrogen liquefaction to show a path to an FOM of 0.5, (2) enable the scale-down of liquefaction plants to capacities that can be optimally located to both utilize low cost hydrogen sources and minimize liquid delivery costs to customers. The team will achieve this by addressing a fundamental reality of liquefaction—the ortho-para conversion of hydrogen spin isomers.

Efficient small-modular hydrogen liquefiers have not been developed due to the difficulty of refrigerating below 77 K. Below 77 K the largest entropy change of any material is orthohydrogen-parahydrogen conversion which is an exothermic reaction that significantly hinders liquefaction efficiencies. In this work we will develop a proof of concept small-modular hydrogen liquefaction system that uses vortex tubes to enable kinetic parahydrogen-orthohydrogen separation and conversion via vortex tubes. This approach allows for an endothermic parahydrogen-orthohydrogen reactions to be catalyzed, such that bulk cooling occurs before the orthohydrogen is separated and recycled in a liquid nitrogen bath. This scalable approach is anticipated to significantly increase the efficiency of small-modular hydrogen liquefiers, enabling their use with electrolysis and enabling low-cost liquid hydrogen to supply backup power and hydrogen fueling stations.

APPROACH

The team will develop and optimize the concept of vortex tube separation for para- and orthohydrogen. The vortex tube will not only separate the two allotropes of hydrogen, but will use para to ortho conversion within the device to drive bulk cooling.

First, WSU will optimize and then, at the bench scale, verify the operation of the vortex tube. Then, NREL and WSU will up-scale the device and build a proof-of-concept system around it. NREL will additionally develop both technoeconomic and liquefaction plant models to further optimize the system design and placement.

RESULTS

The team successfully measured and characterized the thermodynamic state of ternary helium, neon, hydrogen mixtures, and will develop the necessary equations of state. These equations of state will ultimately be implemented in the National Institute of Standards and Technology's Reference Fluid Thermodynamic and Transport Properties Database. See Table 1, which shows sample measurements of a binary system of neon and helium.

The team successfully completed development of first order models of vortex tube performance, using all available literature worldwide. The models show that vortex tubes should be able to perform better than Joule-Thompson throttles under nearly all operating conditions. See Figure 1.

The team successfully completed the first house of quality, identifying the para/ortho conversion rates and refrigerant mixture as critical to quality metrics. The team evaluated a number of vortex tube geometric parameters, which will be more fully explored using detailed CFD studies. See Figure 2.

The team created a steady-state thermodynamic model showing that the goal of FOM = 0.5 is achievable. See Figure 3. This model found an optimal design point at pressure ratio of 2.

TABLE 1. Sample Refrigerant Mixture Properties

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

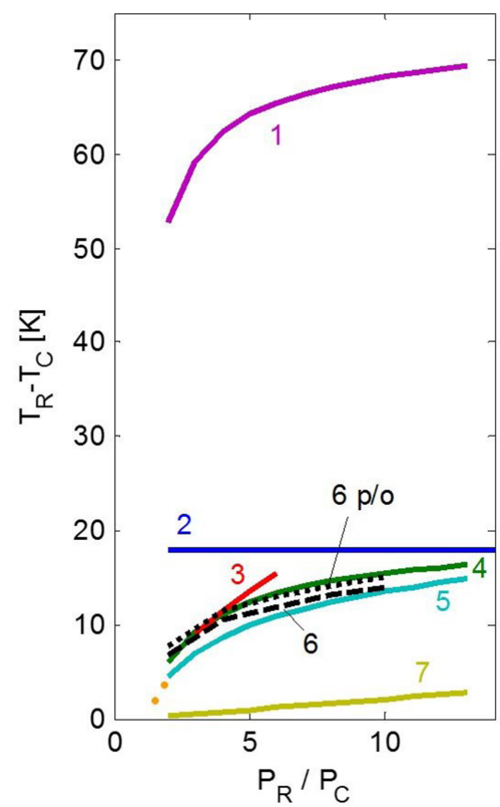
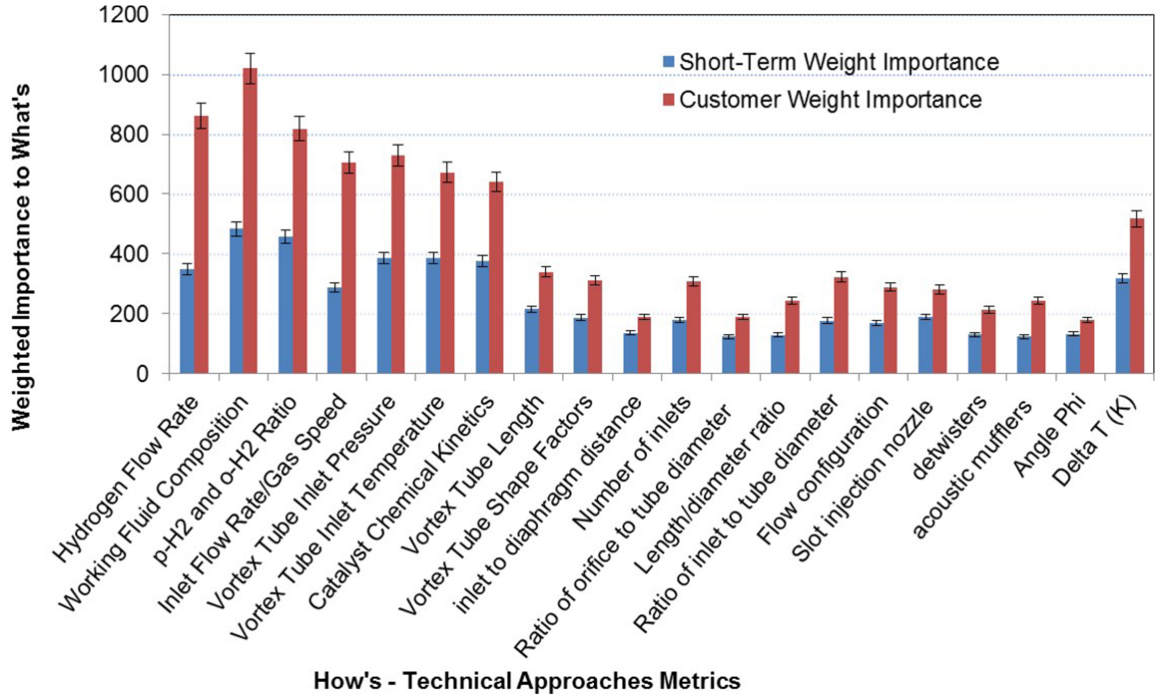


FIGURE 1. First order vortex tube model performance prediction



p-H2 – parahydrogen; o-H2 – orthohydrogen

FIGURE 2. First house of quality identifying critical to quality metrics

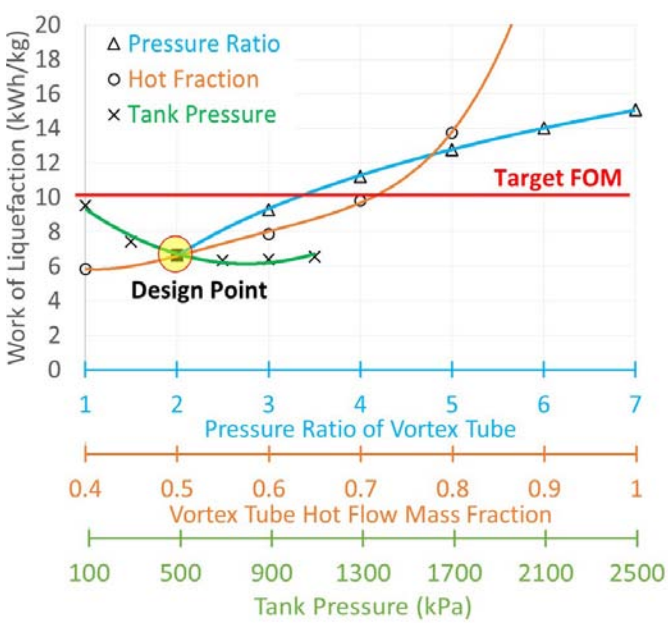


FIGURE 3. Thermodynamic model showing the feasibility of FOM = 0.5

CONCLUSIONS AND FUTURE DIRECTIONS

The team has the following go/no-go milestone to complete by September 30, 2016: while flowing <500 gm/h of hydrogen to a vortex tube, obtain thermal conductivity measurements and calculations showing endothermic para/ortho conversion of 5% of a stream. The team will also complete the first round of technoecoomic analysis by that time.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Ainscough, C., Leachman, J., *Improved Hydrogen Liquefaction through Heisenberg Vortex Separation of para and ortho-hydrogen,* Washington, DC: U.S. Department of Energy, 2016.