## III.5 Improved Hydrogen Liquefaction through Heisenberg Vortex Separation of para- and ortho-hydrogen

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## **Overall Objectives**

This project aims to improve three specific areas of hydrogen liquefaction.

- Improve the thermodynamic efficiency to show a path to figure of merit of 0.5 through the use of a novel separation concept.
- Reduce the delivery cost of liquid hydrogen by enabling small-scale (5–30 metric ton per day [MTPD]) liquefaction systems in optimal locations relative to markets and renewable resources.
- Reduce the installed capital cost of liquefaction plants by enabling efficient scale-down of plants to the 5–30 MTPD sizes.

## Fiscal Year (FY) 2017 Objectives

This project aims to develop the vortex tube (VT) ortho/ para separation concept from technology readiness level (TRL) 2 to a TRL of 4 in three years. The focuses of FY 2017 tasks are:

- Verify the VT performance experimentally and computationally to achieve the performance milestone at Washington State University.
- Small modular liquefier placement analysis for stranded renewable energy used for hydrogen production and delivery.
- Identify candidate cycles that can improve the figure of merit from 0.3 to 0.5 to achieve a work of liquefaction less than 7.92 kWh/kg.

### **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.

- (A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis
- (H) High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

## **Technical Targets**

This research is in an early TRL stage. By developing and validating the performance of VT ortho/para hydrogen separation, the project team will overcome one of the major limitations and inefficiencies that exist in commercial hydrogen liquefaction plants today (i.e., ortho/para conversion).

TABLE 1. Milestones and Deliverables

Characteristic	Units	DOE 2015 Status	DOE 2020 Target
Installed Capital Cost	\$-Million	70	70
Energy Required	kWh/kg of $H_2$	15	12

The baseline analysis on the specific energy consumption of realistic versions of these cycles shows values much higher than the Multi-Year Research, Development, and Demonstration Plan current status. The project has shown through analysis that a VT could reduce the specific energy consumption of a Linde-Hampson cycle from 36 kWh/kg to 29 kWh/kg. This is a 21% reduction. Similarly, with a precooled Claude cycle, the reduction is 15%.

## FY 2017 Accomplishments

- The Heisenberg vortex liquefaction project completed state measurements for combinations of binary mixtures of hydrogen, helium, and neon (H-He, H-Ne, He-Ne). The equations of state developed from these tests will be published in the National Institute of Standards and Technology Reference Fluid Thermodynamic and Transport Properties (REFPROP) database and added to the materials reference database.
- Constructed a cryogenic compatible VT and completed initial testing. A computational fluid dynamics (CFD) model was developed to simulate the VT design conditions.

- Completed a thermodynamic cycle simulation to model the advantages of adding a VT to traditional liquefaction cycles, such as Linde-Hampson and pre-cooled Claude.
- Completed a techno-economic analysis that indicates significant cost benefits from reducing the reliance on hydrogen expanders and heat exchangers, as in current cycles.
- Developed the methodology to incorporate optimization of liquefaction plant placement into existing DOE tools, including Regional Energy Deployment System and Scenario Evaluation and Regionalization Analysis, based on regional forecasts of hydrogen demand and transport network analysis.

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#### INTRODUCTION

This project explores an early-stage approach to lowering the energy requirements of hydrogen liquefaction using catalyst-coated VTs in lieu of conventional mechanical equipment (e.g., compressors, expanders, throttles). The crux of the project is the development of a cryogenic VT, which will be coated with catalysts that convert parahydrogen to ortho-hydrogen. This endothermic reaction is expected to cause bulk cooling. During the liquefaction process, the reverse exothermic reaction (ortho-to-para conversion) typically takes place, and is a source of inefficiency; the heat of conversion between the allotropes of hydrogen is 700 kJ/kg, compared to 420 kJ/kg for the heat of vaporization. Catalysis of para-to-ortho conversion is expected to counter the heat rejection of ortho-to-para conversion at a lower cost than the use of additional heat transfer fluid. Moreover, the motion of the VT is expected to create a pressure drop in hydrogen gas, further contributing the cooling. This project targets enabling liquefaction of hydrogen at 6.0 kWh/kg, the DOE's ultimate target [3].

Liquefaction is a mainstream approach to transport of hydrogen long distances to industrial end users as well as fueling stations. Benefits of liquefaction include the high capacities of liquid tankers relative to gaseous tube trailers, the flexibility of the pathway relative to pipelines, and the high purities of liquid hydrogen relative to gaseous hydrogen. However, conventional mechanical approaches have inherent inefficiencies with little room for improvement, and are not cost-competitive at small scales; hydrogen liquefaction plants today are typically sized for 10–40 tonnes per day. The use of VTs in hydrogen liquefaction has, to the author's knowledge, only been theorized to date. This project is exploring their performance given their potential to lower the energy consumption and enhance the scalability of hydrogen liquefaction.

#### APPROACH

This project will address the barriers of liquefaction efficiency by developing a novel ortho/para hydrogen separation concept, and building a system around the same. This project aims to develop a vortex that separates hydrogen gas by temperature. Higher temperature molecules are expected to migrate toward the walls of the vortex. The vortex will be coated with catalyst capable of converting para-hydrogen to ortho-hydrogen. Catalysis of this endothermic reaction within the tube is expected to cause bulk cooling of the hydrogen gas being liquefied. This approach is expected to lower the energy costs of hydrogen liquefaction, and also to be viable at system sizes of 5–30 MTPD.

In FY 2017, thermodynamic modeling was performed to characterize the energy consumption of a system wherein VTs are integrated into a Claude cycle using liquid nitrogen (LN2) as a pre-coolant. For reference, Claude cycles in industry typically consume 10 kWh/kg-H<sub>2</sub> and 15 kWh/kg-H<sub>2</sub>. The ideal work of liquefaction is 3.92 kWh/kg.

#### RESULTS

#### Go/No-Go Decision

The project's go/no-go milestone was to achieve 5% para/ortho-hydrogen conversion under catalyzed conditions. By the go/no-go date, the team achieved 1.44% conversion. However, the pressure ratios achieved the VTs were significantly lower than originally anticipated. As a result the team felt that achievement of the go/no-go would require more energy consumption than the project originally targeted. The project team and DOE therefore decided to discontinue the project and identify other research areas with potential to enhance the viability of the overall concept. Areas that the team is now exploring include catalyst performance in a vortical flow reactor, supercritical performance of a VT, additive manufacturing of an optimal VT, and catalyst development and characterization.

#### Summary of Results

Figure 1 shows a conceptual schematic of a Heisenberg Vortex Tube (HVT). Tests were performed on tubes containing internal rifling, smooth bore tubes, and those with and without an internal catalyst coating. To the author's knowledge, this was the first time that a VT has been demonstrated to cool hydrogen to cryogenic temeratures. The inset in the upper left shows a comparison of a noncatalyzed HVT to a Joule-Thompson (J-T) throttle. The throttle results in a temperature drop of 0.18 K, whereas the uncatalyzed tube has a cold end  $\Delta T$  of 1.08 K, **one order of magnitude higher**. When coated with ruthenium catalyst,



FIGURE 1. Test result on various catalyst conditions and comparison to J-T expansion

the performance increases an additional 38% to 1.49 K, as shown in the right inset in Figure 1. This increase in performance indicates that the catalyst likely caused para-to-ortho conversion, and subsequent bulk cooling.

Washington State University subsequently tested the impact of rifling in the VT on cooling power. Figure 2 shows a set of test results (details in the inset), along with expected performance based on thermodynamic models, for comparison. The temperature drop achieved by a ruthenium-coated rifled tube was 57% greater than that of a rifled tube without catalyst, and 205% greater than that of a smooth tube without catalyst.

Experimentation showed that the VT achieved 225% greater temperature drop than J-T valves conventionally used in industrial liquefaction (in Linde-Hampson and Claude cycles). This result is a substantial testament to the potential of this approach in lowering the energy consumption of liquefaction, and is supported by previous research in this space. Table 2 shows tabulated comparisons of experimental

and model data from the current project and prior work in this area.

# Subtask 3.2: Develop Steady State Thermodynamic Simulation of Liquefier Cycle

Using the current best estimates of VT performance at cryogenic hydrogen conditions, we estimate a 19% improvement to the standard pre-cooled, single expander, Claude cycle if the VT is used in place of a J-T valve. See Figure 3. The standard single expander cycle achieves a liquefaction work of 19.49 kWh/kg. Adding a catalyzed VT to this cycle lowers the liquefaction work to 15.44 kh/kg, or about four percentage points.

#### Task 4. Perform Nationwide Techno-Economic Trade Study for Optimal Vortex Liquefier Placement

National Renewable Energy Laboratory has been performing market analyses of hydrogen liquefaction to expand the Scenario Evaluation and Regionalization



**FIGURE 2.** Temperature separation performance comparison of first order models, two dimensional (2D) axisymmetric CFD model, and experimental measurements with and without zoom perspectives, where 1a represents the extended heat exchanger (EHE) model without para-ortho conversion, 1β is EHE model with maximum para-ortho conversion potential, 2 represents the Liew et al. [1] model, 3 is the Ahlborn and Gordon [2] model, 4 is a 2D CFD model, 5 is an HVT experimental test with smooth centrifuge, 6 is HVT experimental test with rifled centrifuge, and 7 shows HVT experimental test with rifled ruthenium centrifuge. PR is pressure ratio of the total stagnation pressure of the upstream reservoir to total stagnation of the cold end outlet.

Report	Year	Analysis type		Results <sup>a</sup>					
		Fluid	Method	PR	T <sub>R</sub>	ΔT <sub>c</sub>	ΔT <sub>H</sub>	ΔT <sub>Total</sub>	μ
A.F. Johnson	1947	normal-H <sub>2</sub>	Experimental	6.6	294	-15.9	-	-	-
Elser and Hoch	1951	normal-H <sub>2</sub>	Experimental	6	285	-	-	74	0.5
T. Dutta et al.	2013	normal-H <sub>2</sub>	FLUENT <sup>®</sup> w/REFPROP	3 3	115 115	-10 -7	25 9	35 16	0.22 0.54
Bunge et al. (this project)	2017	normal-H <sub>2</sub>	FLUENT <sup>®</sup> w/REFPROP	1.73 2	77 75	-2.81 -6.41	1.15 0.46	3.96 6.87	0.36 0.70
Shoemake et al. (this project)	2017	para-H <sub>2</sub>	Experimental w/o catalyst w/Ruthenium	1.79 1.96	73 74	-1.08 -1.70	2.16 1.13	3.24 2.83	0.37 0.42

TABLE 2. Review of Vortex Tube Studies, and Comparison to Modelling and Experimental Work from the Current Project [4]

<sup>a</sup> Where is temperature of the reservoir (inlet fluid) before centrifugal acceleration (K),  $\Delta T_{Total}$  is the total differential in total temperature from hot outlet to cold outlet. Each row corresponds to the respective method.

Analysis model with the ability to optimize liquefaction plant placement. Results for this work are due at the end of FY 2017. Figure 4 illustrates the modelling plan for this task. The demand and supply mapping information and the resource locations will be the basis for a quantitative analysis of optimal liquefaction plant placement for minimum hydrogen resource and delivery cost.



FIGURE 3. Diagram of pre-cooled Claude with vortex tube cycle

H2 Demand and Market Map	FCEV roll out, refinery and chemical plants, industry	
Renewable Resource and H2 Production Map	Including biomass, fossil fuel, wind and solar power	
Renewable Electricity and Electric Grid	Utility study on ISO and RTO for electric pricing, renewable curtailment	
Transportation Distribution Network	Delivery by rail, highway, pipeline	
Liquefaction Plant Placement	Hydrogen liquefaction capacity, electrolyzer integration	Trigger Carry

FCEV - fuel cell electric vehicle

FIGURE 4. Information and simulation flow for the liquefaction plant placement study

#### **CONCLUSIONS AND UPCOMING ACTIVITIES**

This project, represents a multi-faceted approach to improving the efficiency and capital cost of hydrogen liquefaction. The project has been stopped prior to its go/ no-go milestone to re-focus future work. Areas currently being explored for future work include (1) investigation of supercritical vortex tube performance, (2) vertical flow reactor testing, (3) development of an optimal VT through three dimensional printing, and (4) and a sensitivity study of performance parameters for higher activity or surface area ortho/para conversion catalysts.

#### **FY 2017 PUBLICATIONS/PRESENTATIONS**

1. Bunge C.D., Cavender K.A., Matveev K.I., and Leachman J.W., "Analytical and numerical performance estimations of a Heisenberg Vortex Tube," In: 2017 Cryogenic Engineering Conference, (Madison, WI).

**2.** Presentation "Analytical and numerical performance estimations of a Heisenberg Vortex Tube," Carl Bunge, 2017 Cryogenic Engineering Conference poster presentation, July 10, 2017.

**3.** Presentation "Design and experimental measurements of a Heisenberg Vortex Tube for hydrogen cooling," Eli Shoemake, 2017 Cryogenic Engineering Conference poster presentation, July 10, 2017.

**4.** Presentation "Assessment of a Cryogenic Cycle System for Improved Hydrogen Liquefaction through Heisenberg Vortex Separation," Zhiwen Ma, Chris Ainscough, Jacob Leachman, Dustin McLarty, ASME 2017 Power & Energy Conference, June 26–29, 2017, Charlotte, NC.

**5.** Leachman, J., (June 2017). "Heisenberg vortex liquefaction, Delivery Tech Team Update," Presented at DOE FCTO AMR, June 7, 2017, Washington D.C.

#### REFERENCES

**1.** Liew R., Zeegers J.C.H., Kuerten J.G.M., and Michalek W.R., 2012 Maxwell's demon in the Ranque-Hilsch vortex tube *Phys. Rev. Lett.* **109.** 

**2.** Ahlborn B. and Gordon J., 2000 The vortex tube as a classical thermodynamic refrigeration cycle *J. Appl. Phys.* **88** 3645–53.

**3.** U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office Hydrogen Delivery Multi-Year Research, Development, and Demonstration Plan. https://energy.gov/sites/prod/files/2015/08/f25/fcto\_myrdd\_ delivery.pdf

**4.** Dutta T., Sinhamahapatra K.P., and Bandyopadhyay S.S., 2013 CFD analysis of energy separation in Ranque-Hilsch vortex tube at cryogenic temperature, J. Fluids 2013 1–14.