Kinetic orthohydrogen-parahydrogen separation to enable small-modular hydrogen liquefaction

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1. OVERVIEW

ARPA-E Contact:	N/A
Technical Subcategory:	1.2 turbines/engines, acoustic cooling, geothermal, tribology
Funding Request:	$300,000
Project Duration:	12
Project Abstract:	Efficient small-modular hydrogen liquefiers have not been developed due to the difficulty of refrigerating below 77 K. Below 77 K the largest entropy change of any material is orthohydrogen-parahydrogen conversion which is an exothermic reaction that significantly hinders liquefaction efficiencies. In this work we will develop a proof of concept small-modular hydrogen liquefaction system that utilizes kinetic parahydrogen-orthohydrogen separation and conversion via vortex tubes. This approach allows for an endothermic parahydrogen-orthohydrogen reaction to cause bulk cooling before the orthohydrogen is separated and recycled in a liquid nitrogen bath. This scalable approach is anticipated to significantly increase small-modular hydrogen liquefier efficiency; an enabling advance for electrolysis, backup power, and hydrogen fueling stations.

2. IMPACT

North America has only 8 medium to large scale hydrogen liquefiers and only the Praxair plant near Niagara Falls produces this hydrogen with zero carbon emissions. Small to medium scale modular hydrogen liquefiers operating with efficiencies close to large-scale systems is the best possible advance to enable low-cost hydrogen storage and clearly addresses all of ARPA-e's missions.

3. STATE OF THE ART

Heat exchange with helium refrigerant, turbo-expansion, piston expansion, Joule-Thomson expansion, and magneto-caloric systems are currently the state of the art for sub-77 K refrigeration. All of these approaches must remove the latent heat of orthohydrogen-parahydrogen conversion via mass flow through an activated catalyst bed. These beds are operated below 77 K and generate an exothermic heat load that requires either boil-off makeup or directly adds to the sub-77 K refrigeration load. The exothermic latent heat load from orthohydrogen-parahydrogen conversion is nearly equal to the sensible heat load to cool the hydrogen from 77 K to 27 K.

4. INNOVATION

We seek to develop a proof-of-concept that kinetic parahydrogen-orthohydrogen conversion and separation can be used for higher efficiency primary cooling in any hydrogen liquefaction cycle design. The concept of kinetic parahydrogen-orthohydrogen conversion and separation in a vortex is shown in the figures below. The top figure describes operation of the device and the bottom figure shows the properties of parahydrogen and orthohydrogen for reference. Equilibrated hydrogen enters the vortex tube at A from a catalyst bed cooled by liquid nitrogen bath at 77 K, ~50 psi, and 50-50 ortho-para composition. As the hydrogen enters the vortex at B, faster, higher temperature molecules migrate to the outside of the tube and slower, colder molecules migrate towards the inside. The outer, higher temperature fluid is likely near ~120 K. At this elevated temperature the equilibrium ortho-para composition shifts to nearly 70 % ortho, and a catalyst along the outer tube wall catalyzes this endothermic conversion (C in the diagram). Insulation along the outer tube wall (D in the diagram) necessitates that the thermal energy required for the endothermic conversion is provided by the surrounding fluid, driving bulk cooling. The now orthohydrogen rich outer stream is separated from the vortex tube (E in the diagram) where it is returned to the liquid nitrogen bath for re-equilibration. Essential this process entraps energy in the fluid itself (a perfect heat exchanger?) whereby this energy is removed at the 77 K bath. The remaining parahydrogen rich fluid in the core region of the vortex is extracted at point F in the diagram, where it can be fed to a second vortex tube (with potentially higher effectiveness) or through a conventional J-T valve or flash separator for final liquefaction.
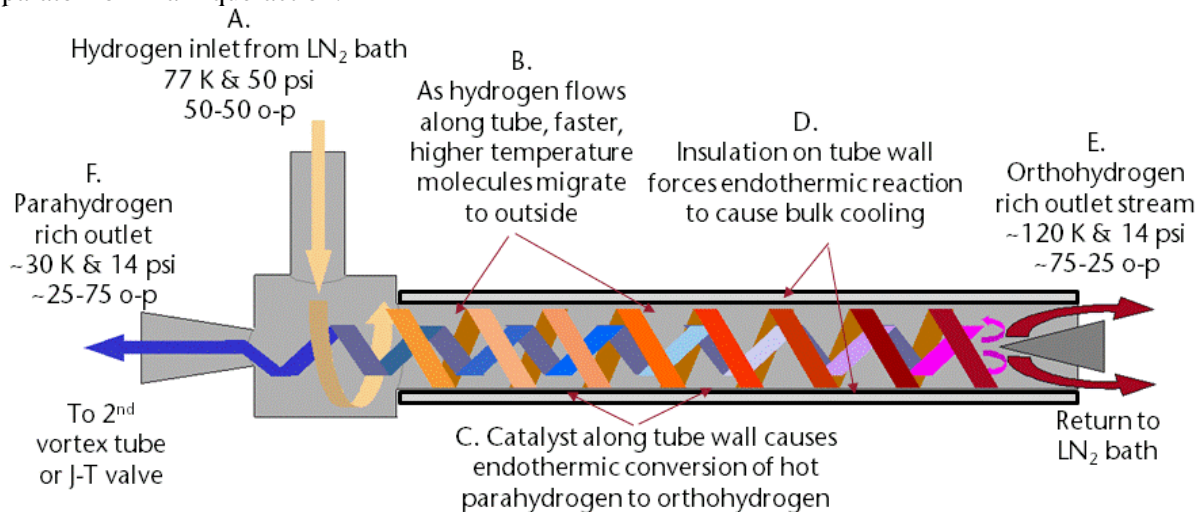

Figure 1: Conceptual diagram of kinetic parahydrogen-orthohydrogen conversion and separation in a vortex tube relying on internal fluid power to accomplish the separation.
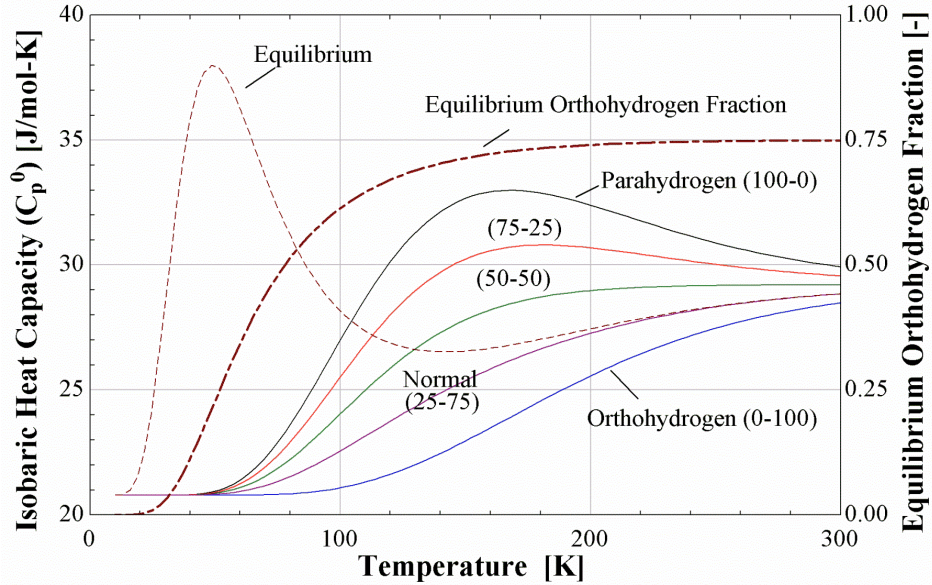
Figure 2: Cryogenic hydrogen heat capacity and equilibrium ortho-para composition.

What must be emphasized is that the vortical separation concept is not limited to utilizing internal fluid power and can be adapted to external work approaches relying on either pistons or an expansion turbine to drive the vortical flow. These concepts are shown in Figure 3 below.
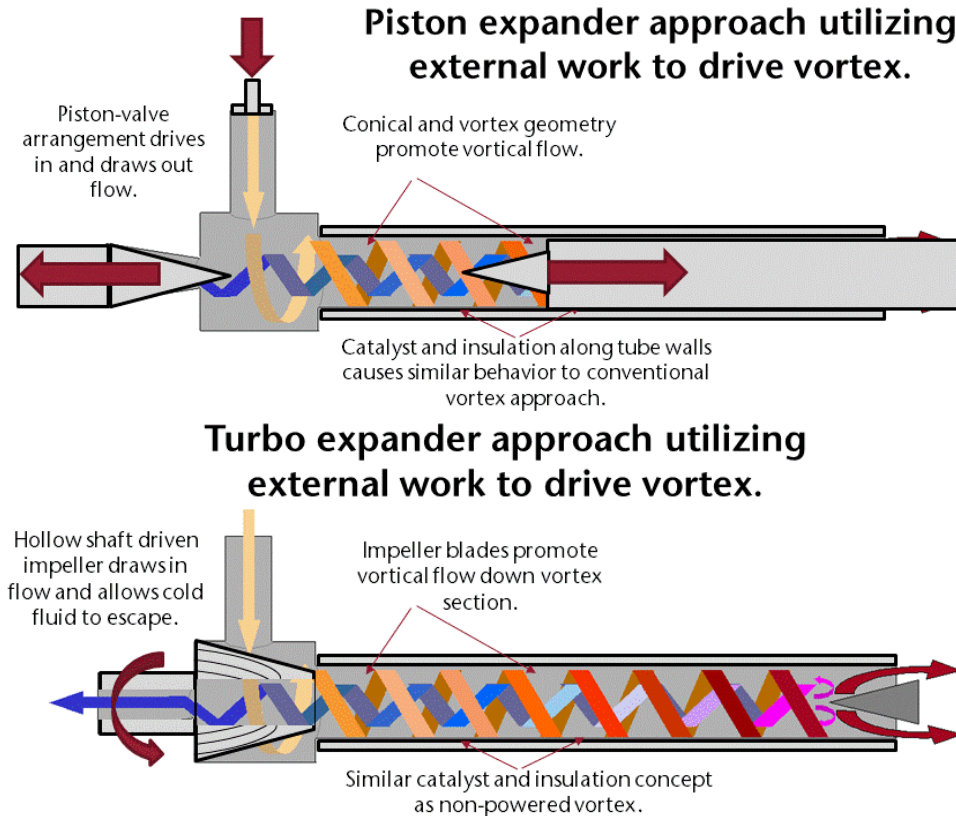

Figure 3: Conceptual diagrams of piston and turbo expander approaches to kinetic separation that rely on external work input to drive vortical flow.

Vortex tubes are well established devices for refrigeration. They are typically less efficient than conventional refrigeration cycles for conventional applications. However, conventional refrigeration cycles are terribly inefficient for sub 77 K cooling due to the lack of acceptable refrigerants. This approach does not suffer the same efficiency declines and has the potential to be superior for sub 77 K cooling. Vortex cooling was considered for slush hydrogen production associated with the National AeroSpace Plane (NASP), however that approach did not utilize orthohydrogen-parahydrogen conversion. This is the first attempt (made public) to utilize parahydrogen-orthohydrogen conversion for primary refrigeration of hydrogen.

Table 1 below shows the minimum work required for liquefaction of several cryogens. Hydrogen has the additional heat of orthohydrogen-parahydrogen conversion that is 20% of the sensible and latent heat removal. Although the enthalpy change of orthohydrogen-parahydrogen conversion is 700 kJ/kg and significantly larger than the latent heat of 420 kJ/kg, this ideal scenario continuously removes the heat of conversion at the highest temperature possible. In reality, six or more catalyst beds are required at different temperature stages. As a result, the catalyst beds are one of the primary sources of inefficiency in hydrogen liquefaction systems. The proposed approach traps the sub-77 K sensible and latent energy within the orthohydrogen and removes the orthohydrogen from the parahydrogen stream to be recycled/converted at the 77 K liquid nitrogen bath, which is the highest temperature catalyst bed in a traditional liquefier. Since this approach potentially removes all catalyst beds from the process, efficiency improvements approaching 20 % over the status quo are possible, placing small modular hydrogen liquefiers at efficiency levels comparable to 500 MW scale liquefaction systems.

Table 1: Minimum work required for liquefaction of various cryogens.

Gas/sub-process	Normal Boiling Point (K)	Minimum work $W=T_0\Delta s-\Delta i$ (kW-hr/kg) to liquefy			
		Cooling/sensible	Condensing/latent	Ortho-Para	Totals
Oxygen	90.19	0.0372	0.1345	--	0.1717
Nitrogen	77.36	0.0524	0.1557	--	0.2081
Parahydrogen	20.27	1.735	1.681	0.6529	4.07
Helium	4.22	1.465	0.3956	--	1.861

5. RISKS AND CHALLENGES

The key risk/unknowns for this proof-of-concept primarily pertain to understanding how the vortex tube itself operates. Whether vortex tubes separate flow primarily via molecular kinetics (solid rotation model) or thermal transport remains unknown in the literature. The ability to closely monitor the orthohydrogen-parahydrogen outlet stream compositions in an uncatalyzed vortex tube will help to solve this fundamental science challenge as the molecular kinetics of the isotopologues are precisely known from statistical mechanics. This issue of solid rotation vs. thermal transport will ultimately determine the maximum effectiveness of the cooling achieved. For example, a parahydrogen molecule that converts to orthohydrogen on the outer wall will be cooled, whether this molecule is then replaced by a new hot parahydrogen molecule and 1) migrates inwards or 2) is transferred heat from the surrounding fluid to remain in radial position within the vortex is an open question. The ideal situation is actually a combination of these two scenarios. Some radial migration inward towards the core of the vortex allows new parahydrogen exposure to the catalyst while drawing thermal energy directly from the core and if balanced, without migrating too close to the core to prevent separation of the orthohydrogen at the hot fluid exit. This is the only entirely new innovation required for the design to be successful.

Vortical separation can be integrated with traditional piston or turbine expander systems in existing liquifiers, and have the advantage of increasing the performance of small-modular systems. Therefore no techno-economic barriers are anticipated should the approach have superior efficiency.

6. PROJECT PLAN

We will demonstrate a proof-of-concept small-modular hydrogen liquefaction system implementing kinetic parahydrogen-orthohydrogen separation and compare the actual and anticipated energy performance directly to large-scale liquefaction systems.

We will develop a COMSOL multiphysics model linked with a statistical thermodynamics code. We will validate performance of the code with experimental measurements and predict theoretical optimal operating conditions.

7. TEAM

The team consists of Dr. Jacob Leachman's Hydrogen Properties for Energy Research (HYPER) laboratory at Washington State University. The graduate students involved with the project are Mr. Elijah Shoemake, Mr. Patrick Adam, and Ms. Hanna Raine. This team has initiated a start-up company, Protium Innovations LLC, which will commercialize the invention once demonstrated.

Dr. Leachman wrote the current leading equations of state for parahydrogen, orthohydrogen, and normal hydrogen as his Master's Thesis and won the Western Association of Graduate Schools Distinguished Thesis Award for 2007. He initiated the HYPER laboratory in 2010 with the goal to efficiently advance the Technology Readiness Level of hydrogen systems for the betterment of humanity. Since this time the HYPER lab has made several relevant accomplishments with orthohydrogen-parahydrogen research:

1) Demonstrated endothermic parahydrogen-orthohydrogen conversion for vapor cooled shielding of liquid oxygen tanks for extended stage rockets.
2) Designed and obtained a provisional patent for 3-D printing Type 4 hydrogen pressure vessel liners for vapor cooled shielding of liquid hydrogen. This work is being transferred to the aerospace industry.