PARAHYDROGEN-ORTHOHYDROGEN CONVERSION FOR

BOIL-OFF REDUCTION FROM SPACE STAGE

FUEL SYSTEMS

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of Ronald M. Bliesner find it satisfactory and recommend that it be accepted.

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Konstantin Matveev, Ph.D.

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I dedicate this thesis to all of you.

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Abstract

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Long-term space missions require minimized boil-off from liquid hydrogen and oxygen tanks to reduce Gross Lift Off Weight (GLOW). Leading rocket technologies utilize liquid hydrogen boil-off vapors to refrigerate and potentially eliminate boil-off from the liquid oxygen tank. The use of liquid hydrogen allows a substantial amount of heat to be conveyed out of the system. Statistical thermodynamic calculations estimate that the amount of heat carried with the hydrogen refrigerant can be increased up to 50 % through catalysis of the parahydrogen-orthohydrogen conversion. This thesis discusses development of the Cryo-catalysis Hydrogen Experiment Facility (CHEF) in the HYdrogen Properties for Energy Research (HYPER) laboratory at Washington State University. Initial experimental results are presented that validate statistical thermodynamic predictions of cooling capacity while catalyzing parahydrogen-orthohydrogen conversion. This proof-of-concept indicates that the mass of hydrogen vented to space can be reduced nearly 33 %. Initial system capabilities and a plan for future measurements are presented.

Table of Contents

Nomenclature

E	Electrical potential
I	Moment of inertia
j	Nuclear rotational energy level
k_B	Boltzmann constant
k	Thermal Conductivity
L	Length
N	Number of molecules
Nu	Nusselt number
P	Statistical weight
Pr	Prandtl number
Q	Heat
R	Electrical resistance
Re	Reynolds number
T	Temperature
x	Concentration (mole fraction)
ε	Energy of a state
θ	Characteristic temperature

Introduction

Hydrogen's history in space technologies lifted off with a bang. A liquid hydrogen and liquid oxygen (LH$_2$/LOx) fueled Centaur upper stage rocket exploded 54 seconds after liftoff during its maiden voyage in May of 1962 (1). The failure, haven taken place less than a year after President John F. Kennedy's famous declaration to send men to the moon, was demoralizing. Yet despite the significant technical challenges that had to be overcome, NASA scientists remained committed; liquid hydrogen was the United States' best hope to land mankind on the moon.

Figure 1: Image of the liquid hydrogen fueled Centaur upper stage during construction. (1)

Liquid hydrogen was not the first space bound rocket fuel to be researched. In the early 1950's at the dawn of the space age, the most popular rocket designs employed the use of RP-1 kerosene fuel and liquid oxygen. Kerosene is a leading rocket fuel because of its low cost, high density, and high stability at room temperature. This made RP-1 easier to work with and far safer than many alternatives. However the specific impulse of RP-1 was comparatively low and many rocket scientists and engineers recognized the enormous potential for liquid hydrogen fuel. Specific impulse (I_{sp}) is the ratio of thrust to the required mass flow rate of fuel and oxidizer. In this way, I_{sp} is effectively a measure of an engine's efficiency and is largely influenced by the selection of propellants. Though less dense than RP-1, the improvements in specific impulse, and exhaust velocity (which determines a vehicles maximum speed) justified the need for advanced research with liquid hydrogen fuel. Before the advantages could be realized however, many serious design challenges had to be solved.

Unlike Hydrocarbon fuels, hydrogen must be stored at temperatures below 25K (-250°C) to be maintained in liquid form. Although engineers had successfully used cryogenic liquid oxygen for years, the extremely low temperatures of liquid hydrogen created significantly more problems. During the design and construction of the Centaur rocket, the first LH$_2$/LOx fueled vehicle in space, engineers had to employ many unique design features to account for the significant fuel volume and extreme thermal shielding requirements. In an effort to save weight, Centaur engineers employed the use of a pressure stabilized tank, by which the tank was in effect turned into a stainless steel balloon to create a rigid structure for the rest of the rocket. The addition of thermal shielding on the nose of the rocket also had to be added to prevent the tank from overheating during lift-off as air rushed over the tank. Ultimately, these challenges would be overcome and Centaur would successfully prove liquid hydrogen as an essential fuel for future space exploration. Although many of the technical challenges in harnessing hydrogen as a fuel have been solved, hydrogen's largest limitation for future space exploration lies in the storage and transfer of this cryogenic liquid.

One of the largest drawbacks to using cryogenic fuels is the extremely low temperatures that must be maintained to prevent the fuel from boiling. As heat from the sun irradiates the fuel tanks in the upper stage rocket, the boil-off vapors must be vented to prevent the tanks from rupturing due to the increased pressure. This can be mitigated by increasing the thermal shielding around the rocket; but without an active cooling system (such as a cryocooler), there will always be a small fraction of fuel lost to boil off. For short duration missions, such as positioning satellites into earth orbit, boil-off is not a concern. However, the importance of mitigating boil-off scales with increases in mission time and becomes a significant concern. Figure 2 shows a relationship between GLOW, boil-off rate, and mission duration.
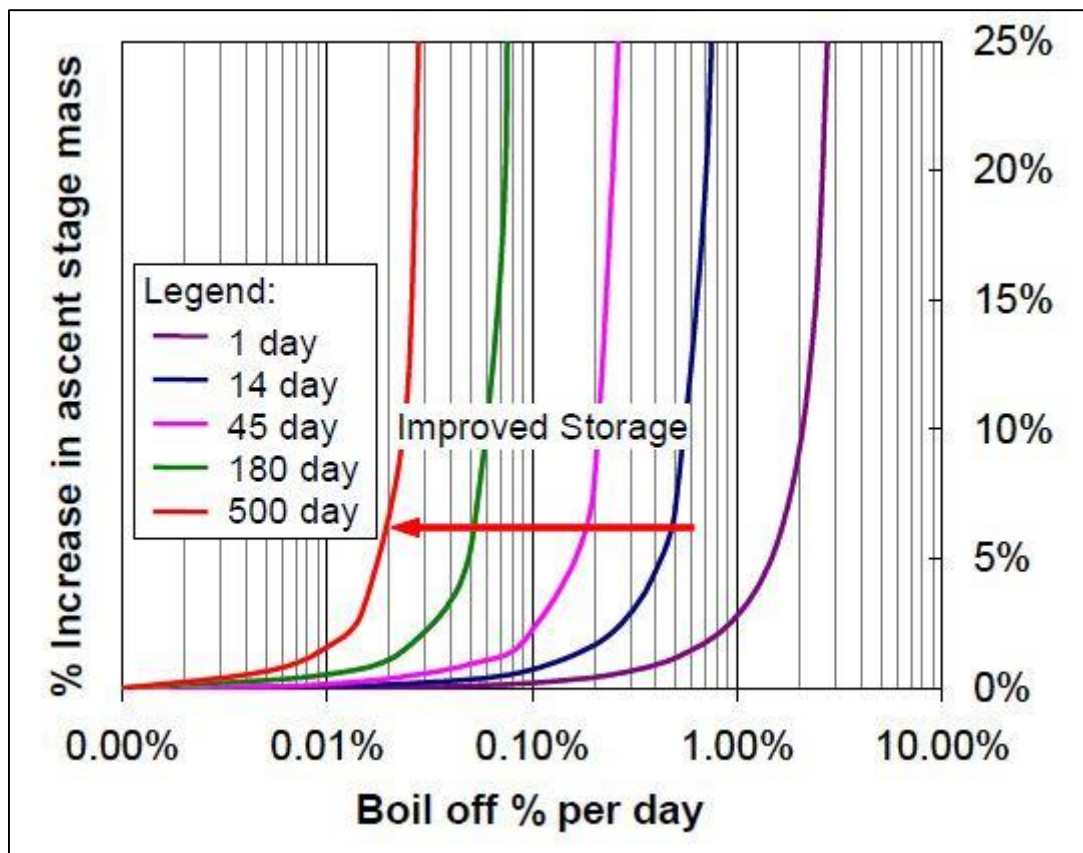

Figure 2: Percentage increase in ascent stage mass plotted versus boil off rate per day for various mission durations (adapted from Kutter 2010). This plot shows that a boil-off rate of less than 0.03% is required for mission durations exceeding 500 days.

Boil-off rates as high as 2% per day were common in second stage fuel systems during the Apollo program (1). This high boil-off rate meant that a significant amount of excess fuel had to be launched into space for long duration flights to ensure enough fuel would be available. This excess fuel greatly increases the ascent stage mass and leads to in-space boil-off being the single largest factor in GLOW and therefore launch cost.

Modern liquid hydrogen space stages utilize passive cooling via boil-off hydrogen vapors to refrigerate the liquid oxygen tank and common thermal shielding. Using the hydrogen boil-off vapors is ideal because hydrogen's specific latent heat of vaporization is nearly twice that of oxygen's, and the change in enthalpy from the boiling point to 220K is nearly ten times higher. Hydrogen is therefore intentionally vented to cool the thermal shielding and eliminate oxygen boil-off. (2) Passive venting of hydrogen for heat shielding is an effective strategy for GLOW reduction and standard practice; however a quantum mechanical characteristic unique to hydrogen molecules can increase the specific vapor cooling load as much as 50 % (1). If functionalized, this characteristic can reduce the required hydrogen boil off by as much as 33%, leading to substantial reductions in GLOW. United Launch Alliance (ULA) has funded this research to design, build, and run experiments in a new test facility designed as a proof of this concept.

Theory
Quantum Mechanics and Hydrogen Spin States

In 1932, physicist Werner Heisenberg was awarded the Nobel Prize "*for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen.*" (4) Quantum mechanics stands as one of the crowning achievements in physics during the 20th century, and has completely changed the understanding of reality.
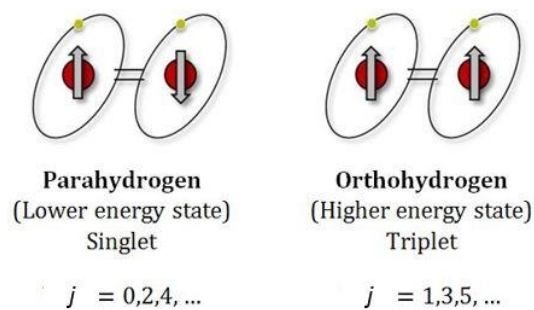
Figure 3: Parahydrogen and Orthohydrogen nuclear spin isomers of the hydrogen molecule. Parahydrogen occupies even rotational energy levels and orthohydrogen occupies odd rotational energy levels.

Quantum mechanics asserts that at the atomic scale particles do not behave the way we might expect by Newtonian mechanics. Instead, events are determined by probability. The implications of this theory have had far reaching effects in both technological progress and our basic understanding of how the world works. Quantum mechanics was developed, in part, to solve one of the leading problems in all of science at the time: The odd behavior of hydrogen's specific heat at cryogenic temperatures.

During experimentation with liquid hydrogen in 1912, German experimentalist Arnold Eucken recorded an odd phenomenon that could not be explained by the physics of the day. While measuring heat capacities of hydrogen at cryogenic temperatures down to the boiling point (~20K), Eucken observed a distinct hysteresis when comparing the curve he measured as the hydrogen was cooling, and the curve created as the hydrogen was warming. For years, many of the world's greatest minds were unable to find an explanation. (5) It wasn't until 1929 when Paul Harteck and Karl Bonhoeffer made the connection between Heisenberg's quantum theory and Eucken's odd data that the existence of two spin isomers of hydrogen was finally discovered. (6)

Hydrogen naturally exists as a diatomic element, with two hydrogen atoms covalently bonded together to form a molecule of hydrogen[I]. Each hydrogen atom has a single proton for a nucleus (neglecting the insignificant fraction of deuterium and tritium) and one electron orbiting it. These protons are not stationary however, and have a "spin" associated with them.[II] When two hydrogen atoms combine to form a hydrogen molecule, they align along the axis of rotation. The direction of the two proton's spins can therefore either line up the same direction or oppose each other. This gives rise to the two spin states of hydrogen; the opposed spin parahydrogen and the aligned spin orthohydrogen. The concentration of the two forms depends greatly on the available energy in the system because there is an energy difference between quantum levels. (6)

Orthohydrogen is a triplet restricted to odd rotational states (j=1,3,5…). This gives rise to three forms of orthohydrogen that are identical in energy, but differ in wave-function. Parahydrogen is a singlet with even rotational states (j=0,2,4…), with only one wave-form. At temperatures above ~200K, enough energy is present such that all four possible wave-functions exist in equilibrium, resulting in a 3:1 orthohydrogen to parahydrogen ratio. The lower energy wave function corresponding to the parahydrogen state (j=0) becomes favored as the temperature of the hydrogen decreases. 99.8% of hydrogen is in the para form at the normal boiling point. (6) There is a temperature dependent equilibrium ratio between the two forms.

This concentration is governed by Boltzmann's distribution law, which states that the fraction of molecules (N_J) of the total number (N_0) in the rotational state J is given by

$$N_j = N_0 P_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)$$

[1]

[I] It should be understood that the word 'hydrogen' refers to diatomic hydrogen; context will indicate when a single atom is meant (i.e. hydrogen atom, monatomic hydrogen etc.).
[II] A proton has a spin of ½ in units of $h/2\pi$, where h is Planck's constant.

Where k_B is Boltsmann's constant, P_J is the statistical weight, and ε_J is the energy of state j. Because the ortho

form consists of all odd rotational states, and para of the even, the ratio between the two forms becomes

$$\frac{N_p}{N_o} = \frac{\sum_{j=even} P_j \exp(-\varepsilon_j/k_B T)}{\sum_{j=odd} P_j \exp(-\varepsilon_j/k_B T)}$$

[2]

If we consider that

$$\varepsilon_J = \frac{j(j+1)h^2}{8\pi^2 I} = j(j+1)\theta_r k_B \qquad \theta_r = \frac{h^2}{8\pi^2 I k_B}$$

[3] ... [4]

$$P_j = \left\{ \begin{array}{ll} 2j+1 & \text{for } j = \text{even} \\ 3(2j+1) & \text{for } j = \text{odd} \end{array} \right\}$$

[5]

then

$$\frac{N_p}{N_o} = \frac{\sum_{j=even}(2j+1)\exp(-j(j+1)\theta_r/T)}{\sum_{j=odd} 3(2j+1)\exp(-j(j+1)\theta_r/T)}$$

[6]

and expanding the sum, we have

$$\frac{N_p}{N_o} = \frac{1 + 5\exp\left(-\frac{6\theta_r}{T}\right) + 9\exp\left(-\frac{20\theta_r}{T}\right) + 13\exp\left(-\frac{42\theta_r}{T}\right) + \cdots}{3(3\exp\left(-\frac{2\theta_r}{T}\right) + 7\exp\left(-\frac{12\theta_r}{T}\right) + 11\exp\left(-\frac{30\theta_r}{\theta_r T}\right) + \cdots}$$

[7]

$$\frac{N_p}{N_o} = \frac{1 - x_{o,eq}}{x_{o,eq}}$$

[8]

For hydrogen, the characteristic rotational temperature is $\theta_r = 84.837[K]$. (6) Using equations [7] and [8], we can calculate the equilibrium concentration of parahydrogen in a hydrogen sample at a given temperature.[III] A plot of the equilibrium composition versus temperature is provided in Figure 4. The plot shows that at temperatures near the boiling point, the equilibrium composition is almost pure parahydrogen, and at elevated temperatures, the composition asymptotically approaches a 3:1 ratio. Because the two hydrogen atoms are tightly bonded together however, the conversion between the ortho and para forms is not free.
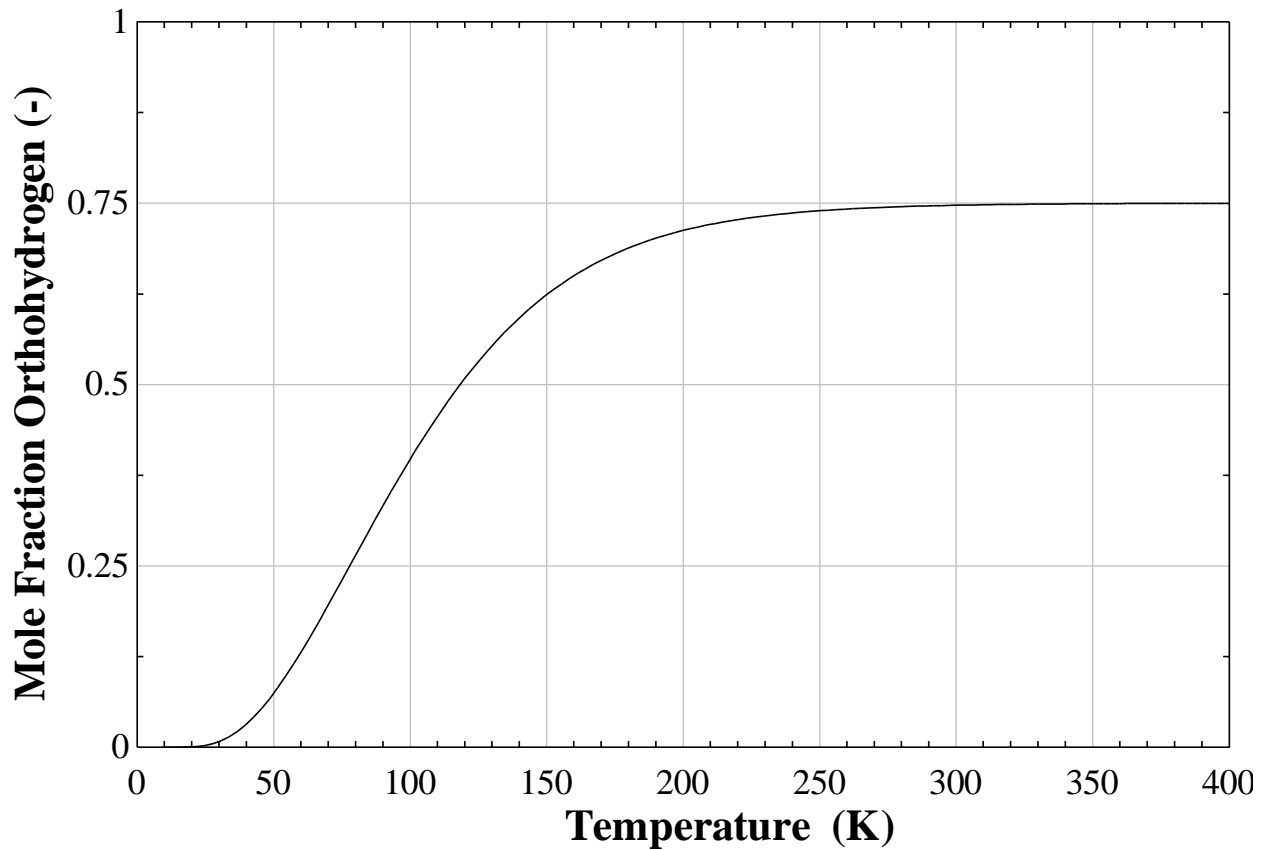

Figure 4: Equilibrium orthohydrogen percent composition plotted versus temperature.

[III] This derivation was paraphrased from *Farkas pg 13-15* (6)

In order for an orthohydrogen molecule to become parahydrogen (or vise versa), the bond between them must be broken and re-formed in the opposite orientation. If there are only other hydrogen molecules to interact with this becomes a very rare event, with half lives[IV] in excess of a year. (6) If the gas interacts with a catalytic material however, conversion between the two states occurs much faster with half lives on the order of minutes to seconds. Complete conversion can occur within a few weeks in aluminum and brass containers and in only seconds for activated catalyst beds. In addition to a catalyst however, an energy source (or sink) is also required else the conversion energy will be extracted from the fluid, lowering the temperature and resulting equilibrium composition.

The difference in energy associated with the different rotational levels means that energy is released when orthohydrogen converts to parahydrogen, and energy is absorbed in the reverse. This phenomenon can be thought of as a latent heat of conversion, in that adding energy to the gas may not result in an increase in sensible heat, but rather be absorbed in the rotational energy of a molecule as it converts from parahydrogen to orthohydrogen. At the dawn of industrial liquid hydrogen production, this presented a major problem.

Liquid hydrogen is often produced from separation from hydrocarbons and then stored in vacuum insulated Dewars. This storage method significantly reduces heat flux from the outside of the container and is the standard for cryogenic liquid storage, however this storage method cannot shield the hydrogen from stored ortho-para conversion energy. When orthohydrogen converts to the para form at the normal boiling point, 525 kJ/kg of heat is released, which is nearly 15% greater than the latent heat of vaporization at the normal boiling point, 476 kJ/kg. The ideal-gas enthalpies and conversion energies of orthohydrogen and parahydrogen are shown in Figure 5. Modern hydrogen liquefying processes now ensure that the liquid hydrogen has reached equilibrium concentration at 99.8% parahydrogen before being transported and stored for use. Though the two spin isomers of hydrogen have been a hindrance to liquid storage in the past,

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[IV] The length of time required for half of a sample to convert from one form to the other.

by making use of the right conditions, the ortho-para characteristic can be used to improve passive cooling
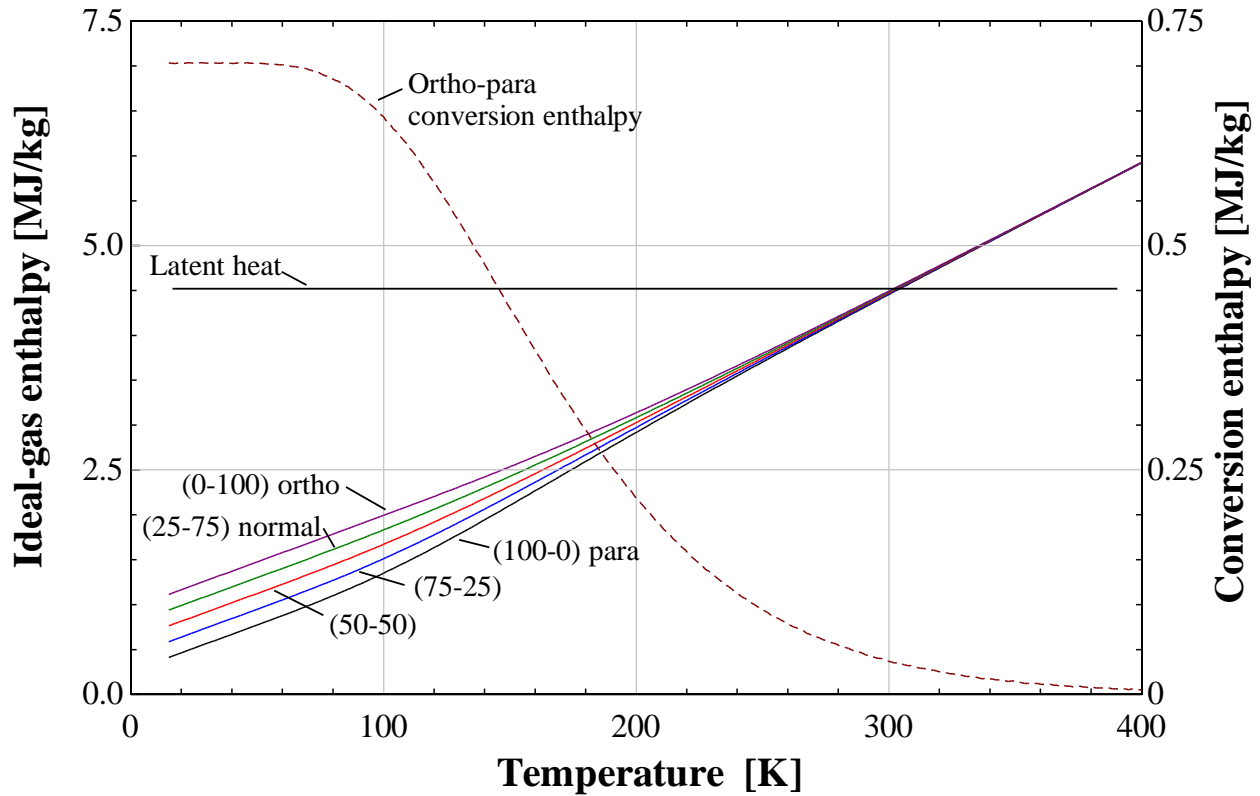
systems.

Figure 5: Variation in ideal gas enthalpy and conversion enthalpy with temperature.

Improved Passive Cooling System Using Catalysts

Liquid hydrogen and liquid oxygen are held in separate thermally insulated tanks in upper stage

rockets. Each tank is maintained at its respective boiling point; about 20K for hydrogen and 90K for oxygen

(depending on pressure). To mitigate the loss of the heavy (and therefore expensive) liquid oxygen, the

hydrogen is intentionally vented through heat exchanger tubes to cool the oxygen tank. This passive cooling

system effectively eliminates oxygen boil off, but requires excess hydrogen fuel. However because only

standard metal materials are used in the heat exchanger vent tubes, the hydrogen being evacuated into

space at 90K is still nearly all in the parahydrogen form. If an active catalyst was introduced, significant

improvement to the current passive cooling systems for rocket LH2/LOx fuel storage is possible by taking advantage of the parahydrogen to orthohydrogen conversion. (3)
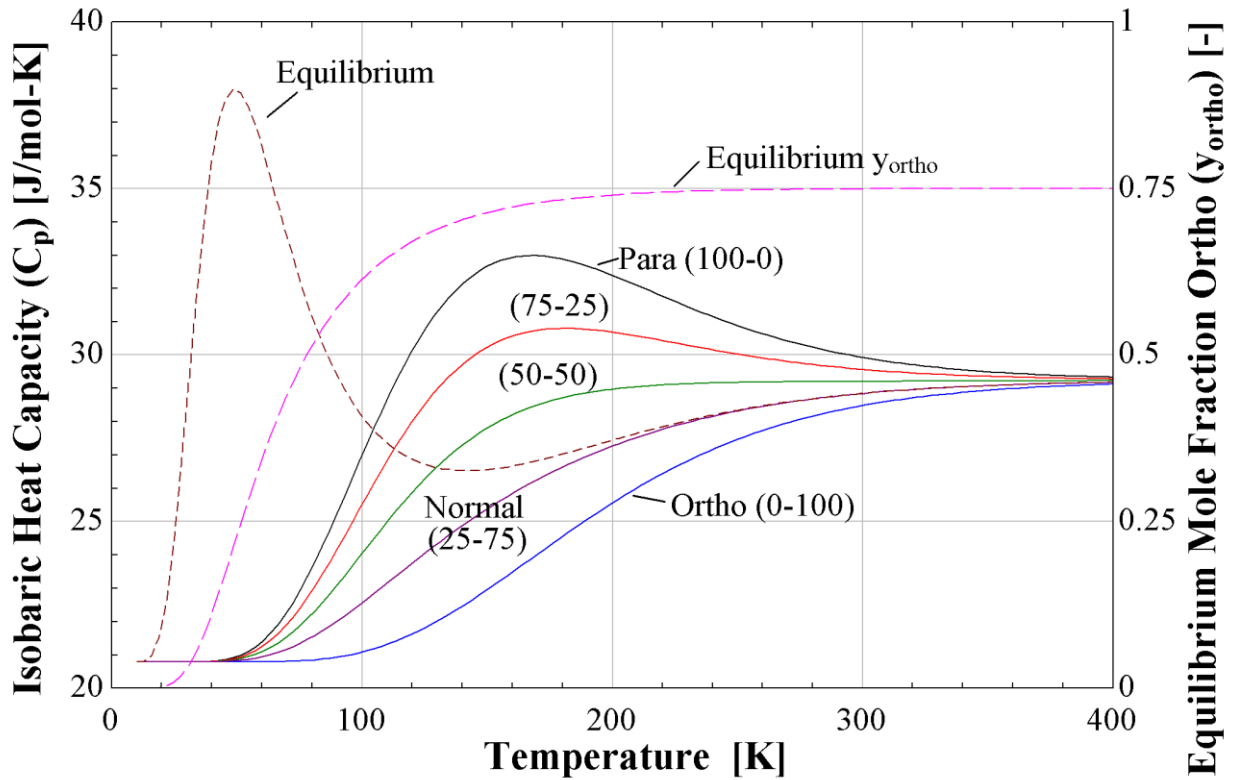
Figure 6: Isobaric Ideal-Gas Heat Capacities plotted versus temperature for various orthohydrogen-parahydrogen compositions. The equilibrium composition and heat capacity curves are also plotted to show the correlation between the change in composition and effective heat capacity.

The heat capacity of a fluid governs the amount of heat capable of being absorbed during transition between temperatures. A plot of isobaric heat capacities for various compositions of hydrogen vs temperature is shown in Figure 6. When The heat capacity follows well defined curves and is unable to convert to follow the equilibrium concentration curve when hydrogen is locked in a particular composition. If the hydrogen is freely and continuously exposed to a perfect catalyst, the hydrogen will continuously convert to equilibrium as temperature increases. This latent heat of conversion can be combined into an effective

heat capacity. By integrating this curve and comparing to the energy absorbed by pure parahydrogen, a theoretical increase of 50% in cooling capacity between 20 and 90 K is possible for passive cooling systems.

Common commercial catalysts are currently available in the form of powdered or gelled paramagnetic ferric oxide intended for packed fixed bed reactors for liquefying hydrogen. Since this is a cheap and effective catalyst, very little research has been done on possible new types of conversion catalysts theorized since the late 1960's. For use in upper stage rocket fuel management systems, advanced catalysts like nano-porous iron oxides and ruthenium surface coatings could vastly improve performance and lifetime of the heat exchanger.

Comparison of Para-Ortho Conversion With Throttling

The concept of increased cooling power using a catalyst is a somewhat abstract idea. For this reason many question why controlled throttling of pressurized hydrogen is not considered as a more feasible alternative. To compare the two cooling methods, a simple thermodynamic model was programmed to calculate the power absorbed by the processes.[v]

In the case of the throttling it is assumed that the hydrogen has been brought to the temperature to be cooled (90K for LOx cooling), and then is throttled from the tank pressure to the vacuum of space. Likewise, in the case of p-o conversion, the energy required for the hydrogen gas to increase in temperature is neglected and only the energy required to convert at the set temperature is considered. Additionally, the equilibrium concentration of hydrogen's allotropes is dependent on this final temperature, limiting the maximum amount of power that can be extracted. In both cases, the change in enthalpy is used to determine the total power required for the process.

The analysis confirmed that ortho-para conversion far outperforms throttling for cooling at 51K and above. In isothermal expansion at 90K, throttling can extract 5.8 kJ/kg. Under the same conditions, para-

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[v] EES code and summary of results presented in the Appendix

ortho conversion can absorb as much as 384.1 kJ/kg. Throttling's poor performance is due largely to the fact that hydrogen has a Joule-Thompson inversion temperature of ~140K (pressure dependent). At any temperature above this point, the cooling effect of throttling will be reverse. Because of this, novel, non-pressure based methods for improving passive cooling systems are needed.

Previous Catalyst Studies and Goals of Experiment

The vast majority of research into the reaction rates of the parahydrogen-orthohydrogen conversion and catalyst activities has been focused on isothermal reactor conditions with various pressures over a range of flow rates. (7) (8) This experimental design is logical for characterizing commercial catalysts intended for use in liquefaction and fundamental studies of the conversion kinetics, and isothermal reactors were easy to create by immersing the catalyst bed in a boiling liquid cryogen, like nitrogen at 77 K. However in a passive cooling heat exchanger, the temperature of the hydrogen will increase from 20K to 90K through the reactor while cooling the liquid oxygen. No experiment has yet been performed to measure catalyst activities, or more importantly, the necessary space velocity[VI] to achieve the desired increase in cooling capacity.

Additionally, there has been very little published research on the performance of newly developed catalysts for ortho-para conversion. Although current commercial interest in them suggests a benefit in performance, a freely available study has yet to be performed. For this reason, the test reactor will be designed to accommodate a variety of exotic catalysts.

[VI] A non-dimensionalized flow rate that is defined as the volume flow rate of gas divided by the volume of the reactor.

Experimental Design

The goals of the experiment require a unique design for the test apparatus. Whereas previous

experiments in catalysis research have used liquid nitrogen to maintain a cryogenic isothermal reactor at 77K,

this experiment requires a range of temperatures and long duration testing to reach steady state. For this

purpose, the Cryo-catalysis Hydrogen Experimental Facility (CHEF) was designed.
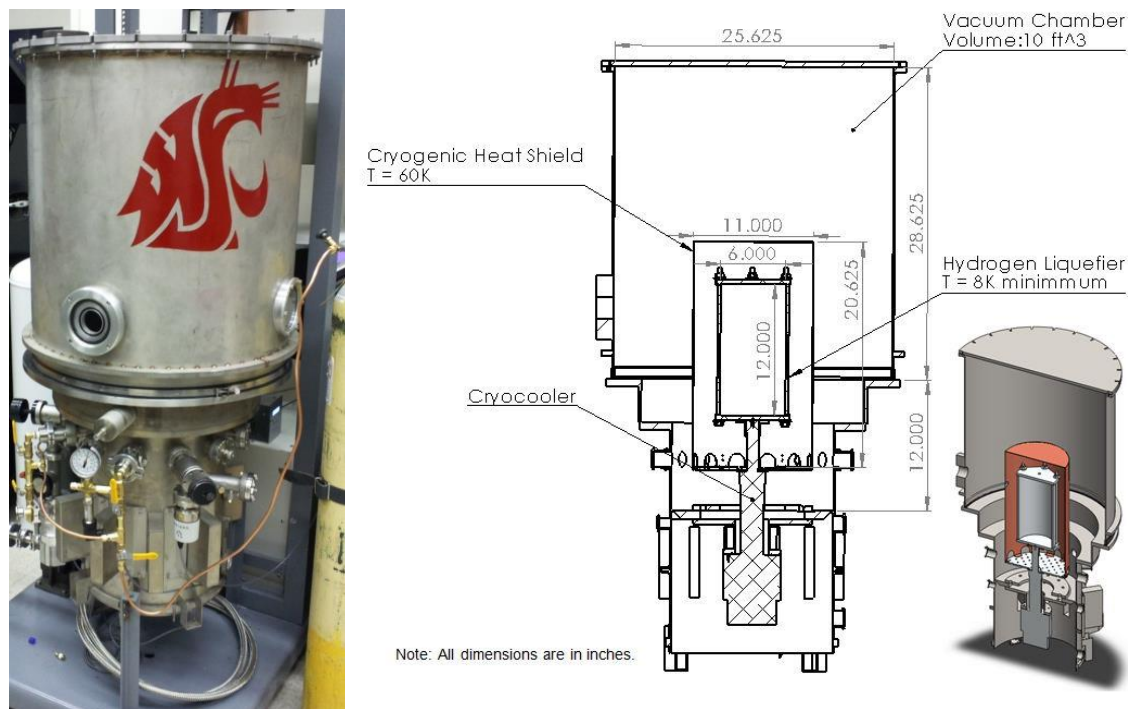
Figure 7: (Left) Image of the Cryocatalysis Hydrogen Experiment Facility (CHEF). (center) Wire-frame drawing with CHEF dimensions. (right) Cross-sectional rendering of CHEF.

Cryocooler

CHEF uses an inverted Gifford-McMahon (GM) cycle Sumitomo CH-204SFF cryo-cooler and HC-4E1

helium compressor to achieve temperatures below the boiling point of hydrogen. With the addition of a

Lakeshore 336 temperature controller, CHEF can operate from 8 to 300 K; a much wider range of

temperatures than previous ortho-para catalyst testing systems.

The system can reach a minimum temperature of 50K on the first stage and thermal shield, and 7.8K on the second stage with high vacuum and thermal radiation insulation. The second stage can absorb 9.0W of power (rated) at 20K, allowing CHEF to liquefy up to 1/8 L of hydrogen per hour.

Vacuum Chamber and Pumps

Isolating the cryostat from the environment with the use of a High Vacuum (HV) system is essential to maintaining cryogenic temperatures with the limited cooling capacity of the cryocooler. The HV system thermally insulates the cryostat with the use of thermal radiation shielding. Without the aid of an insulating vacuum, the necessary temperatures for the experiment would be unattainable with the available cooling power.

A High Vacuum is generally defined as any vacuum lower than 1×10^{-4} Torr[VII]. Below this point is the free molecular flow regime, where the mean free path of the molecules is larger than the container holding them. This means that pressure gradients no longer govern flow, and instead further pumping relies on molecules randomly finding their way to the pump opening. Convection is effectively eliminated as a heat transfer path without bulk fluid motion in the chamber.

Achieving HV requires a series of specialized pumps. CHEF uses two pumps, a roughing pump and a turbomolecular pump. The roughing pump is a Leybold Trivac D-60B rotary vane pump. The D-60B is used first to bring the chamber down to a medium vacuum (1 to 1×10^{-3} Torr), at which point the turbomolecular pump, located in series between the chamber and the roughing pump, takes over. The Varian Turbo-V 81-M turbopump traps molecules that hit the turbine blades spinning at up to 81,000 rpm, pushing them downstream towards the roughing pump. When combined with the cryo-pumping effect of the cryostat, the chamber can reach an ultimate pressure of 2.8×10^{-7} Torr. Pressure is measured using a Varian model FRG-700

[VII] 760 Torr is one atmosphere; space is around 1×10^{-9} Torr.

Inverted Magnetron Pirani Gauge. The FRG-700 is a wide range gauge capable of measurement between 5×10^{-9} to 1000 mbar with accuracy of ±30% of measurement.

The roughing pump is turned on and off via a power switch opening and closing the 3 phase 208V power lines. The turbomolecular pump, vent valve, and vacuum gauge are controlled via the Turbo-V 81-AG rack controller. The turbo can be operated directly through the controller or using the T-Plus software installed on a computer, however pressures must be read on the controller's display.

Hydrogen Flow Management

Hydrogen can react violently with the oxygen in the air from 4–80 % concentrations, so it is therefore important to manage hydrogen in a safe manor and with fuel and oxidizer isolated. For this reason hydrogen in the lab is stored in low pressure reservoirs before it is introduced into the experiment, and all components must pass a helium leak test.

The majority of connections in the system are ¼ brass NPT pipe fittings using ¼ copper tubing and compression fittings for longer expanses. This is the same both outside and inside the cryostat, except copper tubing is joined using metal face-seal VCR fittings brazed on to the ends of the tube. This creates a near perfect seal and is not as sensitive to temperature cycling as the compression fittings.

To begin an experiment on a new catalyst material, hydrogen gas from the reservoir is slowly introduced into the condenser which is being maintained near 20K, filling it to a maximum pressure of 50psig. As the hydrogen liquefies, the pressure in the condenser drops and hydrogen is cryopumped from the reservoir. When the reservoir has been drained to atmospheric pressure, it may be necessary to refill the reservoir and repeat this process until a significant volume (~1.5L) of liquid hydrogen has been condensed.

To ensure that all of the liquid hydrogen has converted to parahydrogen in the condenser, active catalyst contained in a cylindrical mesh container is suspended within the condenser. As the hydrogen vapor
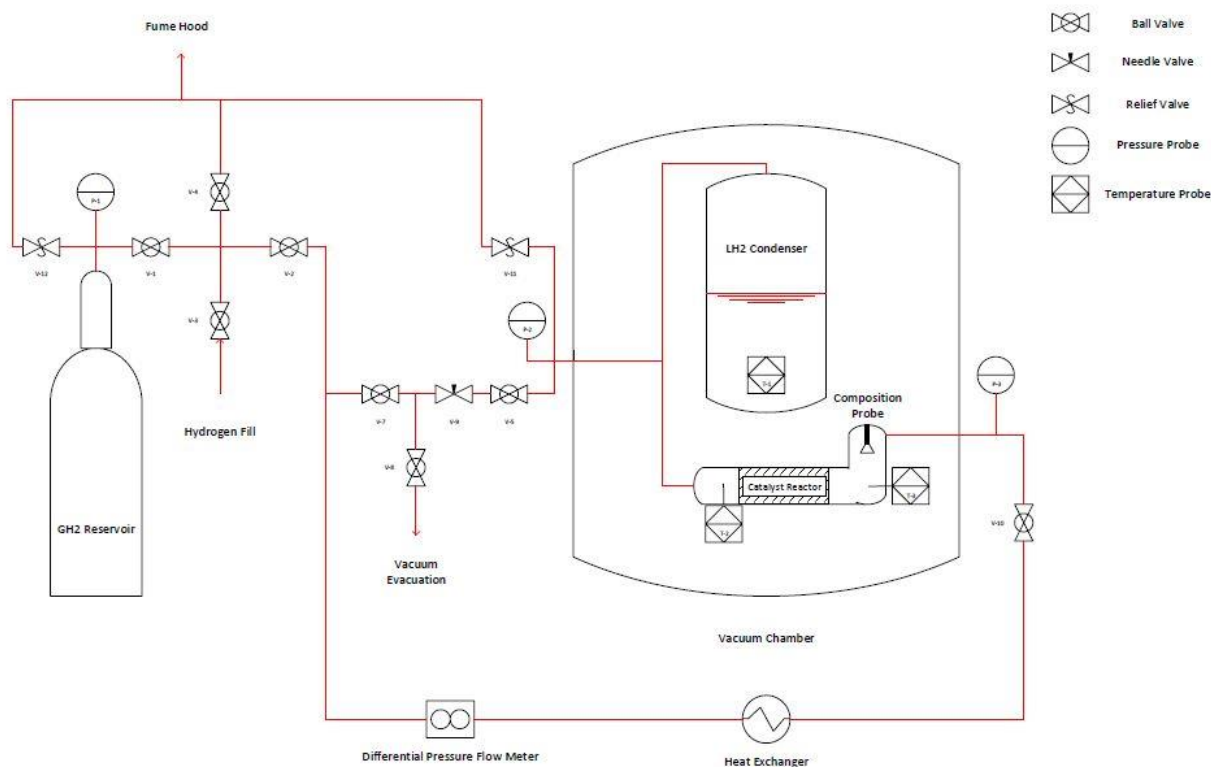
Figure 8: CHEF Piping and Instrument Diagram (P&ID)

cools, the molecules are continuously exposed to the catalyst ensuring that equilibrium concentration is maintained as it is condensed.

Once ready to begin testing, the hydrogen condenser is pressurized by raising the temperature via the condenser heater to increase the vapor pressure of the hydrogen. This pressure is then used to drive hydrogen flow back to the hydrogen reservoir, or out the vent to the laboratory's fume hood through the reactor bed.

The hydrogen passes over a thermal conductivity probe that is used to determine the ortho-para composition at the exit of the reactor bed. The gas then flows through a length of tube to warm the hydrogen from 90K to room temperature before reaching the differential pressure mass flow controller.

Thermal based mass flow controllers would not be suitable for independent mass flow measurement because the thermal properties of the hydrogen are dependent on ortho-para composition. For this reason,

17

the Alicat™ MC-20SLPM was chosen to measure and automatically control gas flow. The Alicat™ flow meter is unique in that it uses small pressure differentials to calculate mass flow rate, allowing measurement independent of composition.

Parahydrogen-Orthohydrogen Conversion Reactor

A unique reactor design was necessary for validating improvements in cooling capacity using para-orthohydrogen conversion catalysts. Basic requirements for the reactor in CHEF include:

- Interchangeable catalysts

- Non-catalytic, insulating walls

- Helium leak-tight construction

- Imbedded heater to create reactor temperature gradient

- In-flow temperature sensors before and after catalyst bed

- Thermal conductivity probe in flow at the reactor exit

To meet these requirements, the reactor chamber was designed and constructed using brass NPT pipe fittings. Brass has been shown in previous experimental systems in literature to be minimally catalytic, and PTFE sealed pipe connections were experimentally verified to be helium leak tight at cryogenic temperatures. Because the pipe fittings can be quickly disassembled and reassembled, the catalyst can be easily changed and sensor repairs can be done relatively simply.

The catalyst chamber itself is a 5 inch section of standard ½ inch pipe with male threads. The downstream end of the packed bed reactor is capped with a 100 mesh screen preventing the catalyst material from escaping, but still allowing flow of hydrogen gas. The other end uses a removable synthetic filter to allow the catalyst material to be changed. At the inlet and outlet of the reactor chamber are platinum RTD's to measure the hydrogen gas temperature. Figure 9 shows an image and conceptual rendering of the reactor bed.
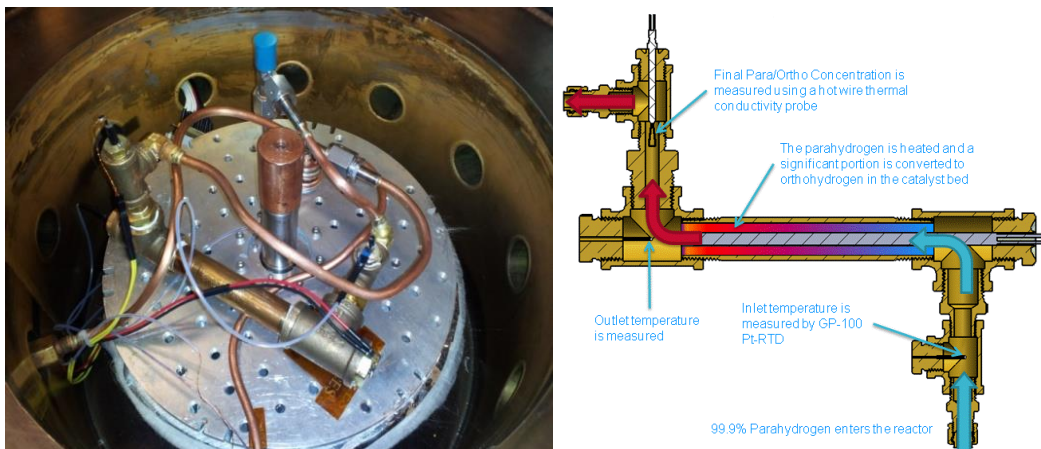
Figure 9: (Left) Image of the catalyst bed in CHEF. (Right) Cross-sectional rendering of the flow through the reactor bed.

Just before the hydrogen leaves the reactor, it passes over the hot wire thermal conductivity probe to measure the composition of the two different allotropes of hydrogen. In previous experiments, it was common to batch-sample the hydrogen gas to analyze the ratio of orthohydrogen to parahydrogen extracted from a continuous process. Thermal conductivity cells (as described by Stewart et. al (7)) make use of the difference in thermal properties between the two allotropic forms. Figure 10 shows the difference in thermal conductivities between normal hydrogen (3:1 ortho to para) and pure parahydrogen. Devices like those used by Stewart and Hutchinson (8) required a sample of gas be taken once steady state in the reactor had been reached. For this experiment, an in-situ, instantaneous method of measuring the hydrogen allotrope composition was desired. To accomplish this, a constant temperature hot wire probe was used.
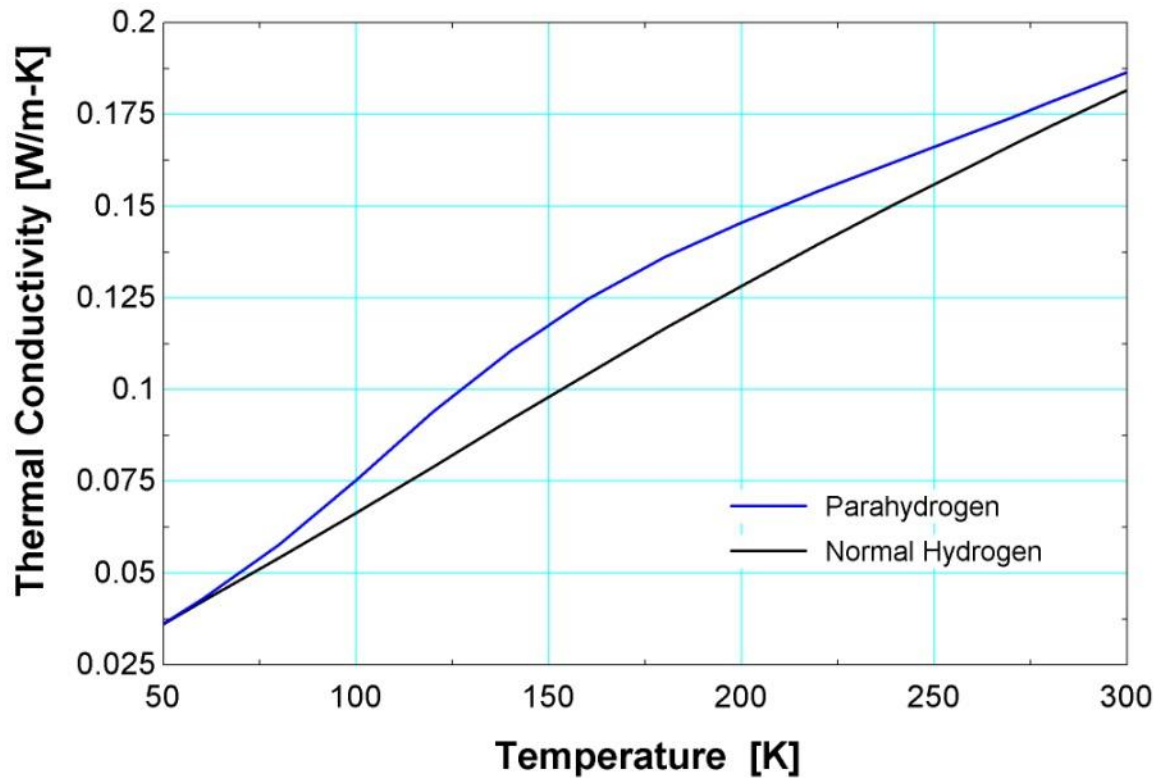
Figure 10: Thermal conductivity as a function of temperature for parahydrogen and normal hydrogen.

The basic principles that allow composition to be measured this way are based on an energy balance between the heating of the wire with convection heat transfer into the hydrogen. The power dissipated in the wire is straight forward and is given by Ohm's law.

$$Q_{total} = \frac{E^2}{R}$$

[9]

An energy balance then relates the power dissipated to heat transfer through convection.

$$Q_{total} = \mathrm{Nu}k\pi L_w(T_w - T_\infty) + Q_{cond} + Q_{rad}$$

[10]

In the energy balance, heat loss from the wire due to conduction through the wire supports and radiation to the surroundings must also be considered. However since they are independent of fluid properties, conduction and radiation losses remain constant regardless of parahydrogen-orthohydrogen concentration. In addition to the thermal conductivity (k) in eqn. [10], the Nusselt number (Nu) is also a very important. For small cylinders with very large length to diameter ratios, it is valid to use Kramer's law, which matches empirical data well over a very wide range of Reynolds numbers (Re). (9)

$$\mathrm{Nu} = 0.42\mathrm{Pr}^{1/5} + 0.57\mathrm{Pr}^{1/3}\mathrm{Re}^{1/2}$$

[11]

Because the Prandtl number (Pr) is also dependent on k and the heat capacity, the Nusselt number must also be considered. If equations [9] and [10] are combined and re-arranged, the variables that are dependent on the composition can be written in terms of the output voltage from the hot-wire circuit.

$$\mathrm{Nu}k = \frac{E^2}{R\pi L_w(T_w - T_\infty)}$$

[12]

Using a software computer algorithm and properties of parahydrogen and normal hydrogen, it can be shown that the product Nu-k is approximately linear with respect to the parahydrogen-orthohydrogen composition. Since composition is proportional to Nu-k, a simple relation between the thermal conductivity probe voltage output and composition can be written that requires only two calibration points at 99.8% parahydrogen (E_p), and normal hydrogen (E_n).

$$x_o = 0.75\frac{E^2 - E_p^2}{(E_n^2 - E_p^2)}$$

[13]

Much like other devices used to measure thermal conductivity of a gas, the sensor implemented in CHEF uses a tungsten filament heated above the ambient gas temperature. In this case however the sensor is placed in the flowing hydrogen gas as it leaves the reactor bed. This presents additional challenges in that the variable flow rate of the gas greatly influences the heat transferred to the hydrogen, and must be compensated for. To account for this, calibration was done at each flow rate of interest for both normal hydrogen and parahydrogen. Although some manufacturers do sell gas composition sensors like the one described, none were available that were designed for cryogenic gases, nor were they programmed to detect the difference between hydrogen's allotropic forms. For these reasons, the decision was made to design a custom hot wire control circuit.

Hot wire circuits for thermal conductivity or flow rate measurement can be either constant temperature or constant current. Constant current hot wires supply a uniform current at all times through the sensor, as the thermal conductivity of the gas drops, the wire heats up and its resistance increases resulting in a measureable voltage increase across the sensor. The advantage to this design is the simplicity of the control and measurement circuit. However, because the temperature of the wire changes with variations in flow rate and thermal properties, calibration and determination of the composition becomes overly complex. Constant temperature sensors instead maintain a constant wire resistance (and therefore temperature) using a Wheatstone bridge and a feedback loop. The voltage across the bridge necessary to maintain the wire temperature can then be measured and related to the composition. Because the wire is maintained at a constant temperature, the calibration of the sensor and the composition measurement are straight forward. It was decided that the extra effort be spent designing the more complicated constant temperature hot wire circuit to simplify calculations during experimental runs.

The hot wire control circuit can be broken down into three main components: The Wheatstone bridge, the differential amplifier, and the current amplifier. A Wheatstone bridge is a common circuit in measurement systems used to convert a change in resistance to a voltage. Figure 10 shows the layout of a
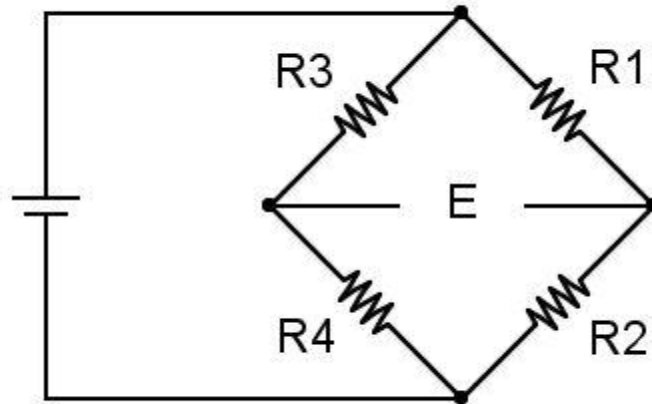
Figure 11: Diagram of a Wheatstone bridge.

Wheatstone bridge. When the resistor values of the bridge satisfy $\frac{R_1}{R_2} = \frac{R_3}{R_4}$ then the potential between the

two legs $E = 0$, however when one of the resistors changes, the change can be correlated to a change in the

potential E. In the case of the constant temperature circuit, R_4 is the tungsten filament located in the fluid

flow, and the bridge is used to detect when the hot wire's temperature deviates from the temperature set

using a potentiometer for R_2. This potential however is a differential voltage with a DC offset from ground,

and cannot be used directly by a current amplifier.

To combine the two voltages into a single potential relative to ground, an instrumentation amplifier

is used. Although instrumentation amplifiers do come in monolithic packages, because LM324 quad amplifier

chips were on hand, a custom instrumentation amplifier was assembled. The output of this circuit is then

delivered to the current amplifier.

Although the instrumentation amplifier has enough gain to step the potential to the necessary

voltage for the Wheatstone bridge, the amplifiers in the LM324 cannot supply the current necessary to

maintain the temperature of the wire. For this purpose a TCA0372 duel amplifier chip capable of supplying up

to one amp of current at 12 volts is used to supply the Wheatstone bridge and power the hot wire.

When the tungsten filament's resistance drops below the set point (temperature too low), the circuit acts by increasing the voltage across the bridge, increasing the heat output of the wire. As the wire heats up above the set point, the circuit compensates by reducing the voltage. This results in a steady equilibrium voltage output that is dependent on the power dissipated into the fluid and can be measured using the NI DAQ. Because the flow rate is determined independently, the voltage can be directly correlated to the composition of the hydrogen.
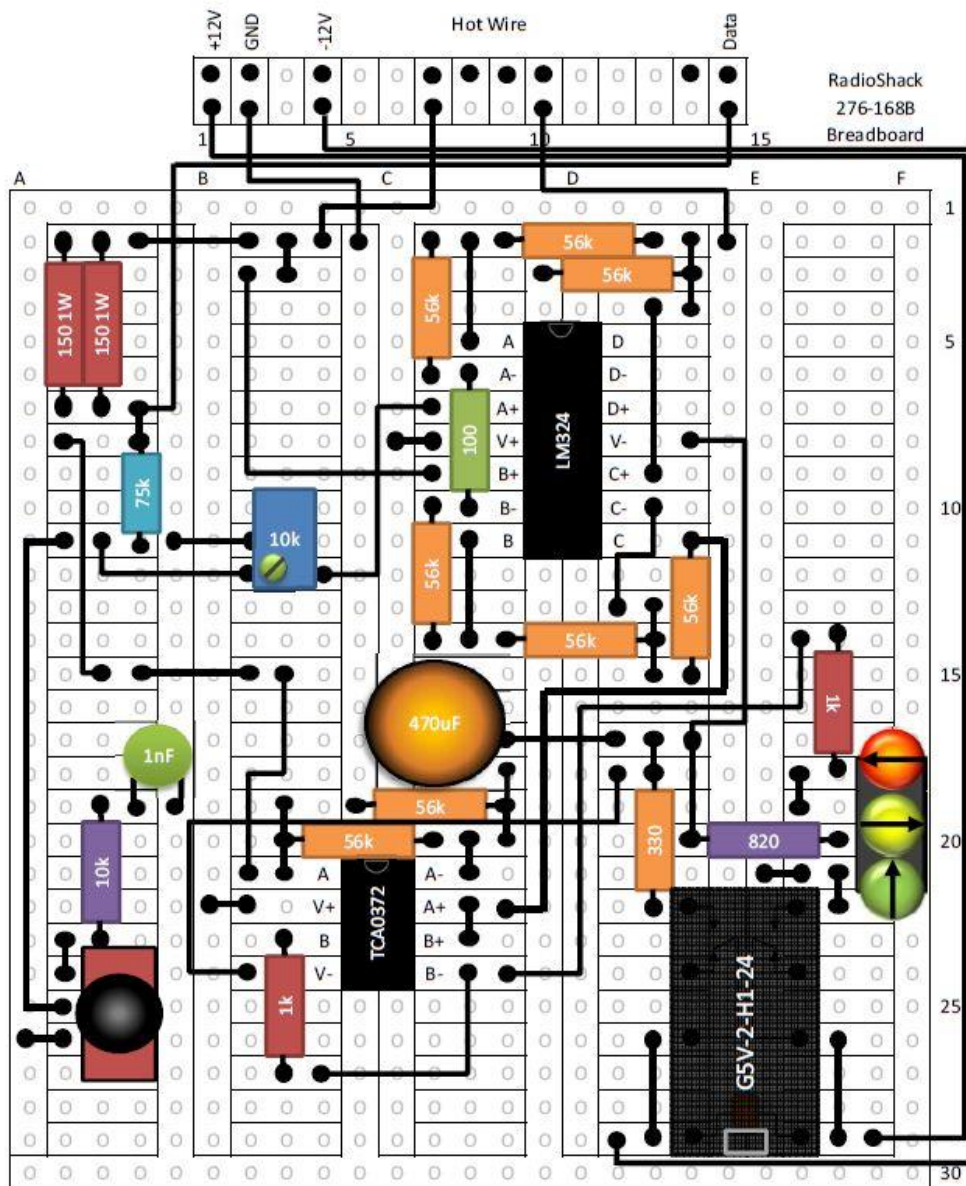

Figure 12: Detailed circuit board schematic for the control and measurement circuit.

Electrical and Measurement System

The ability to accurately control the temperatures within the system is the major attribute that separates CHEF from previous catalyst experiments. To accomplish this, CHEF uses a LakeShore 336 Temperature Controller. The LakeShore Controller can monitor up to four temperature sensors as well as control two heater outputs. Three different temperature sensor types are used in CHEF: two platinum RTD's, one silicon diode, and one Cernox™ sensor.

Platinum Resistance Temperature Detectors (RTD) utilize changes in a metal's electrical resistance with temperature. Platinum RTD's remain sensitive over a wide range of temperatures (20K to 1235K) and follow a standard curve. Additionally, platinum RTD's are available in very small sensor packages, reducing error from self-heating, thermal response time, and increasing sensitivity. This combination of attributes makes Platinum RTD's ideal for measuring temperatures within the catalyst reactor. Two GP-100 Platinum RTD's from Cryogenic Control Systems inc. are connected to inputs C and D on the temperature controller to measure the temperature of the hydrogen gas at the inlet and outlet (respectively). Silicon Diodes are often considered to be the best choice for general cryogenic measurement. Between 30 and 100K, they have a calibrated tolerance of ±0.2K. Silicon Diodes are also sensitive over a wide range, but unlike Platinum RTD's, are available in packages that are easily mounted to surfaces in a vacuum. For this reason, a silicon diode temperature sensor from Cryogenic Control Systems Inc. was chosen for monitoring the thermal shield temperature. Cernox™ temperature sensors are thin film resistance sensors that are highly sensitive at very low temperatures making Cernox™ temperature sensors ideal for monitoring the lowest temperatures in the system, which occur in the hydrogen condenser attached to the second stage of the cryo-cooler. The Cernox™ sensor in CHEF is mounted at the bottom of the hydrogen condenser on the flange connecting the condenser to the cold head of the cryocooler. Figure 12 shows the location of each sensor in the experiment. Because there are no temperature settings on the cryocooler itself, heaters are used to maintain temperature. A PID loop using temperature sensor inputs at specific locations allow the LakeShore 336 to maintain precise control over two key temperatures within the system. The first heater is mounted at the

base of the hydrogen condenser. This heater is used to precisely control the temperature and vapor pressure within the condenser. This is necessary to prevent the system from dropping below atmospheric pressure, and maintain enough positive pressure to drive flow through the reactor. The heater was selected to provide up to 10W of power at the maximum compliance voltage (50V) of the controller.
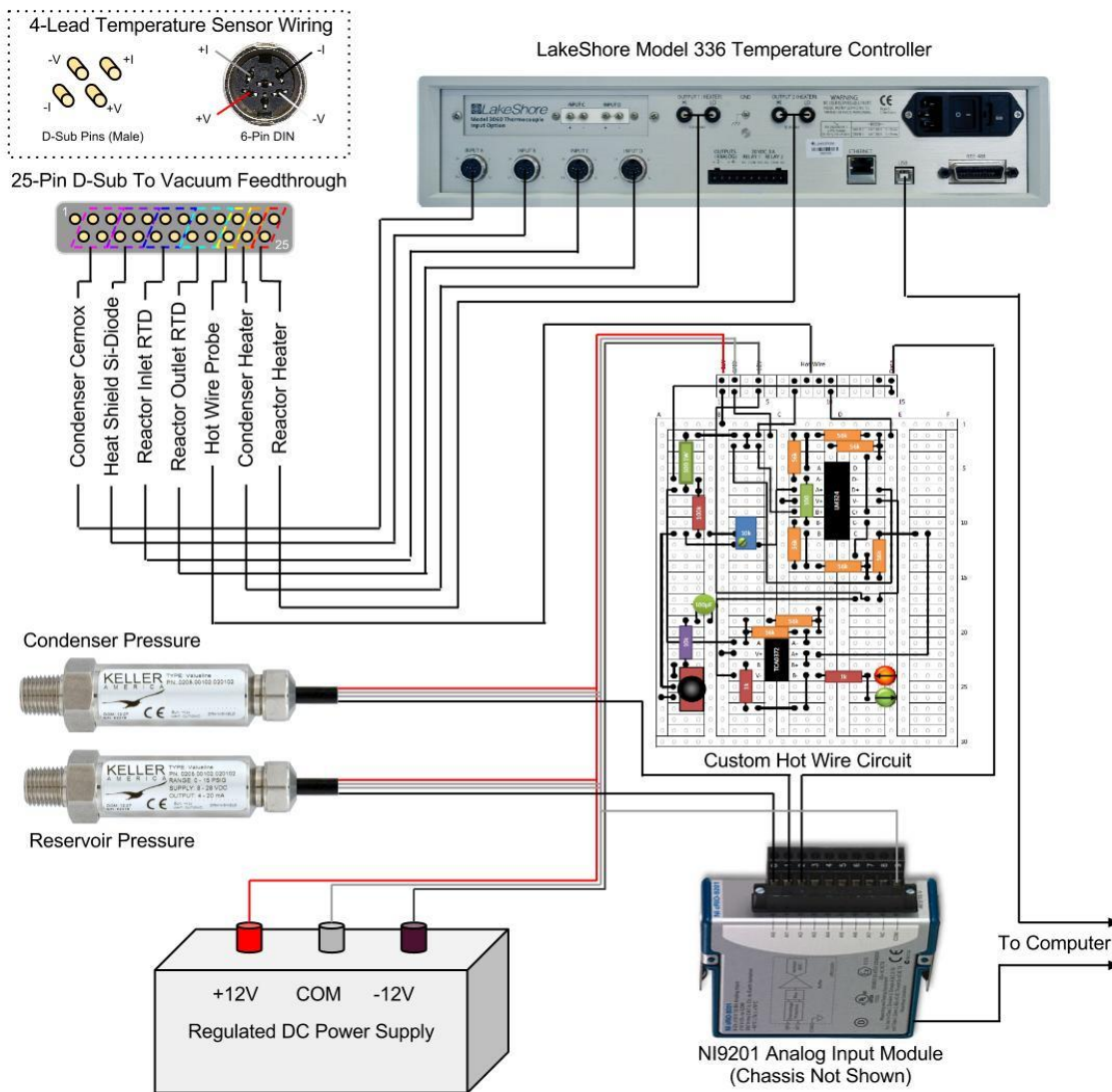
Figure 13: Wiring schematic for CHEFs measurement and control systems.

The heater imbedded within the reactor can provide a maximum of 27.5W. The power to the heater is regulated to maintain a constant outlet temperature. The control circuit is limited by the same 50V compliance voltage as the first heater.

As with many modern experiments, a large majority of the measurements are based on electrical signals and computer data acquisition. To gather the data, CHEF uses a National Instruments Modular DAQ (NI-cDAQ-9172 Chassis) with a NI-9201 analog input module. A custom LabVIEW Virtual Instrument was programmed to track, and log the data, as well as control many subsystems. The front panel for the program is shown in figure 14.
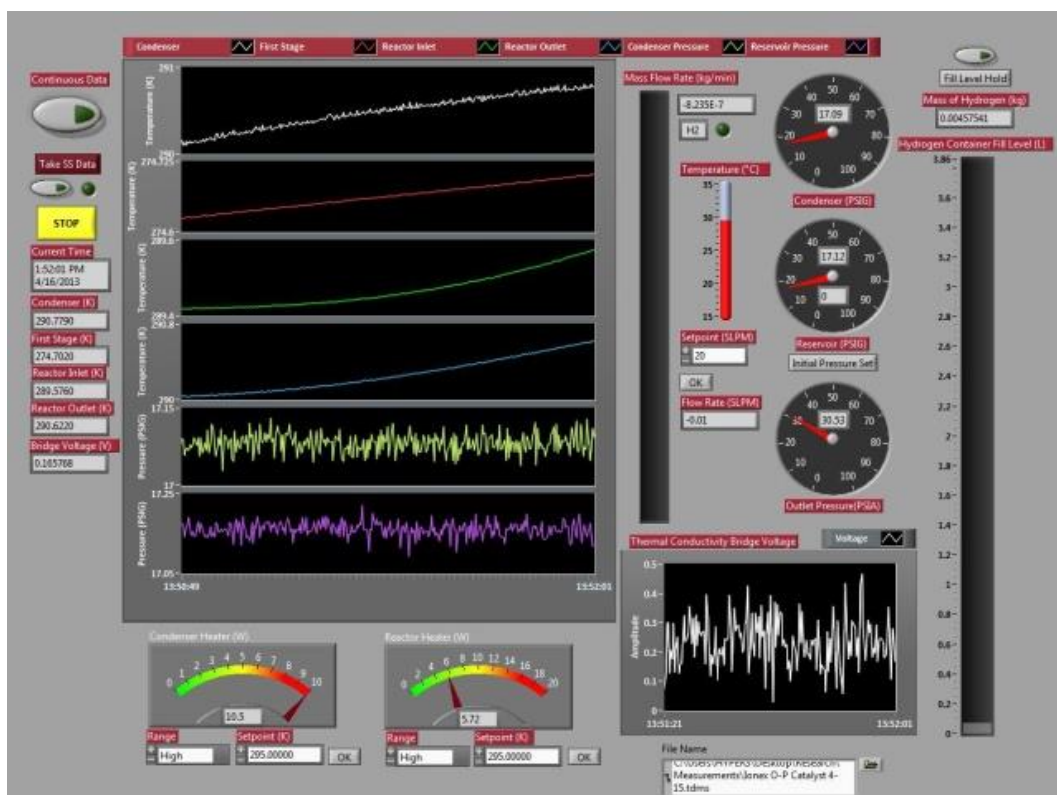
Figure 14: CHEFs LabVIEW VI front panel

Ionex™ O-P Catalyst

 To benchmark CHEF and validate its measurement capabilities, commercial grade Ionex™ orthohydrogen-parahydrogen conversion catalyst was selected for the experiment. Ionex™ catalyst was developed for use specifically in hydrogen liquefaction processes to ensure that the liquid is delivered to the customer as pure parahydrogen to eliminate self-heating due to natural conversion. The catalyst is a 30-50 mesh paramagnetic hydrous ferric oxide (Fe_2O_3) powder. Although many different catalysts have been developed, Ionex™ was chosen because it is readily available, safe to handle, and cost effective. Figure 15 shows the catalyst compared with aluminum powder. The aluminum powder does not catalyze the reaction and so can be used for direct comparison to a system without conversion, as well as calibration runs for the hot wire composition probe.

Figure 15: (Left) Ionex™ O-P catalyst compared with (Right) non-catalytic aluminum powder.

Experimental Method
Safely Working with Hydrogen

Before any experiment with hydrogen is designed or built, it is essential that safety is made the number one priority. Because of hydrogen's wide flammability range, small leaks of hydrogen out, or air into the experiment could be extremely dangerous. To mitigate the risk, several safety systems are installed and procedures are carefully followed to ensure the safety of researchers working with CHEF.

CHEF is protected from overpressure via two safety relief valves, one for the reservoir and another for the condenser. If a pressure above 200 psig is reached, the valves will vent the hydrogen into the fume hood. Additionally, due to the large volume of the reservoir, high pressure hydrogen in the condenser can be internally vented and the pressure relieved without bleeding in to the fume hood. All vented hydrogen exits through non-conductive plastic tubing to prevent sparking and ignition at the exit of the vent tube. Before hydrogen is ever introduced to the system, all fittings are leak checked.

Using a helium leak detector, NPT, compression and VCR fittings are tested for potential leaks. Because monatomic helium is smaller than diatomic hydrogen, any connection that does not allow helium through will also be hydrogen leak tight. The system is tested by pressurizing to 25-50 psig with helium, using a sniffing probe to detect any leaks. If any component fails, the system is depressurized and the fitting is fixed. Once the CHEF is verified leak free, the system can be purged for testing.

By purging the system with inert gas, the chance of a combustible mixture forming within the system is significantly reduced. Nitrogen is the preferred gas for this task because it is inert and much cheaper than helium. Purging and evacuating the system twice is sufficient to ensure that no oxygen remains in CHEF's hydrogen system.

Finally, the system is continuously monitored to ensure everything is operating normally. All data logging and controls in the LabVIEW VI are available via remote desktop connection, allowing researchers to

monitor the system from anywhere, or receive alerts when drastic changes occur. This is especially important for cool-down, fill, and warm-up operations, which can take more than a day to complete.

Cool-Down

To prepare CHEF for hydrogen liquefaction, the system must be brought down to temperature. But before starting the cryocooler, an insulating vacuum must be pulled within the chamber.

With all external ports closed and the lid down, the large rotary vane pump is started and a rough vacuum is pulled. The exhaust is plumbed in to the fume hood to prevent oil vapors from building up in the laboratory. Once a pressure below 10 Torr is reached, it is safe to start the turbomolecular pump.

Once a vacuum below 10^{-4} Torr has been reached, the cryocooler can be started. Before turning on the compressor however, the liquid cooling system should running and supply water entering the compressor must be below 75°F. With the cooler running, the vacuum pressure will drop even further due to the addition of cryopumping to an ultimate chamber pressure of 2.2×10^{-7} Torr. With full heat shield and condenser mounted on the second stage, the system takes roughly 12 hours to reach a minimum temperature of about 11.5K.

Filling Procedure

After the system has reached the operating temperature, hydrogen is slowly introduced to the condenser through a needle valve. As the hydrogen from the gaseous reservoir enters the condenser, it cools and liquefies, reducing the pressure within the system and drawing more hydrogen from the reservoir. In this way, hydrogen can be cryopumped from the reservoir effectively until a large enough volume of liquid hydrogen to perform an experimental run is reached.

It has been determined that in order to properly pre-cool a reactor of this size and allow the system enough time to reach steady state at each different flow rate, A volume of about 2 liters (~0.15kg) is

necessary to complete a data set without refilling. Reaching this volume takes about a 12 hours, requiring the reservoir to be refilled as needed.

To ensure all liquid hydrogen converts fully to the para form, the hanging cylindrical catalyst dipper shown in Figure 16 below is suspended within the condenser. Because the hydrogen is not agitated however an incubation period is required to ensure that complete conversion can occur. After filling is finished, 24 hours is given for the hydrogen to completely convert before experimental runs are performed.

Figure 16: Image of the suspended catalyst dipper probe to ensure complete conversion to parahydrogen in the condenser.

Reactor Precooling

Before any data can be collected in an experimental run, the reactor and vapor lines must reach steady-state experimental conditions. Because the reactor is suspended and not thermally mounted to the second stage, the system cool down and liquefaction only bring the reactor temperatures down to about 170K. For this reason it is necessary to run hydrogen through the reactor to pre-cool it to operating temperatures.

Hydrogen that passes through the reactor can either be directed back in to the gaseous reservoir, or out through the vent. In order to drive the hydrogen into the reservoir a continuously increasing overpressure in the condenser must be maintained, and because thermal conductivity measurements are sensitive to large changes in pressure, this is not an ideal operating condition for experimental runs. Hydrogen can only be captured during reactor precooling to prevent unnecessary venting, keeping in mind that the system pressure should not exceed 100 psi.

The process is started by increasing the set-temperature of the condenser to increase the vapor pressure to that above the pressure currently in the reservoir. Opening the valves back to the reservoir through the reactor and entering a set point of 20 SLPM on the mass flow controller should then begin the flow of cold hydrogen vapor. It is left to the researcher's judgment on whether to continue filling the reservoir or to send the hydrogen to the fume hood to the vent. Once the reactor outlet temperature reaches 90K, the reactor heater PID controls should be turned on and the system allowed to stabilize. CHEF should now be ready to begin running experiments.

Experimental Procedure

Beginning with the lowest flow rate (2.5 SLPM), change the flow rate set point in LabVIEW and adjust the condenser temperature set point such that a constant pressure between 5 and 7 psig is maintained. With hydrogen flowing, it is safe to connect the thermal conductivity probe to the control board. A steady green and amber light indicate the circuit is measuring (if only the green comes on, press the reset button or disconnect and reconnect the BNC cable). Continuous data may be taken but steady state should be observed before taking single averaged data.

Reaching full steady state requires about 30 minutes at each flow rate due to the thermal mass within the reactor and researchers should wait until reactor power is steady and no fluctuations or large period oscillations are observed in temperatures. Then a 100-data-point averaged steady state point can be recorded using the LabVIEW VI and the researcher can move to the next flow rate.

This procedure is repeated for each flow rate until all desired points are measured. The averaged data points record nearly all system parameters (excluding liquid volume) and allow for post experimental analysis of catalyst activity and heat required for conversion.

Shutdown and Warm-up

Before the cryocooler can be safely shut down, all hydrogen within the condenser should be vented. To drive the hydrogen out, the condenser set temperature can be set above its boiling point and hydrogen vented either to atmosphere or to the reservoir. A sharp change in condenser temperature indicates that all the liquid hydrogen has evaporated. If the hydrogen was being vented to atmosphere, the vent valve should be closed and the reservoir valve opened to allow the hydrogen warming in the condenser to expand slowly into the larger reservoir volume.

After shutting down the cryocooler, the heaters can be used to bring the system back to room temperature faster. The vacuum system must remain running until the lowest temperature in the system is above 273K (freezing point of water) to prevent condensation from forming.

With the system back up to room temperature, the vacuum system can be shut down and atmosphere slowly reintroduced to the chamber. Once the CHEF is back to atmospheric pressure, the upper chamber can be lifted to access the condenser and reactor to prepare for the next experiment.

Activating the Catalyst

Ionex™ O-P catalyst is an Iron(III) Oxide powder that requires activation to remove contaminants from catalyst sites that reduce effectiveness. The catalyst can become deactivated from prolonged exposure to moisture in the air.

When the catalyst is purchased from Sigma-Aldrich, it is delivered with an unknown level of contamination and must be activated to ensure consistent performance. The catalyst can be activated by

heating and flowing dry nitrogen over the catalyst. Results from Essler (11) provided an effective procedure for activating the catalyst within the reactor.

Using the imbedded heater, the catalyst was heated to 353K and nitrogen was slowly bled through the reactor with a mean pressure of 0.01 to 0.05 MPa for 16 hours. Because the catalyst can be activated within the reactor, it is not exposed to atmosphere before experimental runs and can be tested with minimum contamination.

Results and Raw Data

Calibration

Although the heat transfer from the reactor and the thermal conductivity probe can be estimated using some simplifying assumptions, it is more effective to use calibration points of pure parahydrogen and normal hydrogen.

Without the catalyst dipper in the condenser, the hydrogen converts at a very slow and consistent rate. By liquefying and immediately running an experiment using non-catalytic aluminum particles, a calibration curve for a known composition of hydrogen can be created. Results for a 27.8 % parahydrogen mixture (near normal composition) are provided in Table 1.

Mass Flow Rate (kg/min)	Condenser Temperature (K)	Inlet Temperature (K)	Outlet Temperature (K)	Reactor Power (W)	Reactor Pressure (psig)	Bridge Voltage (V)
±0.000001	±0.1	±0.25	±0.25	±0.125	±0.1	±0.01
0.000206	21.9	52.8	90.0	2.7	7.3	7.07
0.000412	22.2	44.6	89.9	3.5	6.8	7.49
0.000618	22.6	35.4	89.9	4.9	6.5	7.78
0.000824	22.9	29.7	89.9	7.2	6.4	8.02
0.001029	22.8	26.8	89.8	9.6	6.1	8.23
0.001235	22.7	25.2	89.8	11.8	5.4	8.40

Table 1: 27.8% Parahydrogen calibration data

After replacing the catalyst dipper back in to the condenser, the hydrogen fully converts to parahydrogen form. Again running the experiment with the non-catalytic aluminum, a calibration curve for 99.9% parahydrogen is created. Additionally, the data for reactor heater power required to heat the parahydrogen is the metric of comparison that can be used to justify the inclusion of para-ortho catalyst in upper stage rocket fuel systems. 99.8 % parahydrogen calibration data is shown in Table 2.

Mass Flow Rate (kg/min)	Condenser Temperature (K)	Inlet Temperature (K)	Outlet Temperature (K)	Reactor Power (W)	Reactor Pressure (psig)	Bridge Voltage (V)
±0.000001	±0.1	±0.25	±0.25	±0.125	±0.1	±0.01
0.000206	21.7	55.7	90.0	1.8	5.9	7.43
0.000412	22.1	39.6	90.0	4.1	5.9	7.88
0.000618	22.3	30.6	90.0	6.5	5.1	8.19
0.000824	22.7	26.7	90.0	8.9	6.1	8.47

Table 2: 99.8% Parahydrogen calibration data

Arbitrary composition measurements at given mass flow rates can now be completed using the parahydrogen and normal hydrogen bridge voltages as interpolation points.

Non-Activated Catalyst

Before the catalyst was activated, it was decided that a test with the Ionex™ O-P catalyst straight from the manufacturer would be a useful measurement of the importance of activation. The test would also verify that the composition measurement probe and heater measurements were sensitive to small changes in composition and conversion rates such that useful data could be collected.

Two tests were run. One test with the catalyst as it had been sitting in storage for the past 18 months without any form of activation. Without changing anything in the system, two weeks later the same test was repeated. Because the catalyst had been sitting under vacuum for greater than one week however, very slight activation was expected.

The data confirmed that although non-activated catalyst was used, at low flow rates a significant portion of the hydrogen was converting from the para to ortho form. During the experiment, as the flow rate was modified between data points, the composition could be seen lagging as the conversion rate changed between the two space velocities, a phenomena not seen with non-catalytic aluminum particles. Additionally, the second run clearly showed a slight improvement with a low level of activation, indicating that a direct comparison between similar performing catalysts could be possible. The data for both runs can be seen in Table 3.

April 15th, 2013						
Mass Flow Rate (kg/min)	Condenser Temperature (K)	Inlet Temperature (K)	Outlet Temperature (K)	Reactor Power (W)	Reactor Pressure (psig)	Bridge Voltage (V)
±0.000001	±0.1	±0.25	±0.25	±0.125	±0.1	±0.01
0.001029	22.9	25.1	88.5	11.6	6.7	8.64
0.001235	22.6	23.4	88.5	13.7	4.8	8.82
0.000206	21.8	55.5	90.2	2.4	7.4	7.30
0.000412	22.3	41.0	89.5	4.9	7.7	7.81
0.000618	22.7	32.3	89.2	6.8	7.7	8.16
0.000823	23.0	28.0	88.8	9.1	7.6	8.43
April 28th, 2013 (slight activation)						
Mass Flow Rate (kg/min)	Condenser Temperature (K)	Inlet Temperature (K)	Outlet Temperature (K)	Reactor Power (W)	Reactor Pressure (psig)	Bridge Voltage (V)
±0.000001	±0.1	±0.25	±0.25	±0.125	±0.1	±0.01
0.000206	21.5	55.1	90.0	2.3	6.0	7.26
0.000412	21.9	38.8	90.0	4.9	5.8	7.74
0.000618	22.4	29.4	90.0	7.4	6.1	8.08
0.000823	22.6	25.6	90.0	9.8	6.3	8.36
0.001029	22.5	23.6	89.7	12.2	4.8	8.56
0.001235	22.6	22.6	88.5	14.6	5.9	8.80

Table 3: Non-activated catalyst data

Activated Catalyst

To conclude the experiments, a test with activated Ionex™ catalyst was completed. The measurements in Table 4 clearly show significant improvement in conversion rate over the non-activated catalyst. Not only was the low flow rate closer to equilibrium concentration, but more complete conversion was measured at higher flow rates. The reactor power measurements also clearly indicated that this conversion resulted in significant increases in cooling capacity. Data shown in table 4.

Mass Flow Rate (kg/min)	Condenser Temperature (K)	Inlet Temperature (K)	Outlet Temperature (K)	Reactor Power (W)	Reactor Pressure (psig)	Bridge Voltage (V)
±0.000001	±0.1	±0.25	±0.25	±0.125	±0.1	±0.01
0.000206	21.8	54.7	90.0	2.5	7.3	7.23
0.000412	22.2	38.4	90.0	5.6	7.5	7.70
0.000618	22.6	29.5	89.9	8.7	7.5	8.02
0.000824	23	25.8	89.9	11.7	7.4	8.27
0.001029	22.9	23.9	89.8	14.7	5.6	8.47

Table 4: Activated catalyst data

Error and Uncertainty

For each measurement, all bias uncertainty in the chain from the instrument to data logging was accounted for. Each of these errors is then carried through using the uncertainty analysis functionality in EES and is presented in the tables and in error bars on plotted results.

Random error is eliminated by averaging a total of one hundred steady state measurements for each data point. Because random error for the noise in the custom hot wire circuit could not be easily determined, an arbitrarily large number of averaged points was chosen to ensure it could be safely neglected.

Analysis and Conclusions

Effect of Space Velocity

The amount of time the hydrogen interacts with the catalyst can be described by a quantity called space velocity. It is effectively the inverse of the total time a unit volume of hydrogen spends in the reactor and is given by the ratio of the volume flow rate of the gas to the total volume of the reactor and has units of one over time. Because the density of the hydrogen changes from one end of the reactor to the other, an average density is used to determine the volumetric flow rate.
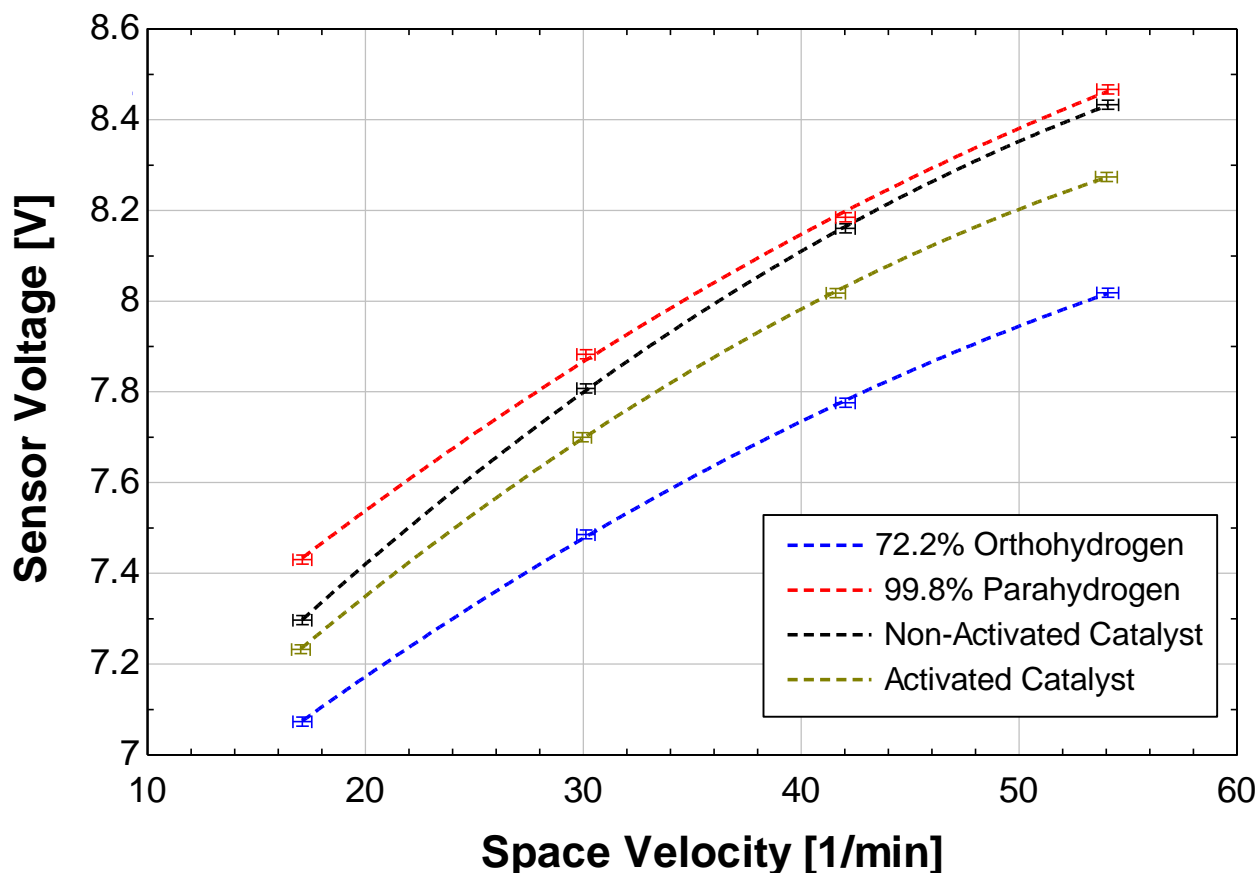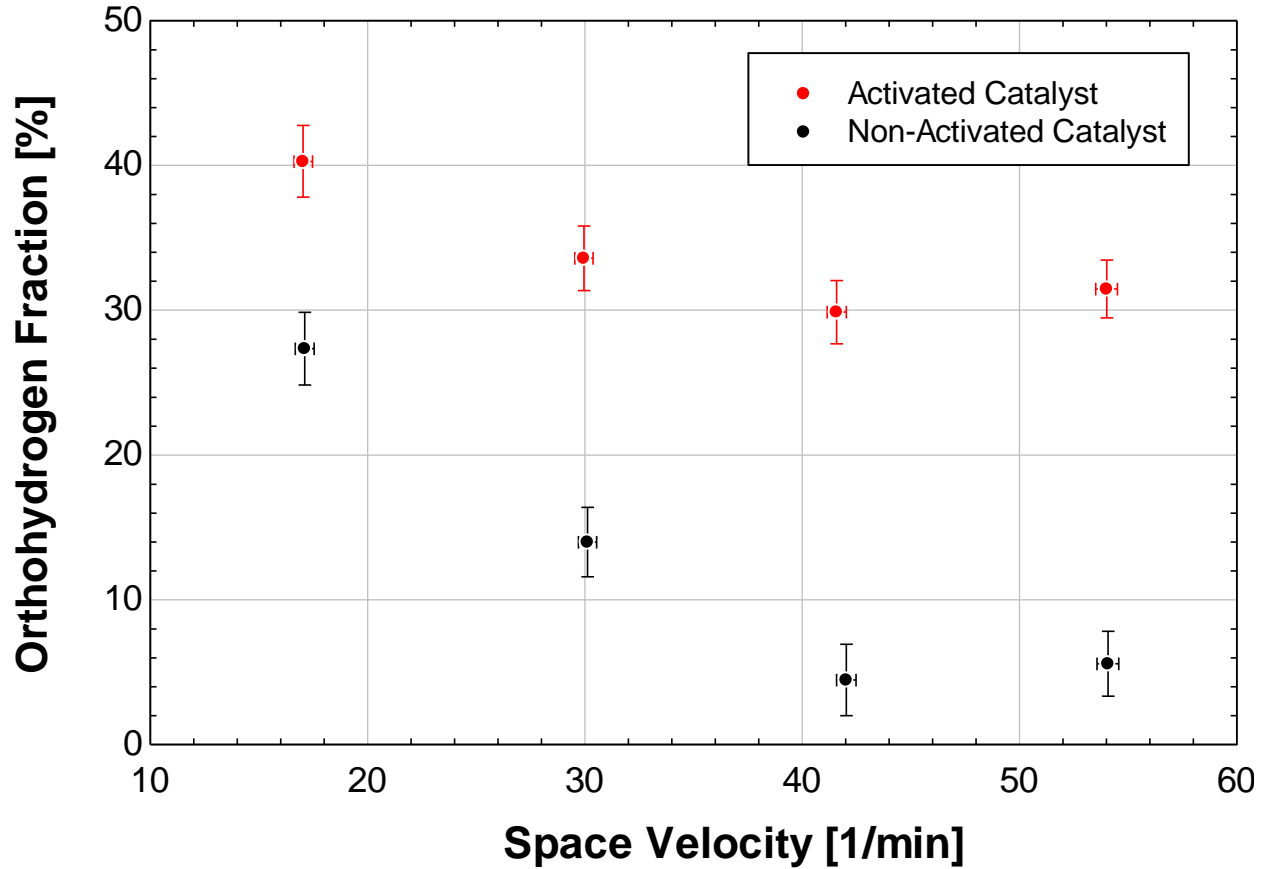

Figure 17: Sensor response vs. space velocity. Calibration curves are shown bounding the data with activated and non-activated catalyst in the middle. Lower points indicate more complete conversion.

Figure 18: Orthohydrogen fraction vs. space velocity. Activated catalyst produces higher concentrations of orthohydrogen at all space velocities, indicating better performance.

The amount of hydrogen that can react is directly related to the amount of time in the reactor, so it is obvious that the lower the space velocity, the more conversion achieved. This trend is illustrated very clearly by the data collected. At low flow rates the hydrogen nearly reaches equilibrium concentration, and at high flow rates little conversion is achieved for the non-activated catalysts.

Figure 17 shows the results of the hot wire probe voltage plotted against space velocity for each of the calibration runs, and for activated and non-activated catalysts. Figure 18 presents the data directly in terms of orthohydrogen fraction using equation [13]. At low flow rates (low space velocities), both activated and non-activated catalysts convert a significant portion of the hydrogen. The activated catalyst however

maintains a relatively high performance level throughout the flow range, whereas the non-activated catalyst drops off at higher space velocities.

Increase in Cooling Capacity

By comparing the power required to heat the pure, non-catalyzed parahydrogen to the test runs with catalyst, we can determine the increase in cooling capacity introduced with the addition of para-ortho conversion. The same trend as was observed in the composition measurement data can be seen here. Lower space velocities result in higher cooling capacity gains.
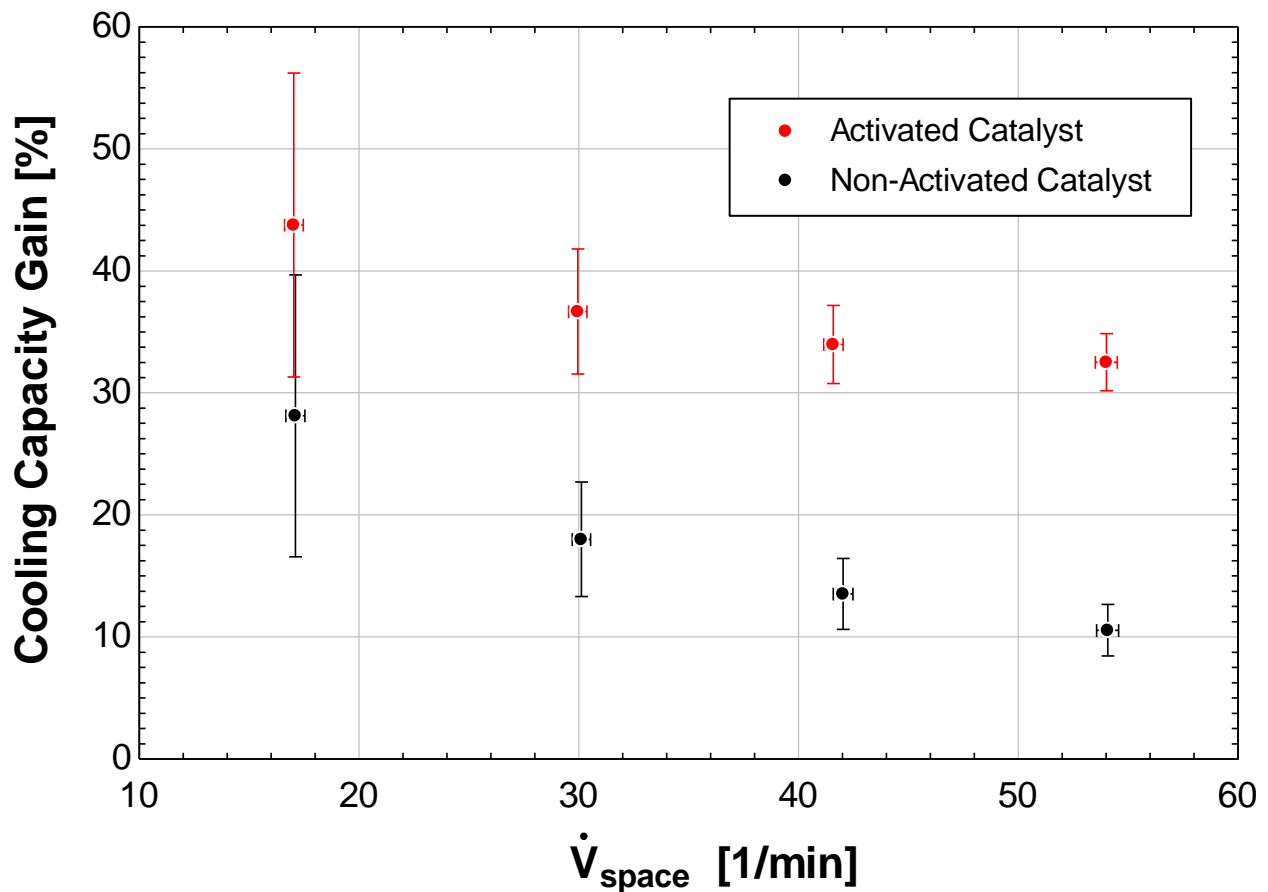

Figure 19: Plot of increase in cooling capacity vs. space velocity for activated and non-activated catalyst.

From Figure 19, it is clear that there is a significant increase in cooling capacity created by the addition of para-ortho conversion catalyst. At the lower end of space velocities, the activated catalyst cooling

capacity approaches the theoretical 50% increase over current passive cooling systems. It should be noted that as the space velocity decreases, the uncertainty increases significantly. This is due primarily to the uncertainty in the reactor power measurement. At the lower end of the tested flow rates, the reactor heater only required about 2.5W to maintain a constant 90K outlet temperature, but the uncertainty in the measurement was ±0.125W due to clipping that occurred in the measurement during data acquisition.

Activated vs. Non-Activated Catalyst

It is clear that the catalyst significantly improved after activation, however even the non-activated catalyst showed significant increases in cooling capacity over current passive cooling. This indicates that inclusion of an o-p catalyst into a space stage fuel system will be robust, and can be a simple retrofit without adding costly testing and overly complex fabrication and installation procedures, yet still greatly improve on current systems.

Conclusion

The research presented here clearly indicates that a passive hydrogen vapor cooling system can be greatly improved by taking advantage of parahydrogen to orthohydrogen conversion. The theoretical maximum of up to 50% increase in cooling capacity has been shown to be very possible and potentially achievable in a carefully designed system. Additionally, CHEF has been proven as a measurement facility, and two years after work began, it is ready to begin characterizing more O-P catalysts for use in passive cooling systems.

Recommendations for Future Work

Although CHEF is capable of taking good data and running a wide range of experiments, there are a few upgrades that would improve the accuracy and widen the range of available test conditions.

1) Install a pre-converter into the condenser.

   Currently, the liquefying hydrogen in the condenser is exposed to catalyst through a dip probe (see figure 16). Although this is effective over a long incubation period, it relies on the self-mixing of the hydrogen to uniformly convert to pure parahydrogen. A much more effective approach would be to install a small pre-converter/reactor in the fill and drain tube within the condenser that the hydrogen would pass through both on the way in to the condenser, and back on the way out to ensure 99.8% parahydrogen is entering the experimental reactor.

2) Add a second heater to the condenser.

   With the single 1/8" cartridge heater that was installed in the base of the condenser, only a maximum of 10.5W is available to drive the flow of hydrogen as it boils off, limiting the maximum flow rate during an experiment. Replacing this heater or adding a second identical cartridge would allow for a much wider range of flow rates to test better performing catalysts.

3) Use an independent reactor power measurement shunt.

   An issue was discovered with the Lakeshore 336's power output measurement when it was found that the data acquisition system was clipping one significant digit from the fraction of maximum power output that is sent to the labVIEW program. It may be possible to contact the manufacturer to get the issue resolved, however in the long term, an independent measurement shunt may be a more reliable and elegant solution.

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