III.11 Innovative Hydrogen Liquefaction Cycle

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- R&D Dynamics, Bloomfield, CT
- Massachusetts Institute of Technology (MIT), Cambridge, MA

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Objectives

Reduce the cost and improve the energy efficiency of hydrogen liquefaction.

- Develop and model a large capacity (50,000 kg/day or greater) hydrogen liquefaction cycle that:
  - Attain efficiencies which are a 33% improvement over present state-of-the-art systems.
  - Significantly reduce the capital expense relative to similar capacity systems.
- Identify and develop the key components needed for the H_2 Liquefaction Cycle that are not commercially available.
- Produce a small-scale (~500 kg/day) hardware demonstration of a hydrogen liquefaction plant to cost effectively demonstrate the large capacity system design and architecture.

Technical Barriers

This project addresses the following technical barriers from the Delivery section (3.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) High Cost and Low Energy Efficiency of Hydrogen Liquefaction

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Introduction

The purpose of this project is to produce a pilot-scale liquefaction plant that demonstrates Gas Equipment Engineering Corp's ability to meet or exceed the efficiency targets set by the Department of Energy. This plant will be used as a model to commercialize this technology for use in the distribution infrastructure of hydrogen fuel. It could also be applied to markets distributing hydrogen for industrial gas applications. Extensive modeling of plant performance will be used in the early part of the project to identify the liquefaction cycle architecture that optimizes the twin goals of increased efficiency and reduced cost. The major challenge of the project is to optimize/balance the performance (efficiency) of the plant against the cost of the plant so that the fully amortized cost of liquefying hydrogen meets the aggressive goals set by DOE.

This project will design and build a small-scale pilot plant (several hundred kg/day) that will be both a hardware demonstration and a model for scaling to larger plant sizes (>50,000 kg/day). Though an effort will be made to use commercial or near-commercial components, key components that will need development for either the pilot- or full-scale plant will be identified. Prior to starting pilot plant fabrication, these components will be demonstrated at the appropriate scale to demonstrate sufficient performance for use in the pilot plant and the potential to achieve the performance used in modeling the full-scale plant.

Background

The simplest liquefaction process is the Joule-Thomson expansion cycle. The gas to be liquefied is compressed, cooled in an after-cooler, and then undergoes isenthalpic expansion across a throttle valve. If the gas is cooled below its inversion temperature in a heat exchanger, then this expansion results in further cooling – and may result in liquid formation at the valve outlet. For hydrogen, this temperature is -95°F. It is obvious that this cycle alone cannot be used for liquefaction of hydrogen without any pre-cooling of hydrogen below its inversion temperature. A modification of this cycle is sometimes used in which liquid nitrogen is used to cool the gaseous hydrogen below its inversion temperature and then Joule-Thomson expansion is used to liquefy hydrogen.

Joule-Thomson expansion is inherently inefficient as there is no work done during expansion. The industrial gas industry departed from using Joule-Thomson as a primary process used in liquefaction of atmospheric gases in the 1960s. Turbo-expanders or expansion engines are now used at most industrial gas plants to provide the necessary refrigeration for liquefaction. The expansion across a turbo-expander is ideally isentropic, or in other words, some useful work is done in expansion. An example of this cycle, now used in most hydrogen liquefaction plants is shown in Figure 1.

We originally proposed to use an optimized combination of the Reverse-Brayton expansion cycle (or a modified Claude cycle) with the Joule-Thompson expansion cycle. At the beginning of the project the scope was expanded to look at a broader range of alternate cycles. The original consultant (AMCS) was dropped, partially because they would not agree to the normal terms and conditions found in DOE-sponsored project contracts and partially because of the nearly year-long hiatus in the project funding. Subsequently they were replaced with MIT. We are working with the Cryogenics Laboratory there, which was originally started by Dr. Samuel Collins and now run by Dr. Joe Smith, with the assistance of Dr. John Brisson. Dr. Brisson collaborated with Mr. Shimko at GEECO and Dr. Smith to select the various cycles that were evaluated. A large portion of the modeling and evaluation, and specifically the investigation of prior work on alternate cycles and modeling was performed by Wayne Staats, a masters degree candidate. This innovative approach to the basic cycle was chosen to be pursued in the "year one" work. The resulting cycle is shown in Figure 2. It is a once-through cycle that uses a helium-based refrigeration cycle employing Reverse-Brayton turbo-machinery. The heat removal from the hydrogen stream is performed by standard two and three channel heat exchangers. The baseline modeling assumes that the catalytic heat exchangers are isothermal, though additional modeling showed the added efficiency gain by using continuous catalytic heat exchangers throughout the cycle. This became the focus of "year-two" component demonstration work.

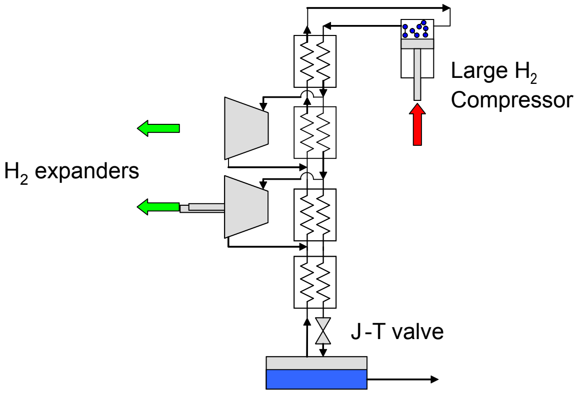

FIGURE 1. Claude Cycle Used for Hydrogen Liquefaction

Accomplishment Summary During the Previous Year (4/1/08 to 3/31/09)

The "second year" work of the project was started this year. Due to limitations in available funding the work was limited to demonstrating the catalytic heat exchanger component determined to be critical to achieving the performance projected for the liquefier cycle design completed in "year-one".

The results of the first year work showed that the unique liquefier cycle design results in both significantly increased efficiency (30% better) and significantly lower capital cost. In the year-two work a numerical model was developed for the catalytic heat exchanger and validated against previous testing performed on simplified catalytic heat exchangers. Based on simulations run using this model it was found that several configurations of "practical, buildable" heat exchangers can be loaded with catalytic material and effectively used in the liquefaction cycle developed in year-one. Work began on the test apparatus to test scaled-down versions of these heat exchangers. The test apparatus design was completed, para-ortho measurement devices were built and successfully tested, catalytic material acquired, compressors run the helium and hydrogen flow loops identified and tested. Work has begun on building the test apparatus.

Project Results

The following is a summary of the major work efforts and accomplishments in this reporting period. More detailed description of the project results follows.

- Completed development and validated accuracy of CHEX numerical model.

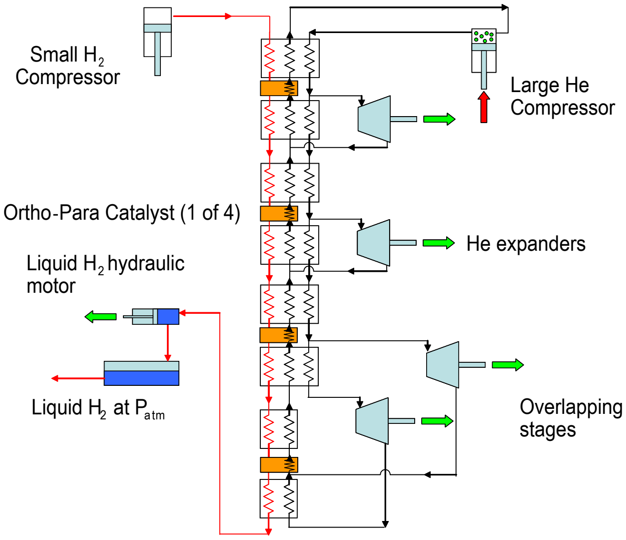

FIGURE 2. Basic Cycle Definition

- Finished design of CHEX article test apparatus.
- Model shows that typical heat exchanger channel dimensions are satisfactory for pressure drop, heat exchange, and catalyst reaction rate criteria.
- Sensor for measuring para/ortho make-up fabricated and performance verified.

The continuous catalyst numeric model was assembled and successfully tested against known data. The model uses MATLAB for controlling inputs, outputs, and referencing thermophysical properties, and COMSOL Multiphysics for the finite element computations.

The model breaks the heat exchanger into alternating lengths of adiabatic catalytic conversion and "normal" heat exchange. Figure 3 shows this arrangement pictorially. Figure 4 shows the significant parameters, inputs, and outputs for the adiabatic catalytic sections.

This numerical model was then applied to a physical configuration that uses "typical" shell and tube heat exchanger dimensions (1/8 inch inside diameter, 5 inches in length). This heat exchanger tube design is also similar to the existing adiabatic catalytic heat exchanger test data where Hutchinson examined the Para to Ortho transition (cold to warm). As Figure 5a and b show, a satisfactory step size was determined so that the model acceptably models a continuous and simultaneous catalytic and heat exchange process. The model was then exercised by comparing it to known data and test conditions from Hutchinson's work. Figure 6 shows good agreement with these results. In addition several parametric runs using the model confirmed the very weak pressure dependence expected for the process.

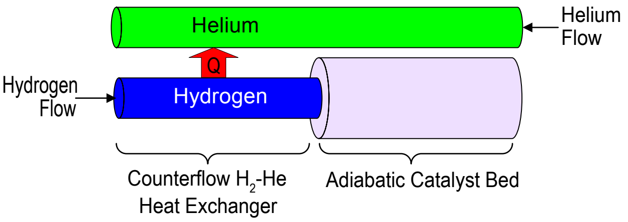

FIGURE 3. Overall Model Basis

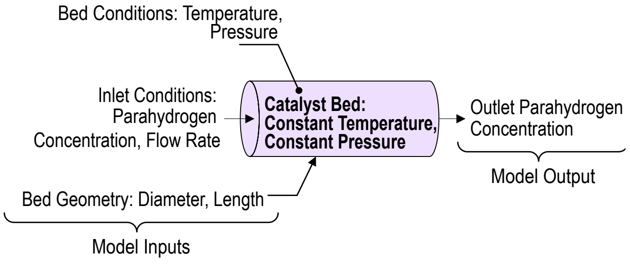

FIGURE 4. Model Parameters for Adiabatic Catalyst Sections

Key Finding: Model shows that typical heat exchanger channel dimensions are satisfactory for pressure drop, heat exchange, and catalyst reaction rate criteria.

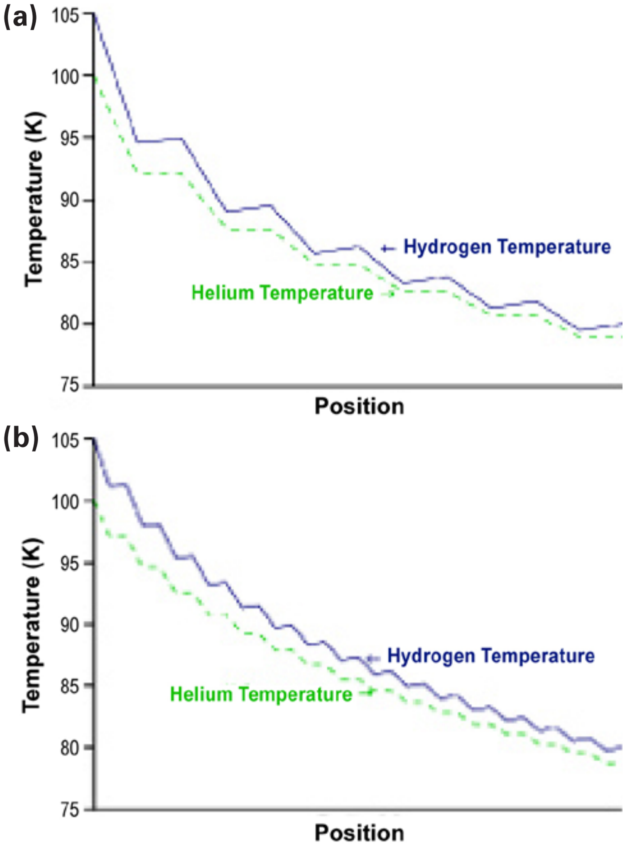

FIGURE 5. (a) Six Section Result (b) Sixteen Step Result

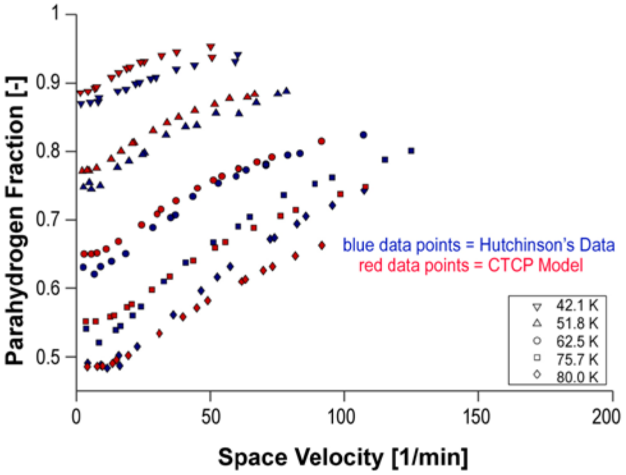

FIGURE 6. Comparison to Hutchinson Test Data

The CHEX model was used to determine what heat exchanger dimensions were needed to meet the combined constraints of pressure drop (not to large), heat transfer (small temperature difference), and conversion reaction rate (catalyst surface area). The initial modeling was done on a channel with constant wall temperature in a 1 cm channel. A second case was run where transverse cooling tubes were placed along the channel.

The results of these two simulations show that a 1 cm channel thickness will not be effective in transferring heat effectively (and therefore limiting the conversion achieved) but that reducing this dimension, even intermittently, with cooling channels had a drastic effect on the heat exchange effectiveness and therefore the conversion achieved within the CHEX channel. The result also had a dramatic effect on the amount of catalyst needed to achieve the effective conversion process within the channel. Pressure drop through the channel set the allowable flow rate and was held to typical heat exchanger values.

The results of the initial modeling set a value for a "reasonable" channel dimension of 2 mm. This size channel should allow simple "filling" of the catalyst material after channel fabrication so that any issues with high temperature brazing processes during fabrication could be avoided. A more detailed model with counter-flowing fluid channels of hydrogen and helium was produced. This model and the simulation results are shown in Figure 7. This configuration is an effective heat exchanger and yields near equilibrium conversion conditions at the hydrogen exit and a significant temperature reduction in the hydrogen flow stream.

Key Finding: The critical sensor for measuring para/ortho make-up at cryogenic temperatures was fabricated and the performance verified.

The commercially available conductivity sensor was successfully modified to accurately measure the ortho/para composition at liquid nitrogen temperatures. The sensor housing was completely redone, especially the upper seal, which was changed from a rotating elastic seal to a face mounted indium seal.

A cryogenic test set-up used to verify the sensor performance at liquid nitrogen temperatures. Dual sensors were submerged in liquid nitrogen and the output voltage from the wheatstone bridge electrical arrangement was measured for two gasses: 1) A normal ambient hydrogen (known ortho/para gas sample composition) and 2) a helium gas sample. Figure 8 shows the results of that testing. The expected para hydrogen value is also shown on the graph to indicate the excellent accuracy expected from the instrument during CHEX testing. This figure also shows the response time of the instrument when switching from one composition gas to another.

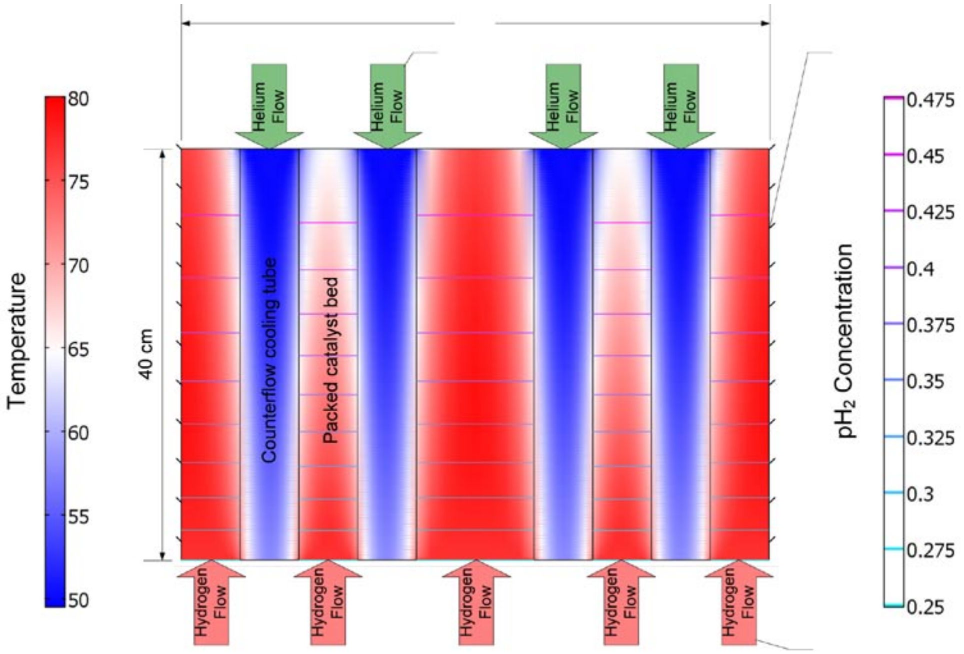

FIGURE 7. Counter-Flow CHEX Heat Exchanger Model and Results

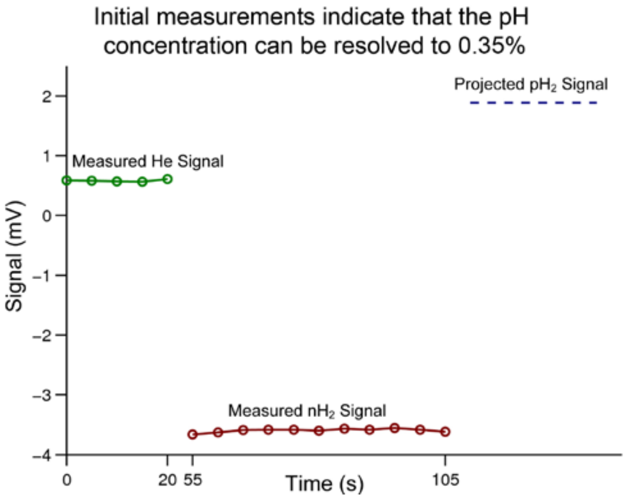

FIGURE 8. Test Results

Future Work

Over the next year we will complete the testing of the catalytic heat exchanger and validate the design approach for applying these heat exchangers to both the pilot plant and full-scale plant applications. We will also update both the pilot- and full-scale plant designs to refine the fabrication cost estimates.