CAREER: Elucidating transport in Ranque-Hilsch vortex tubes via para-orthohydrogen conversion – enabling efficient small-scale hydrogen liquefaction

The PI’s long-term goal is to pioneer new physical concepts for refrigeration that enable low-cost, efficient, small-to-medium scale hydrogen liquefaction. The research objective of this proposal is to test the hypothesis that application of a catalyst to the periphery of a forced centrifugal flow system, e.g. the Ranque-Hilsch vortex tube, will cause endothermic para-orthohydrogen conversion. This is the first attempt to invert the conventionally exothermic ortho-parahydrogen reaction to directly aid in primary cooling – a paradigm-changing advance for cryogenic refrigeration and clean energy storage technologies. This will decisively challenge the leading transport theories in forced centrifugal flow and enable the PI’s educational objective of developing a comprehensive theory of transport applicable to Ranque-Hilsch vortex tubes.

Intellectual Merit of the Proposed Work: Manipulating para-orthohydrogen conversion is the greatest untapped entropy potential available for cryogenic refrigeration. Recent experiments with Ranque-Hilsch vortex tubes measured substantial cryogenic temperature separation sufficient to catalyze endothermic para-orthohydrogen conversion. Optimization of this effect will decisively elucidate the fundamental problems of work, heat, and mass transport occurring in centrifugal flow while enabling low-cost and efficient small-scale hydrogen liquefaction. To enable this advance, the PI developed a Cryo-catalysis Hydrogen Experiment Facility (CHEF) that uses hot-wire anemometry to monitor para-orthohydrogen composition of vortex tube effluent. This capability enables decisive tests of leading vortex tube temperature separation theories; one of which predicts a 69% difference in temperature separation between para- and orthohydrogen in bare vortex tubes. Work and thermal transport is studied via comparing measurements from bare and catalyst coated vortex tube walls while tracking the separation and conversion of inlet para- and orthohydrogen isomers from the 50-50 inlet composition. The PI will extend the results to mass affected binary mixture flows of H2, D2, He, and Ne. These results, when supplemented by ongoing COMSOL CFD modeling, will enable optimization of the vortex tube for hydrogen liquefaction.

Broader Impacts of the Proposed Work: Society will significantly benefit from efficient (>30% of ideal), small (<5 tonne/day) hydrogen liquefiers. Currently, 80-90% of all hydrogen distributed by small-merchants is via cryogenic liquid tanker truck. Therefore, it is predicted that emerging hydrogen fuel-cell vehicles will be sustained by liquid hydrogen. However, only 8 commercial hydrogen liquefaction plants exist in North America. This lack of distributed generation drives up the cost of hydrogen deliveries considerably (~$5/kgLH2 for production, $2-12/kgLH2 for delivery, $2-3/kgH2 for dispensing). At the same time, energy utilities with large percentages of renewables (wind, solar, tidal) face significant viability challenges due to the lack of economical energy storage. These needs converge in a perfect storm – the existing liquid hydrogen infrastructure was established during the 1950-60’s space race, and few engineers have been trained since, resulting in a substantial workforce deficit in cryogenic refrigeration. To help address this need, the PI will supplement an active NSF-IUSE program at WSU to develop affordable Desktop Learning Modules (DLMs) with a Refrigeration Expansion Module (REM). The PI will develop the REMs via a scaffolded curriculum of courses at the junior, senior, and graduate student level and connected internationally through the established NSF-IUSE program network. A student team competition is engaging undergraduate minority students to develop a prototype liquefier system.
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1. OVERVIEW, HYPOTHESIS, & EDUCATIONAL OBJECTIVE

I realized my career goal in 2005 while reading the citation awarding Werner Heisenberg the Nobel Prize in physics: “for the creation of quantum mechanics, the application of which has, *inter alia*, led to the discovery of the allotropic forms of hydrogen” (NobelPrize.org 2010). These separable forms, ortho- and para-, are natural wonders unique in practicality to the hydrogen molecule. Significant differences in thermophysical properties exist between the forms (Leachman *et al.* 2009). Indeed, ortho-parahydrogen conversion is the largest entropy change at cryogenic temperatures useful for refrigeration. *Ortho-parahydrogen conversion, however, remains a leading loss mechanism in hydrogen liquefaction cycles.* Therefore, there is a critical need to develop a device capable of inverting this effect for primary cooling. Doing so will be a paradigm-changing advance for the emerging hydrogen vehicle fleet, while providing a solution to the energy storage challenge for renewable energy.

Only a single mention of harnessing para-orthohydrogen conversion for primary refrigeration exists in the literature. Ray Radebaugh identified changes in rotational energy level as one of 10 known changes in entropy at constant temperature capable of refrigeration (Walker *et al.* 1983). However, when specifying the driving force needed to cause this change, no clear answer is given and only a statement regarding the desirability of achieving this goal is given in the text:

> “Because of the entropy difference between ortho- and parahydrogen, it is tempting to think of some external force which could change the equilibrium concentration at some temperature. Practical levels of electric field gradients or magnetic fields would have only a minor effect on the equilibrium concentration, though further studies may be useful.” (Walker *et al.* 1983, pg. 137)

Changing entropy via rotational energy at a fixed temperature seems a paradoxical violation of the equipartition theorem: energy must be equitably distributed among *available* modes, e.g. kinetic and ro-vibrational, based on a statistical distribution of the thermodynamic temperature. Hydrogen allows a unique opportunity in that the absence of a catalyst allows parahydrogen to only occupy even rotational modes and orthohydrogen the odd rotational modes; presenting an opportunity to test Radebaugh’s paradox.

Flows through centrifugal geometries, such as Ranque-Hilsch vortex tubes, create viscous work and velocity gradients. As little as three atmospheres driving pressure are enough to cause nearly 50 K in cooling with helium at room temperature (Nellis & Klein 2002). The benefits continue to cryogenic temperatures where 12% liquefaction gains and 30% refrigeration gains were realized in helium liquefaction cycles that replaced the J-T valves with non-adiabatic vortex tubes (Miropolsky & Soziev 1990). The key insight for this work is that the imposed temperature gradient and work transfer are sufficient to cause substantial changes in ortho-parahydrogen equilibrium concentration with conventional low-cost equipment. The primary hypothesis of this research is that application of a catalyst to the periphery of a forced centrifugal flow causes endothermic para-orthohydrogen conversion and bulk cooling (Shown conceptually in Figure 1). This effect could ideally double the performance of the vortex tube. Thus, the potential for a paradigm advance in clean fuels exists via a new concept for refrigeration unique to the hydrogen molecule.

![Figure 1: Conceptual diagram of para-orthohydrogen conversion in a Ranque-Hilsch vortex tube.](image)

Project Description-1
Ranque-Hilsch vortex tubes were discovered by accident and liberated from Germany in the waning days of World War II (Ranque 1933, Hilsch 1947). A U.S. Navy technical group returned the device schematics to the Union Carbide (now Praxair) Research Library in Charleston, NC. The document translations created significant cognitive dissonance among Union Carbide’s engineers. The device partitioned a sub 0°F stream from a room temperature, modest pressure air flow, with no moving parts. This was considered a classic Maxwell’s Demon and thought impossible. However the device is easy to manufacture, simple to demonstrate, and theoretically possible from an entropy balance yielding a positive generation. Although calculating and demonstrating that vortex tubes are indeed possible, explaining how the Ranque-Hilsch vortex tube actually achieves flow separation is an unresolved and fundamental challenge to understanding transport processes.

Debate on fundamental operating principles of vortex tubes continues, as echoed by several reviews (Eiamsa-ard & Promvonge 2008, Xue et al. 2010). The vortex tube is essentially a rotor-less turbo-expander, the Holy Grail for cryogenic hydrogen, and an enthalpy (rothalpy) transfer problem (Lyman 1993, Liew et al. 2013, Polihronov & Straatman 2012). Extensive Computational Fluid Dynamics (CFD) studies (Bej & Sinhamahapatra 2015, Dhillon & Bandyopadhyay 2015, Aljuwayhel et al. 2005, Skye et al. 2005) show work (enthalpy streaming) from core to peripheral flow, yet these same studies still show the presence of “negative” heat transfer from the cold to hot streams in the model results. To resolve this puzzle, the research and educational objectives of this research are to use experimental measurements unique to properties of hydrogen to develop or decisively validate a comprehensive theory of transport in vortex tubes and use inexpensive modules to promote student learning about these concepts. I will achieve these objectives through the following specific aims:

Specific Aim 1: **Thermal transport in vortex tubes with para-orthohydrogen conversion.** I will test the primary research hypothesis by flowing variable ortho-parahydrogen compositions through bare and catalyzed vortex tubes to test the effects of variable thermophysical properties. For example, the current leading indicator of temperature separation is the ratio of sound speed squared to the isobaric heat capacity ($v^2/C_p$) (Polihronov & Straatman 2012), a quantity 69% higher for ortho- than parahydrogen near 120 K. I will compare the influence of work streaming from core to periphery flow to COMSOL CFD predictions.

Specific Aim 2: **Analyze mass-affected transport in vortex tubes with binary gas mixtures.** I will test the effect of mass/momentum acceleration on transport in the forced centrifugal flow with He-H2, H2-D2, and He-D2 mixtures. Then I will validate model predictions with He-Ne and H2-Ne, which are candidate mixed refrigerants for novel hydrogen liquefaction cycles.

Specific Aim 3: **Test the theories via development of a Refrigeration Expansion Module (REM) and supplemental content for Low-Cost Digital Learning Modules (LC-DLMs).** I will develop an REM supplement for the LC-DLMs underway through an active NSF-IUSE program at WSU (PD 14-7513). The content includes solid-state refrigeration via elastomers, Joule-Thomson (J-T) cooling through a throttle valve, and customizable air-powered vortex tubes. I will implement and assess the supplemental content through scaffolded curriculum at the junior, senior, and graduate student levels.

Note that these aims can be completed independently and each have merit, yet are complimentary towards developing a comprehensive understanding of vortex tubes for cryogenic hydrogen liquefaction.

The proposed objectives and aims are readily achievable. Preliminary measurements, discussed in Section 3.3 and shown in Figure 4, provide compelling evidence that the vortex tube creates sufficient temperature separation with cryogenic hydrogen to decisively test the primary hypothesis. My uniquely capable Cryogen-catalysis Hydrogen Experiment Facility (CHEF), record of establishing the standards for hydrogen properties (see biosketches), and critical education collaboration with the PI and co-PI of an active NSF-IUSE grant (see letters) ensure that I’m uniquely prepared to achieve the goals of this proposal. I anticipate providing the most conclusive evidence ever on the fundamental operating principles of vortex tubes – a classic problem and demonstration in mechanical and chemical engineering courses. This will greatly enhance applied system development efforts already underway through a student club and partnerships with industry and national laboratories (See Section 5).
2. EXPECTED SIGNIFICANCE

Our Nation is at a junction between our lack of grid-scalable energy storage technologies and the increasing renewable energy demands of the hydrogen fuel-cell vehicle fleet. With this proposed work, I will directly address the reliance on carbon-based fuels. With liquid hydrogen projected to be the dominant transmission method of the hydrogen economy for the coming decades, and with distribution expense potentially tripling the cost of production, one of the best possibilities to solve this challenge is to develop efficient (>30% of ideal), small (<5 tonne/day), low-cost hydrogen liquefiers geographically distributed with renewable energy sources (e.g., wind, solar, tidal) (Elgowainy 2014). Although 30% of ideal efficiency sounds low, it is the status quo for large systems. Conventional cryogenic expanders represent the majority of maintenance as well as inflexibility to demand of current liquefaction cycles. Therefore, a low-cost replacement is essential to achieve small-scale hydrogen liquefaction. Endothermic para-orthohydrogen conversion has the potential to double the performance of conventional vortex tubes, which already surpass the exergetic efficiency of J-T valves, thus superseding or supplementing turbo-expander systems. This will enable zero-carbon emission hydrogen fuel production from distributed locations around the US.

3. BACKGROUND

3.1 Foundational thermodynamic property models needed for this work

Orthohydrogen is a higher energy triplet restricted to odd rotational energy levels \((J=1,3,5\ldots)\) due to parity with nuclear spin in the overall molecular wave function (Leachman et al. 2009). Parahydrogen is a lower energy singlet restricted to even rotational energy levels \((J=0,2,4\ldots)\). When equilibrated at room temperature the two forms exist in a 3:1 ratio of orthohydrogen to parahydrogen, respectively, called normal hydrogen that is traditionally treated as a pure fluid in quasi-equilibrium at all temperatures. Spontaneous conversion between forms is quantum mechanically forbidden and a catalyst is required for conversion. Therefore, an ortho-parahydrogen thermodynamic mixture model is needed. Modern fundamental Equations of State (EOS) are explicit in the reduced Helmholtz free energy \(\alpha\): \[\alpha = \alpha^0 + \alpha^i\]

where \(\alpha^0\) is the ideal-gas contribution and \(\alpha^i\) the residual contribution (Leachman et al. 2009, Richardson et al. 2014, Blackham et al. 2015). Substantial differences in both the ideal-gas and residual contributions exist between the ortho- and parahydrogen forms. It is possible to utilize a hybrid statistical-empirical approach to account for the differences in both the ideal-gas and residual contributions of the EOS. The residual contribution to the EOS is fitted to experimental measurements and ideal-mixing of para- and orthohydrogen real fluid properties produces deviations less than 0.25% for calculated normal hydrogen properties. To calculate ideal-gas properties, the only consistent method that accounts for the ortho-parahydrogen conversion energy is to use the partition function: \[Z_n = \sum_v \sum_J i \left(2J + 1\right) E_{ij}^\nu e^{-E_{ij}/kT}\]

where \(n\) denotes the moment 0–2 of the partition function, \(v\) and \(J\) are the respective coupled ro-vibrational energy levels clamped to the first electronic excitational mode and determined via direct solution of the Schrodinger wave equation, \(i\) is the nuclear degeneracy, \(E_{ij}\) is the tabulated energy level, \(k\) is Boltzmann’s constant, and \(T\) is the temperature (Schwartz & Le Roy 1987). The moments of the partition function, \(n=0–2\), must be summed for only even or odd rotational energy levels, for the respective ortho- and parahydrogen forms and the result treated as an ideal mixture. Figure 2 shows the ideal-gas isobaric heat capacities of various ortho-parahydrogen mixtures. Other relevant properties can be determined from:

\[C_p^0 = R \left(y_{\text{para}} \left[\frac{Z_{\text{para},2}}{Z_{\text{para},0}} - \left(\frac{Z_{\text{para},1}}{Z_{\text{para},0}}\right)^2\right] + y_{\text{ortho}} \left[\frac{Z_{\text{ortho},2}}{Z_{\text{ortho},0}} - \left(\frac{Z_{\text{ortho},1}}{Z_{\text{ortho},0}}\right)^2\right]\right)(kT)^2 + \frac{5}{2}\]

\[K_B = N_a \left(y_{\text{para}} \left[\frac{Z_{\text{para},1}}{Z_{\text{para},0}} + y_{\text{ortho}} \left(\frac{Z_{\text{ortho},1}}{Z_{\text{ortho},0}}\right)\right] + \frac{5}{2}RT + h^0\right) + s^0 = -\left(\frac{g^0 - h^0}{T}\right) - R \ln \left(\frac{P}{P_{\text{ref}}}\right) + s^0_{\text{ref}},\]

where \(s^0\) and \(h^0\) are the exergetic efficiency of J-T valves, thus superseding or supplementing turbo-expander systems. This will enable zero-carbon emission hydrogen fuel production from distributed locations around the US.

Project Description-3
Solution via the partition function also allows for the equilibrium constant \((K_{op})\), equilibrium mole fraction \((\gamma_{ortho})\) and adsorption separation coefficient \((\psi_{op})\) to be readily determined:

\[
K_{op} = \frac{Z_{ortho,0}}{Z_{para,0}}, \quad \gamma_{ortho} = \frac{K_{op}}{1 + K_{op}}, \quad \text{and} \quad \psi_{op} = \frac{(Z_{para,0}/Z_{ortho,0})_{\text{fluid}}}{(Z_{para,0}/Z_{ortho,0})_{\text{adsorbed}}}.
\]

Although properties of ‘equilibrium’ hydrogen can be calculated using a non-segregated partition function, the augmented heat capacity values for equilibrium hydrogen displayed in Figure 2 would never be observable without the continuous presence of a catalyst during temperature change. Therefore, using the partition function in calculating ortho-parahydrogen mixtures eliminates the need to calculate ‘equilibrium’ hydrogen values or the need for an additional step to account for the conversion energy. This simplification eliminates a historical point of confusion and corrects the often misinterpreted ortho-parahydrogen and normal-parahydrogen conversion enthalpies erroneously reported in many texts (McCarty et al. 1981, Barron 1985, Flynn 1997).

![Orthohydrogen, Normal Hydrogen, and Parahydrogen](image)

**Figure 2:** Ortho-parahydrogen molecular wave function and ideal-gas isobaric heat capacities for various mixtures with the equilibrium orthohydrogen concentration.

### 3.2 Technologies pioneered as a result of understanding para-orthohydrogen properties

The statistical thermodynamic property predictions accurately predict real-world energy transitions. The bulk property differences cause preferential adsorption which has been used for separation and enrichment of the spin-isomers (Cunningham et al. 1958, Silvera 1980), a process now used to enhance NMR signals (Hougen & Oka 2005). At the normal boiling point of hydrogen the temperature dependent enthalpy change of the exothermic ortho-parahydrogen conversion is 703 kJ/kg, substantially higher than the latent heat of vaporization at 446 kJ/kg. I used this effect to design a self-pressurization system for liquid normal hydrogen tanks and filed a provisional patent (Leachman et al. 2012). This exothermic release confounded early experimentalists (Gearhart 2010) and resulted in catalytic converters in liquefaction systems that eliminated the need for consideration in most applications. Optimal catalyst selection for para-orthohydrogen conversion has been extensively studied and remains classified in some cases due to space-based applications (White 1989, Illisca 1992, Brooks et al. 1994, Hutchinson 1966, Schmauch & Singleton 1964).
Reducing in-space boil-off of cryogenic fuel is a likely application given the sensitivity to launch cost. Meier et al. (1968) and Benning et al. (1968) developed a re-liquefaction cycle based on endothermic para-orthohydrogen conversion in a conventional catalyst bed and venting of the orthohydrogen. However, venting of liquid oxygen is significantly more mass intensive. I received funding from United Launch Alliance (ULA) to develop the Cryocatalysis Hydrogen Experiment Facility (CHEF) as the first proof-of-concept that catalyzing endothermic para-orthohydrogen conversion can increase the thermal capacitance of hydrogen coolant for LOx tanks (Bliesner et al. 2014). I show experimental measurements from CHEF in Figure 3. To realize CHEF, we had to continuously monitor the ortho-parahydrogen composition of the effluent and create a controlled environment for producing hydrogen at known ortho-parahydrogen composition prior to testing. We coupled a hot-wire anemometry system with a variable orifice mass flow meter resulting in composition accuracy better than ±3.5%. We designed an all-aluminum condenser with non-catalytic materials to allow liquefaction of either para- or normal hydrogen depending on catalyst bag insertion. We designed an annular flow reactor with a concentric heater to continuously expose the parahydrogen flow to catalyst during heating—the necessary scenario to realize the equilibrium heat capacity curve shown in Figure 2. The theoretical heat capacitance increase was 50% between 22-94 K. Careful switching between normal hydrogen and parahydrogen, along with catalytic and non-catalytic flow beds decisively proved the effect. We also performed a parallel test to analyze the performance of a proton exchange membrane fuel cell operating on para- vs. normal hydrogen (Bahrami et al. 2014).

I am also engaged in a project with Insitu, a wholly owned subsidiary of Boeing, to engineer a 3D-printed liquid hydrogen tank making use of para-orthohydrogen conversion to simultaneously insulate the tank while eliminating the need for external vaporizing heat exchangers (Adam & Leachman 2015, Cruz et al. 2015). As part of this project, we developed a COMSOL multiphysics simulation to model the endothermic conversion during heating of the vapors, shown in Figure 3. We will test a flight article later this year and have already filed for a provisional patent (Leachman & Adam 2014).

With these recent applied technology successes, NASA has renewed interest in studies of para-orthohydrogen conversion after a two decade hiatus and recently awarded an SBIR Phase I, of which I am a sub-I, to develop vapor-shielding blankets using the effect. The catalyst coating experience gained ensures a seamless transition to the applied catalysis work proposed here. All para-orthohydrogen technologies developed currently use the hydrogen post-liquefaction in the parahydrogen form. Centrifugal flow geometries, such as the vortex tube, may allow a decisive change to this paradigm. Several of my graduates students and I have started Protium Innovations LLC to commercialize the technologies from this research.

Figure 3: (Left) Measured increase in cooling capacity during heating from 22-94 K in the presence of catalyst in the Cryocatalysis Hydrogen Experiment Facility (CHEF) (Bliesner et al. 2014). (Right) COMSOL multiphysics temperature model in a 3D-printed vapor-shielded tank with catalyzed para-orthohydrogen cooling (Adam & Leachman 2015).

Project Description-5
3.3 Ranque-Hilsch tube operational theory applied to cryogenic hydrogen

The body of literature on Ranque-Hilsch vortex tube phenomena is extensively reviewed elsewhere (Eiamsa-ard & Promvonge 2008, Xue et al. 2010, Yilmaz et al. 2009). The dominant theory is based on the classic Bernoulli-turbine equation that couples kinetic energy gradients with pressure to predict a temperature drop (Lyman 1993, Liew et al. 2013, Polihronov & Straatman 2012, 2015, Alekseeenko et al. 2007). The Bernoulli approach yields good agreement, better than 2-3 % with experiment. Figure 4 below shows the predictions of the Liew et al. (2013) kinetic impinging model, the ratio of sound speed to specific heat ($w^2/2C_p$) model (Polihronov & Straatman 2012), conventional throttling, a 60 % isentropic efficiency turbo-expander, and preliminary measurements of normal hydrogen expansion through a bare vortex tube. The kinetic impinging vortex model of Liew et al. (2013) significantly under-predicts the measured temperature separation for hydrogen at 125 K while the $w^2/2C_p$ scaling rule for normal hydrogen is close. It should be noted however that these are preliminary measurements and while the temperature separation measured with the bare vortex tube boarders on a thermodynamic limit, the cool stream left near the inlet temperature and the temperature separation is almost entirely due to heating of the hot stream. A 5-10 K reduction in measured temperature separation will likely occur when the copper exit lines are replaced with stainless steel.

![Figure 4: (Left) Measured (pre-publication) and predicted refrigeration effects for hydrogen at 125 K. (Right) Ortho-parahydrogen conversion enthalpy and magnitude of temperature separation predicted by the $w^2/2C_p$ model (Polihronov & Straatman 2012).](image)

The measurements I present in Figure 4 initially correspond to the $w^2/2C_p$ scaling rule (Polihronov & Straatman 2012). Whether the model can accurately scale parahydrogen flow is an outcome of Specific Aim #1. I show predictions of the model versus temperature on the right side of Figure 4. The temperature separation for orthohydrogen is 69% larger than parahydrogen near 125 K but decreases with temperature raising concerns of viability in the sub 100 K range. The ortho-parahydrogen conversion energy increases in this range to balance the predicted decrease in performance. Cryogenic vortex tube have been applied to several cryogenic cycles, although no measurements from hydrogen systems are reported (Miropolsky & Soziiev 1990, Nash 1991, Hughes 1950, Prelowski 1969, Schlenker 1978). A non-adiabatic vortex tube (centrifugal section externally cooled by boil-off vapors) with internal riffings was able to increase the liquefaction efficiency by 12% and the refrigeration efficiency by 30% in one superconductor refrigeration configuration (Chernetskiy et al. 1984, Alekseyev et al. 1976). The endothermic heat of para-orthohydrogen conversion (shown in Figure 4) catalyzed on the external vortex tube wall, serves a similar function to the non-adiabatic vortex tube proven by Chernetskiy et al. (1984) but with significantly reduced thermal resistance. The overall efficacy of the effect is governed by work and heat transfer within the vortex tube. Substantial work streaming between the core (cold) flow and the hot flow must be occurring for helium and hydrogen to experience such a considerable cooling effect at room temperature, well above the Joule-Thomson inversion curve. Xue et al. (2010) acknowledged the results of the Nellis and Klein group (Aljuwayhel et al. 2005, Skye et al. 2005, Nellis & Klein 2002) that viscous shearing (work flow) between
layers “is a useful approach in the investigation of the vortex tube.” The Nellis and Klein group’s CFD studies, however, display the same “negative” zones of heat transfer occurring from cold to hot flow near the vortex tube plenum that have yet to be explained (Bej & Sinhamahapatra 2015, Dhillon & Bandyopadhyay 2015). A phenomenon-based explanation of the negative heat transfer is kinetic partitioning within the plenum. Although this is a violation of continuum mechanics, I can readily test this via para-orthohydrogen composition measurements.

In the end, few (if any) studies can simply answer the fundamental question of “how a Ranque-Hilsch vortex tube works”. Several theories provide significant confidence that solutions are close and simply await rigorous experimental validation coupled with educational content. Many simplified educational demonstrations are available despite lack of closure on the actual mechanism (Bruno 1987, Derjani-Bayeh & Olivera-Fuentes 2011, Carrascal & Lizarraga 2013).

3.4 Future applications of this work in hydrogen liquefaction cycles

The dominant hydrogen liquefaction cycle, still in use by industry, is the modified Claude cycle (analogous to a reverse Turbo-Brayton cycle) originally invented for air liquefaction over 100 years ago (Peschka 1992). The key improvement over the original Linde-Hampson (J-T) cycle was the reduced reliance on throttle valves via the use of a cold expander to stream work out of the system, enabling the theoretical performance to drop from 13 kW-hr/kgLH2 to 7 kW-hr/kg LH2. The primary drawback of this approach is the costly and maintenance intensive cryogenic expander that has moving parts exposed to both cryogenic temperatures and hydrogen vapor. The vortex tube still allows for work streaming out of the system via the hot return gas flow of the vortex-enabled cycle, shown in Figure 5. Although untested, maximization of the effect could yield low-cost liquefaction cycles needed for small-modular liquefaction systems. The vortex concept can also be used as a replacement for the J-T valves in modern mixed-gas cycle designs (Valenti & Macchi 2008, Krasae-in et al. 2010). The vortex tube has no moving parts and is cost effective to manufacture. An additional potential gain from the vortex tube approach is the separation of orthohydrogen from the stream to be liquefied. This reduces load on the ortho-para hydrogen catalyst beds, one of the largest sources of irreversibility in hydrogen liquefier design (Staats & Brisson 2008).

![Flow diagram for a modified Claude cycle incorporating the vortex tube and employing cryogenic thermal compression for 700 bar fueling (see H2-Refuel in Section 5.1).](image-url)
3.5 Results from prior NSF support
I have not received NSF support to date aside from mentoring five summer REU students.

4. RESEARCH & EDUCATION PLAN
The primary hypothesis of this work, that application of a catalyst to the periphery of forced centrifugal flow causes endothermic para-orthohydrogen conversion and bulk cooling, is directly linked to the educational goal of using the unique properties of hydrogen to develop a comprehensive theory of transport in vortex tubes. As such, the educational and research aims are highly integrated. Although I present the research aims first here, I will complete the educational aim in parallel to leverage significant student and faculty discussions on the topic.

4.1 Specific Aim #1: Thermal transport in vortex tubes with para-orthohydrogen conversion.
Introduction. In this aim, I will test three aspects of vortex tube kinetics without the presence of mass effects:

1) **Effect of the specific heat on vortex tube operation.** A rule of thumb for vortex tube operation is that the temperature separation achieved is directly proportional to the ratio of specific heats (Han et al. 2014). This is a similar conclusion to the ratio of sound speed to specific heat (\(c_s^2/2C_p\)) model (Polihronov & Straatman 2012). The temperature separation for orthohydrogen is 69% larger than parahydrogen near 125 K. Since ortho-parahydrogen mixtures of known composition can be generated and maintained (Bahrami et al. 2014, Cunningham & Johnston 1958, Silvera 1980), it is possible to directly test the influence of specific heat ratio on temperature without any chemical or mass effects.

2) **Kinetic para-orthohydrogen separation in bare vortex tubes.** The equipartition theorem requires equal distribution of energy among available modes. However orthohydrogen cannot freely transition out of the 1\(^{st}\) rotational energy level and could cause a depletion of kinetic energy. In this scenario, significant separation of ortho- from parahydrogen may occur in the vortex tube without the presence of a catalyst due to kinetic energy gradients alone. Although counter to continuum-mechanics assumptions, preferential adsorption of orthohydrogen at cryogenic temperatures to hinder rotational energy provides further evidence that this could indeed happen (Cunningham & Johnston 1958, Silvera 1980).

3) **Catalyzed para-orthohydrogen conversion and separation in vortex tubes.** This is the primary test of the research hypothesis. With vortex tube operation on para-orthohydrogen mixtures determined from the previous two tests, I will identify an operating state for flow through an identical geometry vortex tube with a catalyst applied to the periphery of the forced centrifugal flow section. I will observe endothermic para-orthohydrogen conversion through changes in outlet temperature, ortho-parahydrogen composition, and potentially even mass flow rates. The degree to which temperature and composition changes between outlets will inform the levels of transport occurring within the vortex. Adding riflings to the vortex tube may be required to decrease the space velocity relative to the catalyst coatings and can improve vortex tube performance (Alekseyev et al. 1976)

*Design. Modification of the procedure previously used to generate known para- and normal hydrogen gas flows at cryogenic temperatures is straight forward (Bliesner et al. 2014, Bahrami et al. 2014). Parallel condensing tanks will generate sufficient quantities of normal/ortho- and parahydrogen within the established CHEF (results shown in Figure 3). The experimental procedure is based on the specific test:*

1) **Specific heat procedure.** I will cycle the effluent vapor from parallel liquid condenser tanks between 1) para-, 2) normal, 3) para-, 4) normal hydrogen, through the same vortex tube operating at steady state and housed within the vacuum jacketed cryostat. The inlets and outlets of the vortex tube are instrumented with cryogenic temperature controllers and custom hot-wire anemometer composition gauges to continuously determine ortho-parahydrogen composition. I will raise the inlet temperature of the flow to 135 K, where the ratio of specific heats of normal hydrogen (1.5119)

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is 11% greater than parahydrogen (1.3558) and comparable to the difference between normal hydrogen and helium (1.666). Due to the elevated temperature, little difference in kinetic energy should exist between forms. The ortho-parahydrogen composition gauges should validate that the hydrogen remains in the para- or normal state emitted from the condensing tanks. Differences in operating performance based solely thermophysical properties will inform future tests.

2) Para-orthohydrogen separation in bare vortex tube procedure. I will liquefy 50-50 ortho-parahydrogen composition in a single condenser tank after flowing through a catalyst bed immersed in liquid nitrogen at 77 K. I will then heat this 50-50 mixture to flow out of the tank and through a bare vortex tube to determine the degree of ortho-parahydrogen separation occurring. I will test three inlet temperatures to the vortex tube (~30 K, 77 K, and 135 K) to investigate the effect of temperature on the kinetic energy of the orthohydrogen and the subsequent degree of separation caused by the forced centrifugal flow.

3) Catalyzed vortex tube procedure. I will identify an optimal inlet condition, based on the prior two tests, to observe endothermic para-orthohydrogen conversion. I will apply a highly active ruthenium catalyst to the periphery of the vortex centrifuge tube (White 1989, Brooks et al. 1994). I will independently monitor the temperature and composition of the outlets to validate the occurrence of endothermic conversion, the achievement of cooling enhancement, and the result of the primary research hypothesis. I will vary the inlet conditions to validate the observation that an optimum for the particular vortex geometry and flow condition. A pure parahydrogen flow into the catalyzed vortex tube at 77 K will determine the degree of spin isomer transport from the outer periphery to the center-core flow through measurement of the orthohydrogen composition of the core flow.

**Expected Outcomes.**

1) Decisive test of the primary hypothesis on the cooling gains made possible by catalyzing endothermic para-orthohydrogen conversion within centrifugal flow geometry. Thus, assessing the potential for this device to revolutionize small-scale hydrogen liquefaction.

2) The amount of molecule transport from the periphery to the core flow from the catalyzed pure parahydrogen test, providing evidence on the turbulence models applicable to the vortex tube.

3) The validity of specific heat ratio, $\frac{w^2}{2C_p}$ and other indicators of vortex tube performance.

4) The utility of the vortex tube to separate ortho- from parahydrogen and minimize load on liquefaction cycle catalyst beds.

5) A simple and adaptable geometry to investigate work and thermal streaming within the vortex tube.

**Potential Problems and Alternative Approaches.** The complex geometry of the counterflow vortex tube creates the potential for recirculation zones and increased turbulence in the device. Therefore, separating the differing transfer effects in the plenum and centrifuge zones of the device could prove difficult. The first step of this aim is to investigate the simplest vortex geometry for experimentation. In close coordination with Specific Aim #3, I will work with students to construct and compare reconfigurable vortex tubes in the counter and parallel-flow configurations that could greatly simplify analysis by eliminating the counterflow friction and back-flow eddies within the device.

4.2 Specific Aim #2: Analyze mass transport in vortex tubes with binary gas mixtures.

*Introduction.* Although the kinetic-impinging model developed by Liew et al. (2013) modeled nitrogen flow through a vortex tube to better than 1% uncertainty, the model does not address the fundamental issue of preferential separation of deuterium leaving the core-flow (cold stream) when mixed with hydrogen despite nearly double the molecular weight and a $10^6 \text{ g cm}^{-2} \text{ s}^{-1}$ acceleration (Schlenker 1978). By testing binary gas mixtures of hydrogen with helium, deuterium, and neon the influence of molecular weight versus chemical and momentum drivers of flow separation can be directly compared to the purely thermal-kinetic differences measured in Specific Aim #1.

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Design. I will use uncatalyzed vortex tubes to directly compare the solid-core rotational model and kinetic impinging model by analyzing centrifugal gas separation of binary mixtures. Although helium, hydrogen, deuterium, and neon are totally miscible, the condensation prior-to testing approach applied in Specific Aim #1 is not possible as the boil-off venting process is analogous to cryogenic distillation and fluid separation will occur prior to entering the vortex tube. I will develop and implement a counterflow heat exchanger using liquid nitrogen in CHEF to precool to the incoming mixed gas flow to near 77 K prior to entering the vortex tube (Leachman et al. 2009b, Nixon & Leachman 2011). Only two tests are essential to determine the chemical and momentum transport: hydrogen-deuterium and helium-deuterium. Since deuterium has an identical molecular weight to helium but a different kinetic energy, differing amounts of preferential separation will provide additional information for predictive model development. I will model helium-neon and hydrogen-helium prior to experiment to validate the predictive model development needed for implementation with mixed gas refrigerant cycles (Quack 2002, Valenti & Macchi 2008, Krasae-in et al. 2010). Additional temperature measurements will not be required after completing Specific Aim #1. I will determine the degree of separation occurring by sample extraction and analysis in a calibrated Gas Chromatograph (GC) (Blackham et al. 2015). I will run the sampled gas through a catalyst bed to prevent ortho-parahydrogen composition from biasing the GC.

Expected Outcomes.
1) Decisive tests of flow separation in molecular mass effected forced centrifugal flow.
2) Predictive model validation with unknown neon-helium and hydrogen-helium flows.

Potential Problems and Alternative Approaches. Extracting gas samples without biasing composition has been a problem in early vortex tube separation studies. Additionally, deuterium and hydrogen are not likely to display significantly different gas chromatography signals and a mass spectroscopy method may be more preferable and will need to be located. Isotopic exchange in the presence of a catalyst can create Hydrogen-Deuteride (HD) which could make deuterium-hydrogen separation difficult. In this case the hydrogen-deuterium separation test is not essential should the other tests prove valid.

4.3 Specific Aim #3: Develop a Refrigeration Expansion Module (REM) for DLMs.
Introduction. In 2014 WSU was awarded an NSF-IUSE (PD 14-7513) titled, “Affordable Desktop Learning Modules (DLMs) to Facilitate Transformation of Undergraduate Engineering Classes.” The goal of the project is “to transform the STEM learning environment making it more effective, exciting and experiential by using hands-on team interactive pedagogy.” The Low-Cost DLM (LC-DLM) are manufactured by 3D printing of molds and vacuforming over the molds thereby creating transparent heat exchangers and fluid flow systems for classroom work. Availability of equipment and educational assessment strategies for expansion of the work to include REMs present an excellent opportunity to develop the conceptual and experiential understanding required of vortex tubes. IUSE PI Van Wie (see collaboration letter) has agreed to collaborate by providing access to the equipment and implementation and assessment strategies, allowing testing of the teaching concepts in new, but related engineering venues. However, the current operational theories of vortex tubes fall outside the bounds of traditional course scopes, and experiments with hydrogen flows of this volume must be conducted within a controlled hydrogen rated laboratory. These compounding issues present an opportunity to use a scaffolded curriculum with junior, senior, and graduate level courses implementing LC-DLM REMs to generate data and theoretical analysis that must be reconciled with laboratory measurements.

Design. Currently, the LC-DLMs do not address the concept of refrigeration. I will develop three low-cost experiments as a general REM for the LC-DLMs to include:
1) Joule-Thomson expansion (throttle). This requires a fundamental understanding of the difference between enthalpy and internal energy, begging the classic question, “What is the physical meaning
of enthalpy?” This will introduce the LC-DLM REM to ME 301-Thermodynamics students. Graduate students in ME/ChE 527 Macroscale Thermodynamics will derive the J-T inversion curve to show the inversion boundary where gas heating occurs with expansion, as demonstrable with hydrogen in the laboratory.

2) **Solid-state phase change (rubber-band).** The temperature and strain differentials of solid-state refrigeration using rubber-bands create cognitive dissonance in ME 301 by causing the students to believe friction is responsible for heating during stretching, but the inverse relaxing process creates identical friction simultaneously with cooling. A working understanding of entropy is required to rationalize this refrigeration process. ME/ChE 527 will use this information to derive a fundamental equation of state, and connect it to statistical thermodynamic concepts (Ritacco et al. 2014).

3) **Centrifugal flow partitioning (vortex tube).** I will test the temperature and pressure differentials of fluid flow through vacuum-molded vortex tube shapes in ME 406 Experimental Design considering concentric, counterflow, conical, and inverse-conical geometries. Unlike the previous two experiments, no single thermodynamic property has been identified that simply predicts vortex tube performance, ME/ChE 527 students will address this. An additional opportunity exists to go beyond reporting of laboratory exercises to integrate the 406 students into assessment of LC-DLM REM testing in ME 301 within the NSF-IUSE pedagogical framework. Additionally, I will permanently maintain the final cryogenic vortex tube experiment as one of the standard ME 406 system-level experiment offerings.

I will adapt the rigorously established pre- and posttest-assessment of learning outcomes methodology for the DLMs in undergraduate hydrology and fluid mechanics courses. This assessment has validated increased long-term learning retention associated with the DLM’s, especially at the higher levels of Bloom’s taxonomy and has standardized the process for data collection and analysis (Brown et al. 2014, Burgher et al. 2014). The approach adapted for the J-T throttle, rubber band, and vortex tube, will begin with interviewing instructors to determine difficult concepts for students, and questioning students who have had lectures on the concepts in the 2015-2016 academic year to identify persistent misconceptions. Then, CAREER supported students and I will design classroom activities to address those misconceptions, mapping pre- and posttest questions to varied levels of Bloom’s taxonomy, from remembering, and understanding, to analyzing, and creating. We will evaluate and administer the tests before and after implementation during ensuing years. We will then use a 10-point scale rubric, from mostly wrong to mostly right, to determine efficacy of the approach. With the help of the external evaluator, we will administer an adapted motivated strategies learning questionnaire to determine the degree to which the LC-DLM REM facilitates student motivation and use of learning strategies.

Additional course synergies outside my experience that are already implementing DLMs within my department include ME 303-Fluid Mechanics, ME 305-Heat Transfer, and ME 306-Thermal and Fluids Lab. Given the ongoing work through the IUSE, Drs. Van Wie, Adesope, and Richards (see letters) invited me to participate in regular team meetings focused on fabrication, implementation, assessment, and dissemination aspects. Additional courses of relevance outside of my department include: ChE 301-Introduction to Transport Phenomena, and ChE 510-Transport Processes, a course that extensively uses COMSOL. The primary instructor for ChE 510, Dr. Ivory (see letter), has invited me to co-develop course content based on this proposal and to utilize opportunities for in-class demonstrations and modeling.

**Expected Outcomes.** The scaffolded curriculum of relevance to the LC-DLM REM ensures both implicit and explicit development of pedagogical content and assessments synergistic to the educational goal of this project. I will assemble the developed content modules in a booklet to supplement with the LC-DLM REM, which I anticipate will either be bundled or sold independent of the DLM. Pedagogical assessment will conform to the established approach of the active NSF-IUSE/TUES-CCLI to ensure seamless comparison and integration to parallel efforts at the four US non-WSU institutions. I anticipate parallel publications to the Brown et al. (2014) study, specifically on refrigeration in undergraduate thermodynamics. An additional interesting test is to compare the in-class exercises with the LC-DLMs to student club students constructing...
the actual prototype machine and vortex tube, thereby directly comparing the simulated hands-on-exercise to reality.

*Potential Problems and Alternative Approaches.* The cost of a pump capable of delivering the air power necessary to measure significant throttling effects may prove cost prohibitive for the LC-DLMs. CO2 cartridges would provide a suitable alternative.

*Evaluation Plan.* The external evaluator, Dr. O. Adesope, associate professor of educational psychology and member of the WSU Learning & Performance Research Center (LPRC), will lead a series of critical reviews and evaluation of the project (See letters). The LPRC provides leadership, training, consultation, and state-of-the-art solutions to challenging educational research questions. The LPRC is highly qualified to evaluate this project because Center staff, including Dr. Adesope, have extensive experience on projects funded by the NSF, the US Department of Education, as well as state and local educational agencies. The evaluation plan is driven by four key questions shown in Table 1.

**Table 1: External evaluation questions, methods, and sources.**

<table>
<thead>
<tr>
<th>Evaluation Questions</th>
<th>Methods &amp; Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Is the project infrastructure established as planned?</td>
<td>Meetings with PI and review of documents.</td>
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<tr>
<td>2. How well are the data collection procedures aligned with the research questions, and to what extent were the data collection procedures conducted to ensure reliability?</td>
<td>Review of project plan. Observation of data collection and statistical analyses of pre/post assessments of learning outcomes and surveys.</td>
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<tr>
<td>3. What challenges were encountered during the implementation of the education plan, and how were these challenges addressed?</td>
<td>Interviews with PI and graduate and undergraduate students.</td>
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<tr>
<td>4. To what extent has the project met its stated goals and objectives, and addressed the research questions?</td>
<td>Summary of all the methods and sources in 1-3.</td>
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The external evaluator and I will implement three components of evaluation, briefly highlighted below:

1) **Implementation/fidelity evaluation.** The evaluation will include assessment of the extent to which the project infrastructure is implemented as planned, including personnel deployment, and how strategies and activities are developed and implemented. Under implementation evaluation, Dr. Adesope will meet with my graduate, and undergraduate students and me to examine personnel and infrastructure in place for the successful completion of the project.

2) **Formative evaluation.** The external evaluation will also include formative aspects that will provide me with useful information to continuously improve the project. Dr. Adesope will review the project plan in relation to the project goals, objectives, and project tasks, and will provide me with constructive feedback to strengthen the plan as needed. During the course of the project, the evaluator will also monitor project progress and interview my students and me to document and understand the effects of modeling. The evaluator will also review all data collection procedures and instruments, and provide me with feedback as needed. Dr. Adesope will provide formative feedback as evaluation highlights at the conclusion of each evaluation activity.

3) **Summative evaluation.** The summative aspects of the external evaluation will focus on the degree to which the project met its goals and objectives to ensure research integrity throughout the course of the project. To address evaluation question 4, the external evaluator will examine all collected data to determine the degree to which the project met its intended goals and answered the research questions. I will detail the results of the implementation/fidelity, formative and summative evaluations in the annual report produced in accordance with NSF requirements and timelines.

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4.4 Timetable of Research and Educational Aims

<table>
<thead>
<tr>
<th>Aims/Tasks</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Year 4</th>
<th>Year 5</th>
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<tr>
<td>Specific Aim #1: Thermal transport in vortex tube</td>
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<tr>
<td>1.1 Effect of specific heat in bare tube</td>
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<td>1.2 Ortho-para separation in bare tube</td>
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<td>1.3 Para-ortho conversion in catalyzed tube</td>
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<td>Specific Aim #2: Mass transport of binaries</td>
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<td>2.1 He-H2, H2-D2, He-D2</td>
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<tr>
<td>2.2 Predictive model validation of He-Ne, H2-Ne</td>
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<tr>
<td>Specific Aim #3: Develop LC-DLM REM</td>
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5. RELATION TO OTHER WORK IN PROGRESS

5.1 By the Principal Investigator

Active relevant research. I currently have four federal or state grants involving cryogenic hydrogen fuel (see current and pending support section). All four grants will end prior to August of 2016 and do not present any conflicts with this research. Two of the grants (NASA-SBIR and JCATI) pertain to the design and insulation of liquid hydrogen storage tanks. The NASA-SBIR grant is related in that the CHEF experiment will be characterizing para-orthohydrogen conversion in heat shielding blankets with catalyst coatings (Bliesner et al. 2014), a very similar process to that proposed in Specific Aim #1. Although the process is similar to that proposed here, the end use application and device are entirely different and the project timelines do not currently overlap. Another grant, NASA-STRF, is producing fundamental measurements and equations of state for binary helium-hydrogen mixtures and has created some of the property models and composition analysis methods necessary to complete Specific Aim #2 (Blackham et al. 2015). The final grant, US-ITER/UT-Battelle, was to characterize the operational performance of twin-screw extruders operating on solidified deuterium and hydrogen fuel for fusion energy machines and is not related to the proposed work.

A state-level grant (Washington Research Foundation, $20k) is supporting equipment purchases and time-slip student wages of the undergraduate student team/club’s effort to develop a system level prototype liquefier using the vortex tube concept (see Hydrogen-related student club research later in this section). I can proceed with applied cycle development without lower TRL progression (the topic of this proposal) because the vortex tube concept works for helium liquefaction.

Pending relevant research. A commercialization gap fund proposal is pending (Murdock Charitable Trust, $60k + $60k WSU match) and will function similarly to the Washington Research Foundation award in support of the student team’s applied prototyping efforts as part of the DOE’s H2-Refuel competition. The funds will also help my graduate students that have started a company, Protium Innovations LLC, to find potential customers. The TRL of this work is 5-8 and not overlapping with the work proposed here.

The closest grant to overlapping with this research is pending through NREL ($666k) as sub-award of an Energy Efficiency and Renewable Energy (EERE) solicitation restricted to participation by national laboratories. This project is also applied and intended at the TRL 3-5 level. Notification of award is coinciding with the due date of this CAREER proposal and the award notification will be immediately communicated to the program manager. The key objectives of the work are optimization of the vortex tube cycle performance for liquefaction through system-level design and prototyping. The major part of the grant is optimal placement and operation of the liquefiers associated with renewable energy resources. The grant is clearly not intended for fundamental/basic research and does not overlap with the Aims of this proposal but is rather complimentary.

A final pending proposal (NIST, $50k) is to develop content modules to educate engineers utilizing standards for capstone design. This proposed work is not related to the NIST proposal and the time allocation on the NIST proposal is small.
Hydrogen-related student club research.

1) 2nd place in the 2012 International Hydrogen Student Design Contest that challenged participants to develop a tri-generation system to produce heat, hydrogen, and power for their university campus utilizing locally available biomass (Pecha et al. 2013).

2) Design and construction of the Genii liquid hydrogen fueled, fuel-cell powered Unmanned Aerial System (UAS) on a sub $30,000 internal WSU budget. Shown in Figure 6 below. The use of cryogenic hydrogen fuel and a proton-exchange-membrane fuel cell, with such a very low budget was novel. The project, from 2012-2014, garnered significant in-state interest from industry and resulted in follow on projects (Adam & Leachman 2014).

3) 1st place in the 2014 International Hydrogen Student Design Contest by challenging participants to design a low-cost drop-in 700 bar hydrogen refueling station for the nascent hydrogen fueled vehicle fleet (Richardson et al. 2015). We pioneered a new concept, called Cryogenic Thermal Compression (CTC) to nearly remove the reliance on conventional piston compressors – the primary cost and failure mechanism of stations.

Figure 6: (Top Left) Genii takes off on 2nd flight. (Top Right) Primary Genii student team. (Bottom Left) 2014 H2 Student winners. (Bottom Right) Conceptual fueling station render.

5.2 Active work by Investigators elsewhere

The US does not have active basic research in hydrogen liquefaction. The DOE Fuel Cell Technologies Office (FCTO) only funds applied research development and does not have an early CAREER program. Monterey Gardiner stepped down as an FCTO program manager in 2014 and informed me that I am only one of three hydrogen liquefaction researchers known in the US and the only one in academia. The recently completed Ideal-Hydrogen project in Europe supported research groups in Norway, Italy, and two in Germany, all of which are currently pursuing mixed-gas (neon-helium) refrigerant approaches to hydrogen liquefaction. This proposed work has the potential to propel the US back to a leading role in this field. Most vortex tube research is happening internationally in Europe, China, Australia, Canada, and India.

6. BROADER IMPACTS OF THE PROPOSED WORK

The progression of the prior student club projects has made it clear that the production, dispensing, and end use technologies required to support the emergent hydrogen economy are at a threshold for a paradigm change experienced by the general public. The recent announcements of ten major auto manufacturers committing to sell hydrogen vehicles in the US further supports the eminent market transformation. The
major remaining problem is the most efficient approach to densification of the hydrogen for transportation, storage, and distribution. Hydrogen liquefaction has a long history of addressing this need, but the lack of distributable liquefier infrastructure adds substantial cost to the delivered product ($5/kg LH2 production expense vs. $2-12/kg LH2 delivery distance expense). Although 80-90% of small-merchant hydrogen is distributed via cryogenic liquid tanker truck (TTC 2010), the classic criticism of hydrogen liquefaction remains – even a perfect liquefier loses 30% of the hydrogen’s energy to liquefaction. Regardless, liquid hydrogen currently retails for $7-17/kg, or $23.1-56/kW-hr – a portable energy product orders of magnitude more valuable than conventional electricity or natural gas. This presents an economical alternative to wind farms that in many cases entirely curtail energy due to insufficient storage capacity and directly enables off-grid or shore locations. The geographic distribution of wind farms provides a unique opportunity to substantially undercut the mileage-based cost of delivery associated with the eight commercial hydrogen liquefiers in North America. Clearly, a low-cost distributable hydrogen liquefaction system is the missing and essential technology to the hydrogen economy. The primary hypothesis of this work will utilize the vortex tube to invert the paradigm of exothermic ortho-parahydrogen conversion to directly aid in primary cooling. Vortex tubes are widely considered a rotor-less turbo-expander – the Holy Grail for cryogenic hydrogen refrigeration. Therefore, the degree to which society benefits from the hydrogen economy directly hinges on the outcomes of this proposal.

In an effort to solve this distributed supply chain issue, in late 2014 the DOE announced the $1M prize H2-Refuel competition to develop an in-home or community-based hydrogen refueling system with on-site generation. Although the competition is open to participation from any organization within the US, the approach of the WSU student team is completely novel. We will use our patent-pending small vortex-enabled liquid hydrogen cycle (a direct extension of this proposed research) to densify the hydrogen prior to cryogenic thermal compression with compatible pressure vessels. Underrepresented groups are already involved with the club per my role on the minority student advisory board (see synergistic activities in biosketches). Industry support, voluntary undergraduate students, and broader faculty participation in system-level application of this CAREER project will accelerate Technology Readiness Level (TRL) advancement efforts. Regardless of whether or not my team is successful in the competition, the companies that have pledge support are very interested. Commercialization of the concept cycle will be key and hiring the students trained in this line of research is an additional motivator due to the long-term shortage of engineers trained in cryogenic refrigeration. Although I am proceeding with the applied cycle design with the support of NREL, these companies, and local foundations, the fundamental science behind the vortex technology central to the cycle is the sole focus of this proposal. We are currently designing the entire cycle around ‘rules of thumb’ for the vortex tube performance and the students already fully appreciate the role of fundamental science to enable the applied cycle design.

The proposed research scope, to use the unique properties of hydrogen to develop or validate a theory for transport in the Ranque-Hilsch vortex tube, will greatly aid in solving a long-standing debate in the field. The fundamental question of how the vortex tube works remains open, despite several recent and credible theories awaiting rigorous experimental validation. Simply communicating and allowing the students to experience how the vortex tube experiments and theory pair is an essential step towards confident application. To this end, developing the REMs to supplement the LC-DLMs in parallel with the active NSF-IUSE program will decisively test the pedagogical system being developed around vortex cooling. The scaffolded classroom implementation ranges from simple device production and experimentation, to complex property modeling and CFD analysis, is comprehensive and synergistic with the research aims. The end results will be long-term experiments maintained at WSU and low-cost pedagogical approaches distributed widely through the established NSF-IUSE network. The pedagogical content will finally allow instructors to resolutely answer the question of how the Ranque-Hilsch vortex tube actually works. The key being a unique characteristic of hydrogen discovered in-part by Werner Heisenberg over 80 years ago. The key that unlocked clean hydrogen liquefaction for the benefit of humanity.

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Ranque, G., “Expériences sur la Détente Giratoire avec Productions Simultanées d'un Echappement d'air Chaud et d'un Echappement d'air Froid,” J. de Physique et Radium, 4(7) (1933), 112S.
BIOGRAPHICAL SKETCHES

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Professional Preparation:
University of Idaho Mechanical Engineering B.S. 2005
University of Idaho Mechanical Engineering M.S. 2007
University of Wisconsin-Madison Mechanical Engineering Ph.D. 2010
University of Wisconsin-Madison Nuclear Engineering Ph.D. Minor 2010

Appointments:
Assistant Professor, Washington State University, 8/2010 to present.
Graduate Research Assistant, University of Wisconsin-Madison, 09/2007 to 08/2010.
Guest Researcher, National Institute of Standards and Technology (NIST), 07/2006 to 08/2006.
Graduate Research Assistant, University of Idaho Center for Applied Thermodynamic Studies (CATS), 01/2006 to 05/2007.

Five Related Publications:

Five Other Publications:


**Five Synergistic Activities:**
Cryogenic Engineering Conference (CEC) board member.
ASME K7 Committee on Thermophysical Properties member.
Community Outreach, “Cryogenics and the Conquest of Cold: Liquid Nitrogen Ice Cream,” Presented to children and families at rural community libraries in Whitman County Washington, Period: 05/2011 to 08/2011, 5 total presentations to over 100 participants.
Research Experience for Undergraduates (REU) Mentor for six students Period: 05/2011 to present.

**Collaborators:**
Ainscough, Chris; Senior Engineer, National Renewable Energy Laboratory.
Baylor, Larry; Scientist; Oak Ridge National Laboratory.
Combs, Steven; Scientist; Oak Ridge National Laboratory.
Lemmon, Eric; Scientist; National Institute of Standards and Technology.
McLinden, Mark; Scientist; National Institute of Standards and Technology.
Meitner, Steven; Scientist; Oak Ridge National Laboratory.

**Graduate Advisors:**
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Jacobsen, Richard; Vice Provost for Research; Idaho State University.
Penoncello, Steven; Professor; University of Idaho.
Pfotenhauer, John; Professor; University of Wisconsin-Madison.

**Graduate Research Assistants:**
Fisher, Jake; 5th year Ph.D. student, Washington State University.
Richardson, Ian; 4th year Ph.D. student, Washington State University.
Adam, Patrick; 3rd year Ph.D. student, Washington State University.
Blackham, Thomas; 3rd year Ph.D. student, Washington State University.
Pedrow, Brandt, 1st year Ph.D. student, Washington State University.
Shoemake, Elijah, 1st year M.S. student, Washington State University.
FACILITIES, EQUIPMENT, & OTHER RESOURCES

1. Facilities

1.1 Hydrogen Properties for Energy Research (HYPER) Laboratory: The PI initiated the HYPER laboratory in 2010. The HYPER laboratory occupies a 55.7 m² (a 20’ x 30’ space) in the Engineering Teaching and Research Laboratory (ETRL) on the WSU Pullman campus. ETRL is the premier engineering laboratory building on campus being recently constructed in 1999. The laboratory space is specifically amenable to hydrogen research for the following reasons:
   1) Separated hydrogen bottle storage area to minimize gas storage in the laboratory,
   2) Chemical fume hood with fire suppression system,
   3) A snorkel attachment to the fume hood system for creation of ventilated experiment systems within the general laboratory space,
   4) A dedicated air handler to exchange the entire air volume of the laboratory every hour.
In summary, the PI’s laboratory space is well suited to cryogenic hydrogen research and the PI is the only faculty member utilizing the space.

1.2 Thermal Fluids Research Building (TFRB) Suites 113 and 108: The PI has over 5000 square feet with adjacent outdoor hydrogen testing area. The space includes a thermophysical phenomena library, high-bay facility with 10 ton rail crane, assembly space, and design space.

1.3 Office Space in Sloan Hall: The PI has sole use of a 14 m² (10’ x 20’) office space in Sloan Hall which is adjacent to the HYPER laboratory in ETRL. The office space has shared printing, fax, and office facilities.

1.4 Core Characterization Facilities: WSU-Pullman is home to the Franceschi Microscopy and Imaging Center. This center will be utilized for X-Ray diffraction, SEM, and TEM images of the synthesized solid-state manipulator materials. The images shown in the Preliminary research section were taken by an REU student utilizing the Franceschi Microscopy and Imaging Center.

1.5 Clinical and Animal Space: (Not applicable)

2. Major Equipment

The following major equipment is available in the HYPER laboratory for this proposal and is organized by facility:

2.1 Cryo-catalysis Hydrogen Experiment Facility (CHEF): The following major equipment components comprise the CHEF:
   1) A Sumitomo Model 204S-N-HC4 cryogenic refrigerator (measurement range 7.5–300 K).
   2) A Varian Turbo-V-81M turbomolecular pumping system with minimum on cryostat attainable pressures down to 10⁻⁸ bar backed by a Leybold D60B roughing pump.
   3) A 1 cubic meter Varian cryogenic vacuum chamber with positionable hoist.
   4) A Lakeshore Model 330 cryogenic temperature controller.
   5) A new DELL Optiplex PC outfitted with Labview software and interfaced with the CHEF via a Labview modular DAQ system.
Additional details on CHEF including images were provided in the preliminary research portion of the Project Description. Additional details can be found in the literature (Bliesner and Leachman 2012).

2.2 Rubotherm Isosorp 2000: The following major equipment components comprise the CHEF:
   1) Cryomech PT405 vibration-isolated cryogenic refrigerator (measurement range 2.7-300 K),
   2) A new vacuum chamber and test cell will be fabricated for this experiment,
   3) A Leybold turbomolecular vacuum pumping system,
   4) An ASL precision thermometry bridge,
   5) Rubotherm Isosorp 2000 with thermal standoff, dual-sinker modification, and electromagnetic coupler.

Additional details on the Rubotherm were provided in the preliminary research portion of the Project Description. Additional details on the facility can be found in the literature (May et al. 2002).

2.3 Helium Leak Detector: The PI will receive bids back the day that this proposal is due for a new helium leak detection system that is critical to the safety and accuracy of this research. The system to be purchased will have the following specifications:
   1) hard, sniffer, and gross leak helium leak detection modes,
   2) a variable AMU system for detecting hydrogen leaks,
   3) a dry pumping system to prevent oil-mist contamination,
   4) the standard suite of helium leak detection capabilities.

In summary the PI has, or unlimited access to, the experimental facilities necessary to complete the objectives of this research.

3. Other Resources

3.1 Engineering Instrument Shop and Metal Fabrication Shop: The PI’s graduate students are trained for open access to the WSU Metal Fabrication Shop. This space is available for supervised use should minor machining and fabrications be necessary. For advanced fabrications, both the Engineering Instrument Shop and Technical Services on the WSU campus competitively bid for inter-WSU machining contracts. The PI has worked with all of these facilities and is confident that all of the fabrications required of this proposal are achievable via WSU facilities.

3.2 Software & Computing: The PI has active COMSOL CFD and Solidworks seats for research. A custom computer with a 20 core-2.2 Ghz processor, 192 GB ram, 500 GB harddrive space, and Quadro K2200 graphics card was designed for operating COMSOL.
DATA MANAGEMENT PLAN

In order to secure funding for this study, this Data Management Plan (DMP) was created on July 8th, 2015 for submission to the National Science Foundation as required by NSF guidelines. The objective of this DMP is to guarantee the preservation of data collected, as well as analysis of the subsequent data. This DMP covers the experimental measurements to be collected as part of this CAREER award at Washington State University. The study period will be from January 1st 2016 through December 31st 2020. The PI is committed that all raw measurements of technical importance will be preserved as part of this study and the analyzed measurements disseminated broadly.

The study will collect experimental measurements on orthohydrogen-parahydrogen catalysis from a Cryo-catalysis Hydrogen Experiment Facility (CHEF) and preferential adsorption measurements from a retrofitted Rubotherm Isosorp 2000. These measurements include temperature, pressure, concentration of orthohydrogen-parahydrogen mixtures, electromagnetization, catalyst reactivity, adsorption, absorption, X-ray diffractometry, TEM, and SEM. Measurements will be archived in thesis publications, provided in electronic format upon request, and posted to the PIs faculty website. Data posted to the faculty website will be within a self-contained report such that it is easily understood and utilized by the general public. No biological testing of any kind will be conducted as part of this research.

It is anticipated that the primary point of dissemination for results published as part of this work will be the journals Cryogenics, Engineering Education, and the International Journal of Hydrogen Energy. These journals are peer-reviewed, highly reputable, and well known. A secondary source for dissemination will be presentations at the bi-annual Cryogenic Engineering conference with corresponding publications in Advances in Cryogenics: Proceedings of the Cryogenic Engineering Conference. A tertiary source for dissemination will be the PI’s website: hydrogen.wsu.edu

There are no requirements stipulated by the funding or partner organizations regarding this data. The PI is trained on institutional guidelines regarding the collection of this data. There are no additional requirements (including copyrights) associated with this data collection. Although there are no requirements to make this data available publicly, the PI is electing to do so by December 31st 2020. This DMP will be reviewed to ensure compliance at that time.
Current and Pending Support

Current Support:

Use of a vortex-tube for H2-Refuel Challenge. Description: This award is funding the acquisition of equipment for the applied cycle/system design development effort as part of the student club effort for the DOE’s H2-Refuel Challenge. [Washington Research Foundation; Amount: $20,000, Duration: 7/2015-8/2016]

Parahydrogen-Orthohydrogen Catalytic Conversion for Cryogenic Propellant Passive Heat Shielding. Description: We will utilize the established Cryocatalysis Hydrogen Experiment Facility (CHEF) to conduct catalytic activity measurements of heat shielding blanket materials. [NASA SBIR Phase I sub-award; Co-I: M. Wright (Ultrade); Amount: $27,500; Duration: 7/2015–12/2015]

Development of an Insulation-Free Cryogenic Hydrogen Fuel Tank for ScanEagle. Description: In this project, we are finishing the design and production of a 3D printed liquid hydrogen fuel tank with vapor cooled shielding. [Washington Joint Center for Aerospace Technology & Innovation (JCATI) and Insitu; Amount: $125,000; Duration: 7/2014–10/2015]

Hydrogen-Helium mixtures: Fundamental Measurements, Neutral Droplet Buoyancy, Evaporation, and Boiling. Description: We are using an established magnetic-suspension cryogenic densimeter to develop fundamental property models of binary helium-hydrogen mixtures. [NASA Space Technology Research Fellowship; Co-I: I. Richardson (student); Amount: $139,480; Duration: 8/2014–8/2016]

Deuterium Modeling and Measurements in support of US-ITER Extruder Development. Description: We are using an established twin-screw extruder to characterize solid fuel pellet production for the ITER fusion tokomak. [US ITER/UT-Battelle; Amount: $106,063; Duration: 10/2013–8/2015]

Pending Support:

Standards and Standardization Curriculum Modules: An Open Access Educational Repository. Description: My wife (the engineering librarian at WSU) and I are seeking to develop standardized curriculum modules for finding standards relevant to engineering design problems. [National Institute of Standards and Technology (NIST) Standards Services Curricula Development; Co-I: C. Leachman; Amount: $50,000; Duration: 8/1/15-12/31/16]

Improved Hydrogen Liquefaction through Heisenberg Vortex: Separation of Para and Orthohydrogen. Description: This project seeks to design and implement a prototype liquefaction cycle utilizing catalyzed vortex tubes and to assess optimal placement locations throughout the US. The TRL will be transitioned from 3-5 during this project. [DOE/NREL sub-award; Co-I's: C. Ainscough (NREL), D. McLarty (WSU), J. Schwartz (Praxair); Amount: $666,591; Duration: 9/2015–8/2018]

Optimization of vortex tube performance via para-orthohydrogen conversion to enable small-modular hydrogen liquefaction and storage. Description: Similar to the Washington Research Foundation grant above, this proposal will purchase equipment for the applied system development as part of the student club’s design for the DOE’s H2-Refuel competition. The grant also includes funds to commercialize the technology as part of business plan. [M.J. Murdock Charitable Trust Commercialization Gap Fund; Amount: $60,000 ($60,000 additional match from WSU); Duration: 8/15/15-8/31/16]

CAREER: Elucidating transport in Ranque-Hilsch vortex tubes via para-orthohydrogen conversion – enabling efficient small-scale hydrogen liquefaction. Description: This proposal. [NSF; Amount: $500,000; Duration: 1/1/16-12/31/20]