III.7 Innovative Hydrogen Liquefaction Cycle

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

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Estimated Project End Date: August 1, 2011

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

Project Overview

The purpose of this project is to produce a pilot-scale liquefaction plant that demonstrates the ability to meet or exceed the efficiency targets set by the DOE. 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-Thompson Expansion Cycle (Figure 1). 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.

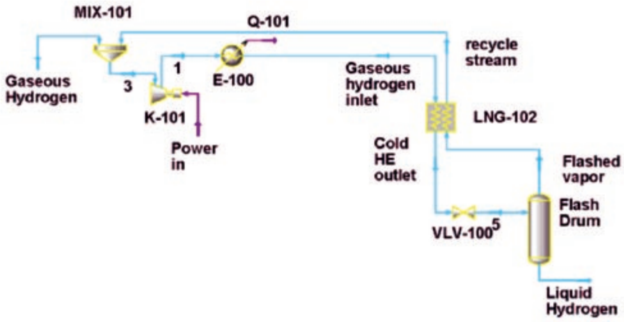

FIGURE 1. Joule-Thompson Expansion Cycle

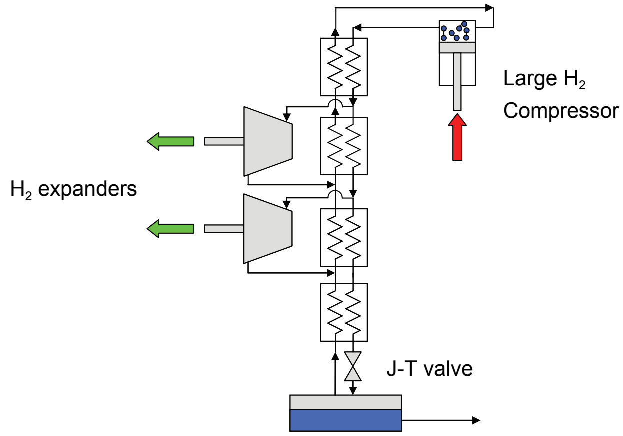

FIGURE 2. Claude Cycle Used for H_2 Liquefaction

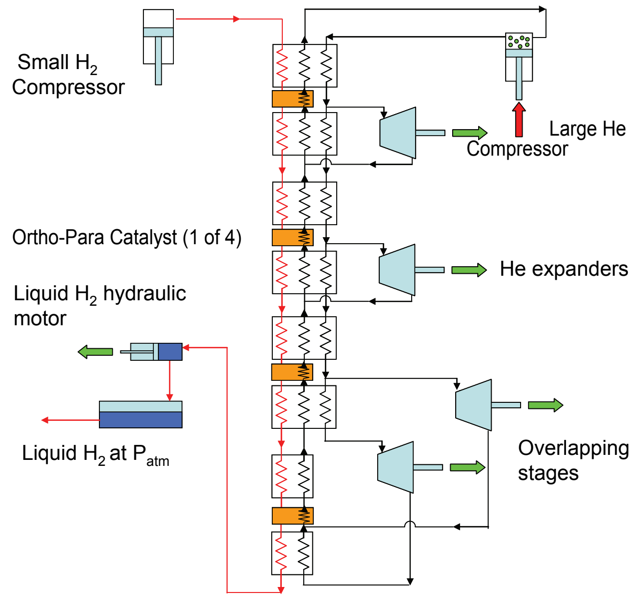

FIGURE 3. Basic Cycle Definition

Joule-Thompson expansion is inherently inefficient as there is no work done during expansion. The industrial gas industry departed from using Joule-Thompson 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 H_2 liquefaction plants is shown in Figure 2.

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. We are working with the MIT Cryogenics Laboratory to select the various cycles that were evaluated. The cycle chosen is shown in Figure 3. It is a once-through cycle that uses a helium-based refrigeration cycle employing Reverse-Brayton turbomachinery. 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.

Accomplishments

The "first year" work of the project was completed this year. The final presentation was given and the project was given the go ahead to move into year two work. Due to limitations in available funding the work will be 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.

Project Results

As reported in the 2007 annual report, the selection of the operating parameters for the cycle were selected to maximize the potential efficiency using a conventional Reverse-Brayton refrigeration approach to a He loop. One key parameter was the selection of the H_2 pressure. Thought the smaller of the two compressors (He and H_2) due to the once-through approach to the H_2 side, the H_2 pressure had a large impact on the "evenness of the cooling load, especially in shifting as much of the cooling to higher temperature regions. Unlike on existing cycles where the H_2 pressure ratio was also used to supply the cooling, we were free to select the pressure that struck the balance between the heat load distribution and H_2 pressure ratio driving compressor input power. Figure 4 shows the effect of increased pressure on smoothing the heat load, while Figure 5 shows the importance of keeping the pressure above the two phase dome on the temperature-entropy (T-S) diagram to allow the use of the liquid expander, thus enabling once-through liquefaction (100% yield).

Various parametric studies were performed to optimize the heat exchanger design. The goal was to identify the point of diminishing returns relative to increasing the heat exchanger size (and therefore cost) versus the impact on increased cycle efficiency. Figure 6 displays typical results that clearly show that cycle efficiency only increases marginally after a ΔT/T of 0.03 (inversely proportional to heat exchanger area).

Table 1 shows the efficiency predictions for both the full-scale and pilot-scale plants based on this modeling and constrained by the practical limits of available compressor and heat exchange components. As expected, the component size of the full-scale plant allow much higher efficiency components.

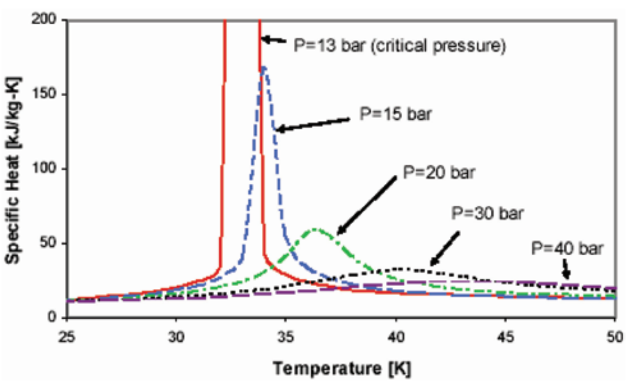

FIGURE 4. Effect of Pressure on Specific Heat

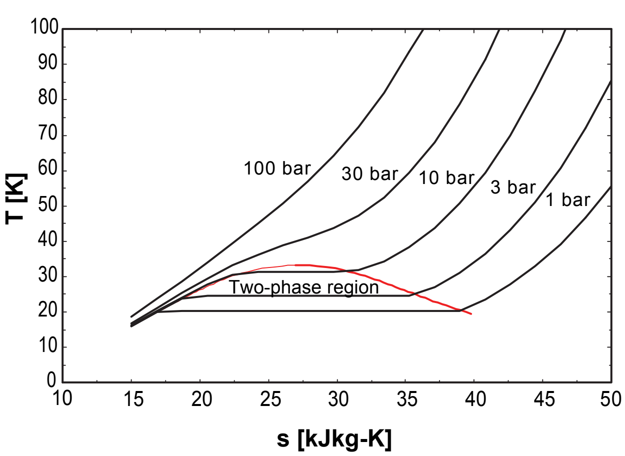

FIGURE 5. Pressure Required to Avoid the Two Phase Region

Further refinements to the model allowed the comparison of different approaches to the ortho/para conversion in a catalytic bed and the removal of the exothermically produced heat from the process.

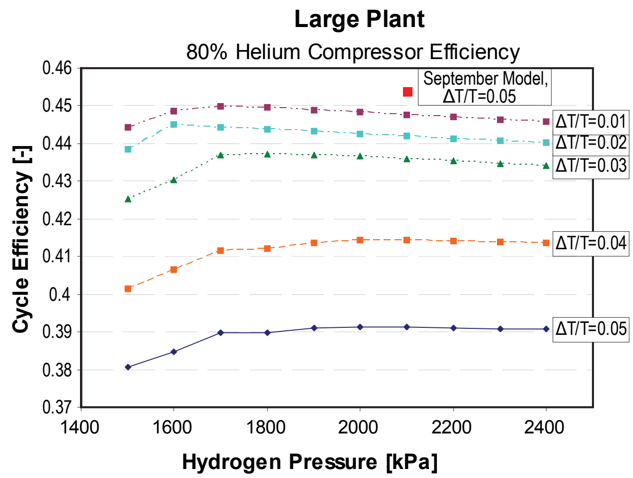

FIGURE 6. Effect of Increased Heat Exchanger Size on Cycle Efficiency

TABLE 1. Efficiency Predictions for Both the Full-Scale and Pilot-Scale Plants

Liquefier Performance		Pilot	Large
System parameters	ΔT/T	0.03	0.03
	η_{exp1}	0.6	0.85
	η_{exp2}	0.7	0.83
	η_{exp3}	0.75	0.86
	η_{exp4}	0.65	0.86
	$\eta_{comp,He}$	0.65	0.8
	$\eta_{comp,H2}$	0.6	0.8
	$\eta_{wet\_expander}$	0.9	0.9
	P_{H2} [bar]	21	21
	$P_{He,high}$ [bar]	15	15
	$P_{He,low}$ [bar]	2.5	2.5
Environmental and final properties	T_{atm} [K]	300	300
	P_{atm} [bar]	1	1
	$x_{para,in}$ [-]	0.25	0.25
	T_f [K]	20	20
	P_f [bar]	1	1
	$x_{para,f}$ [-]	0.95	0.95
Simulation result	η_{cycle}	0.2214	0.4455
	W_{ideal} [kWh/kg]	3.89	3.89
	W_{net} [kWh/kg]	17.57	8.73

Figure 7 is a graphic display of the results of the temperature profiles resulting from the three approaches. This strong effect coupled with the lack of commercially available catalytic coated or filled heat exchangers identified this component as requiring a development and demonstration segment in the project that takes precedence over both the He cooling turbines and the wet expander.

R&D Dynamics completed their design of the He turbines for both the pilot- and full-scale plants. These results were used in the cycle model described above. In addition, their cost estimates were used in the plant cost estimates that were used to demonstrate the potential cost reduction of the full-scale plants using this cycle and to help put a realistic cost on the pilot-plant. These estimates were combined with vendor cost estimates for the heat exchangers and compressors and engineering estimates for the remaining components. The resulting costs are shown in Table 2. This summary shows that the full-scale system has the potential for significant cost reduction relative to present systems (as estimated by the H2A program). It also shows that the cost of fabricating the pilot-scale plant far exceeds the estimate in the original proposal. The breakdown of plant costs are compared to the H2A model in Table 3.

The detailed layout of the system components was completed. One view of the layout of the cold box is shown in Figure 8. Figure 9 shows the overall layout and scale of the pilot-plant.

The results of the efficiency and cost studies are summarized as follows:

- Increases efficiency by 30% over present state-of-the-art:

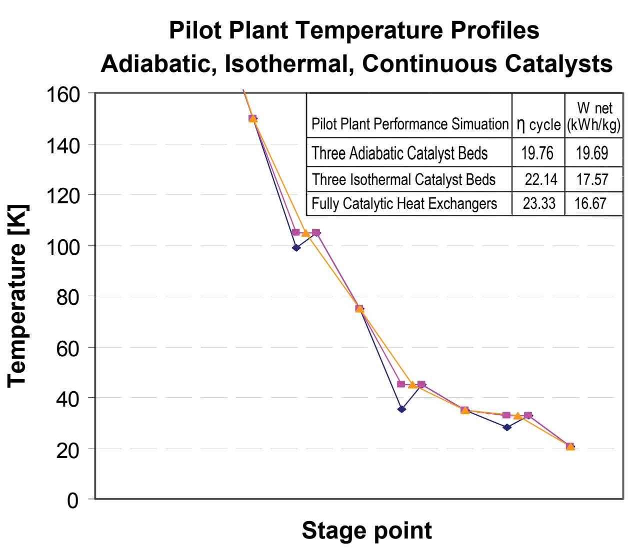

FIGURE 7. Temperature Profiles resulting from Catalytic Conversion Assumptions

TABLE 2. Full-Scale Plant Cost Estimate

Major Equipment	Qty	Pilot (500 kg/day)	Qty	50,000 kg/day
Compressor, H_2	1	$400,000.00	3	$5,700,000.00
Compressor, He	1	$900,000.00	10	$24,000,000.00
HX 1-2-3	1	$160,000.00	10	$4,084,000.00
HX 3A	1	$37,000.00	1	$183,000.00
HX 4-5	1	$67,000.00	4	$1,322,000.00
HX 5A	1	$35,000.00	1	$130,000.00
HX 6-7	1	$45,000.00	1	$187,000.00
HX 7A	1	$33,000.00	1	$104,000.00
HX 8	1	$31,000.00	1	$136,000.00
Catalyst Bed	6	$6,000.00	6	$120,000.00
TBX 1	1	$150,000.00	1+1	$350,000.00
TBX 2	1	$150,000.00	1	$250,000.00
TBX 3	1	$150,000.00	1	$250,000.00
TBX 4	1	$150,000.00	1	$250,000.00
Control Valves	4	$6,000.00	5	$75,000.00
Check Valves	13	$25,000.00	13	$130,000.00
Control System	1	$75,000.00	1	$100,000.00
Instrument Air Supply	1	$5,000.00	1	$10,000.00
H_2 Expander	1	$25,000.00	1	$125,000.00
Piping		$10,000.00		$250,000.00
Insulation		$10,000.00		$150,000.00
Structures		$10,000.00		$200,000.00
Electric Switchgear		$100,000.00		$500,000.00
Miscellaneous		$100,000.00		$500,000.00
TOTAL		$2,680,000.00		$39,106,000.00

  - From 30% to 44% of Carnot, or
  - From 9.7 kWh/kg to 7.4 kWh/kg
- System “equipment” cost ~40% of H2A estimate:
  - Could be significantly higher, but also not included in H2A Model
  - Largely conventional component use
  - Development risk and cost uncertainty minimized

Future Work

Over the next year we will demonstrate a sub-scale version of the catalytic heat exchanger. This work will start by reviewing existing literature on catalytic reactors and working with existing suppliers of catalytic material to understand the options. In parallel we will begin

TABLE 3. Comparison of Project Estimated Costs to H2A Costs

	DOE H2A Model Results	Project Estimates
Liquefier Capital Cost	$102.3M	$39.1M
Annual Energy Cost ($0.05/kWh)	$9.5M	$7.1M
Operational and Maintenance plus Misc Annual Costs	$5.1M	$5.1M
Capital Cost Contribution to the Liquefier Share of Real Levelized Delivered Hydrogen Cost ($(2005)/kg)	$1.08	$0.42
Energy/Fuel Cost Contribution to the Liquefier Share of Real Levelized Delivered Hydrogen Cost ($(2005)/kg)	$0.60	$0.45
Other Cost Contribution to the Liquefier Share of Real Levelized Delivered Hydrogen Cost ($(2005)/kg)	$0.32	$0.32
Liquefier Portion of Real Levelized Delivered Hydrogen Cost ($(2005)/kg)	$2.00	$1.19

Annual H_2 Production of 15.9M kg
Amortization Period of 7 years

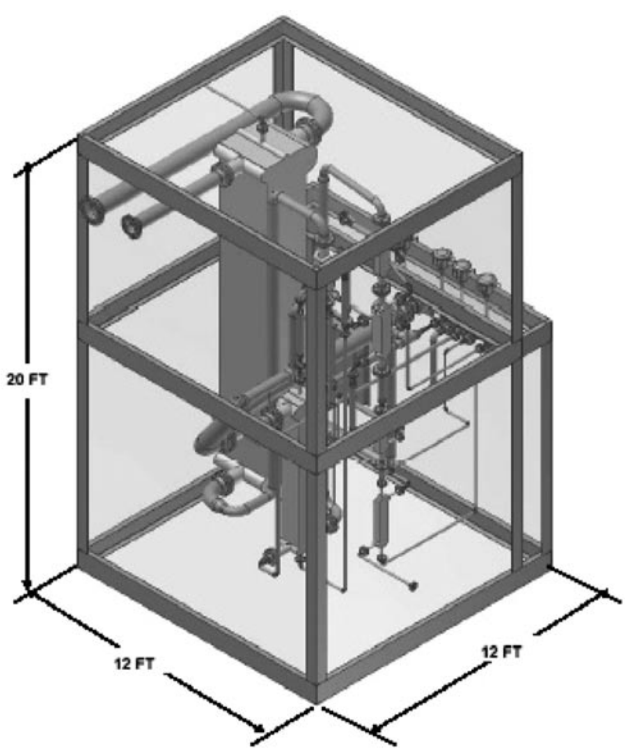

FIGURE 8. Pilot-Plant Cold Box Layout

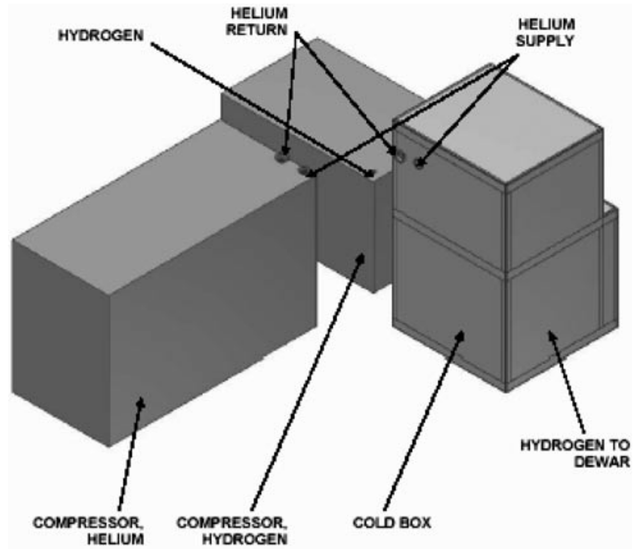

FIGURE 9. Overall Pilot-Plant Layout

fabricating the test apparatus with a primary concern on the sensor that measures the para/ortho percentage make-up of the hydrogen. Initial testing will be performed on test coupons of potential heat exchanger configurations – different materials, applications, and spacing. Finally the selected catalytic heat exchanger design will be fabricated and tested.