III.14 Thermodynamic Modeling of Rapid Low Loss Cryogenic Hydrogen Refueling

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Linde LLC, Hayward, CA

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Projected End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 Objectives

- Demonstrate rapid refueling of cryogenic vessels.
- Refuel cryogenic vessels even when warm and/or pressurized.
- Refuel at high density (>80 kgH_2/m^3).

Technical Barriers

This project addresses the following technical barrier from the Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(J) Refueling Site Operations

TABLE 1. Progress toward Meeting DOE Hydrogen Delivery Technical Targets

Pressurized LH_2 pump				
DOE Targets for Forecourt Compressors	**Units**	**2010 Target**	**2015 Target**	**Pressurized LH_2 pump**
Reliability	-	Improved	High	High
Compression Energy Efficiency	%	94	95	95
Installed Capital Cost	k$/(kg/hr)	4	3	5
H_2 Fill Pressure	Peak psi	6,250	12,000	12,000

LH_2 – liquefied hydrogen

FY 2011 Accomplishments

- Developed model of vessel fill processes.
- Calculated final fill density as a function of initial vessel conditions (temperature, T, and pressure, p).
- Completed LH_2 pump contract negotiation with Linde LLC.

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Introduction

Cryogenic pressure vessels have demonstrated highest performance for automotive hydrogen storage, with weight, volume, cost, and safety advantages [1,2]. One of the outstanding challenges for cryogenic pressure vessels is refueling. Today's hydrogen storage technologies (compressed and liquid hydrogen) operate at fixed temperature. Cryogenic pressure vessels, however, drift across the phase diagram depending on the level of use. The challenge is demonstrating rapid, inexpensive refueling that minimizes evaporative losses regardless of the initial thermodynamic state of the vessel.

Approach

We have identified a promising technology for cryogenic pressure vessel refueling: a liquid hydrogen pump. This pump takes LH_2 at low pressure (near atmospheric) and delivers it as high-pressure (200-880 bar) low temperature (30-50 K) high-density (>80 g/L) hydrogen that can be directly dispensed into a cryogenic pressure vessel, even when warm and/or pressurized. In this project we plan to install a LH_2 pump in the LLNL campus and demonstrate its virtues for rapid and efficient cryogenic vessel refueling.

Results

We have developed a model for vessel fill processes in an effort to evaluate the potential for future LH_2 pump high density refueling. Based on REFPROP [3], the model considers real gas hydrogen properties and enables quick calculation of relevant thermodynamic properties.

We start by considering a simplified case: a large forecourt vessel storing hydrogen at temperature T_i and pressure p_i. This vessel fills a (relatively small) vessel onboard a vehicle. The fill process is modeled with the first law of thermodynamics for open systems [4]:

$$Q + m_i h_i = U_f - U_o + m_e h_e + W \quad (1)$$

Mechanical work W is negligible for typical (rigid) pressure vessels, and we neglect heat transfer into the vessel Q as a first approximation. Mass flow out of the vehicle vessel m_e=0 during refueling, and the specific enthalpy h_i of the hydrogen flowing into the vessel is calculated at the conditions of the forecourt vessel (p_i, T_i), assumed constant due to its large relative size. The equation for the vehicle vessel therefore reduces to,

$$m_i h_i = U_f - U_o \qquad (2)$$

Assuming an initially empty vessel with negligible thermal mass, the initial internal energy U_o=0. The final internal energy in the vehicle vessel $U_f = m_i u_f$, which leads to h_i=u_f, where u_f is the specific internal energy inside the vessel. From thermodynamics, $h_i \equiv u_i + p_i v_i = u_f$. The term $p_i v_i$, frequently named flow work, explains the heating that occurs when substances are forced into a vessel.

Figure 1 shows results for the fill process of an initially empty vessel with negligible thermal mass and heat transfer. The figure shows vessel temperature and density during the fill process as a function of pressure, for forecourt vessel conditions p_i=700 bar and T_i=100, 200, and 300 K. The figure shows that hydrogen flowing into the vehicle vessel heats substantially in the process, considerably reducing the vessel fill density. Temperature is nearly constant during the fill process, changing only slightly due to hydrogen's non-ideal behavior, especially at lower temperature. It is worth pointing out that hydrogen heats up as it flows into the vessel regardless of the value of the Joule-Thomson coefficient (negative at ambient temperature, near zero at 200 K, and positive at 100 K): vessel fill processes are not isenthalpic and therefore not controlled by the Joule-Thomson coefficient. Flow work plays the key role in understanding the process.

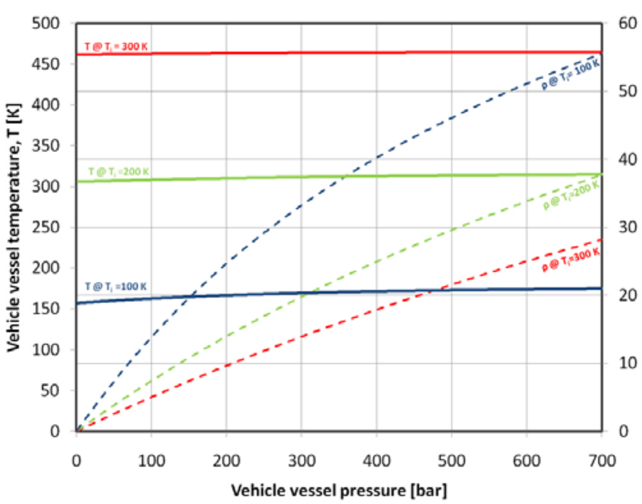

FIGURE 1. Automotive vessel temperature and density during the fill process as a function of pressure, for forecourt vessel conditions p_i=700 bar and T_i=100, 200, and 300 K, assuming an initially empty vessel with negligible thermal mass and heat transfer.

Results in Figure 1 can be generalized by varying p_i and T_i over broad ranges. Figure 2 shows vehicle vessel temperature (blue) and fill density (red), at the end of the refueling process, when pressure equilibrium is reached with the forecourt vessel (p=p_i), for an initially empty vessel with negligible thermal mass, for any combination of forecourt vessel pressure and temperature (p_i, T_i). As an example, assume that the forecourt vessel is filled with hydrogen at 100 K and 300 bar. From the figure, the vehicle vessel at the end of the fill process (when both vessels equilibrate at 300 bar) would be at 150 K and 40 g/L.

Figure 2 once again shows the considerable heating that occurs during the fill process. For an ideal gas with constant specific heat, heating is constant ($T = \gamma T_i$, where γ is the specific heat ratio c_p/c_v), and therefore temperature lines are fairly horizontal at low pressures and high temperatures. At higher pressures, deviations from ideality increase the heating. Minimum heating (minimum density losses) occurs at low temperature and pressure, where hydrogen's compressibility factor drops as hydrogen approaches liquid phase. This is observed by the 50 K blue line reaching a local maximum at ~50 bar.

Figure 2 also shows the exergy of the hydrogen inside the forecourt vessel (black lines). Exergy is defined as the minimum theoretical work necessary to compress and cool down hydrogen from the reference state (1 bar and 300 K) to any condition p_i, T_i in the diagram. Exergy is therefore an indication of the energy necessary for densifying hydrogen. Figure 2 shows that hydrogen compression is exergetically inexpensive compared to cooling: any level of densification from 10 to 60 g/L is achieved with minimum possible exergy by maximizing pressurization and minimizing cooling.

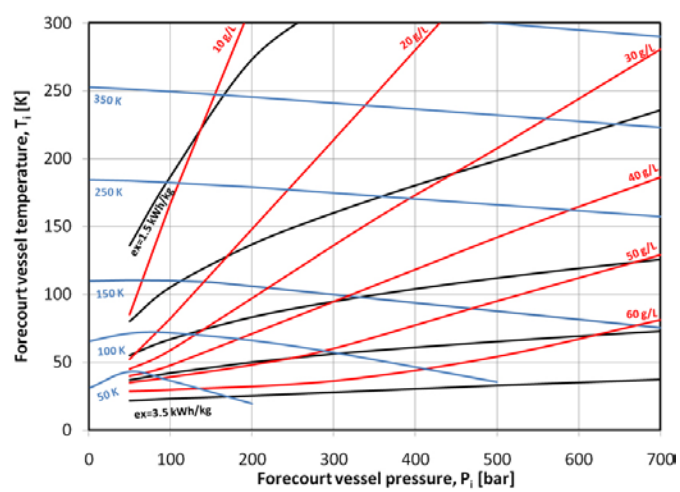

FIGURE 2. Vehicle vessel temperature (blue) and fill density (red), at the end of the refueling process, when pressure equilibrium is reached with the forecourt vessel (p=p_i), for an initially empty vessel with negligible thermal mass, for any combination of forecourt vessel pressure and temperature (p_i, T_i). The figure also shows the exergy of the hydrogen inside the forecourt vessel (black lines).

Hydrogen liquefaction is well known to be exergetically expensive (3.92-3.27 kWh/kg depending on whether para-ortho hydrogen conversion is included or not [5]). Investing energy in liquefaction, however, has the virtue of minimizing station energy consumption and capital cost, because liquid hydrogen can be pressurized with little exergy input as indicated by the nearly horizontal 3.5 kWh/kg exergy line (Figure 2).

The fact that pressurizing liquid hydrogen is exergetically inexpensive enables rapid compression and efficient densification with low evaporative losses. Demonstrating the potential for this technology is the purpose of this project. While LLNL moves forward issuing the pump contract and preparing for construction, we have applied our thermodynamic model to predict expected fueling performance.

Predicting pump refueling is similar to predicting vessel refueling, and Equation (2) still dominates the process. However, delivery temperature is a function of pump performance details, and it is therefore hard to predict. For this preliminary analysis, we estimate delivery temperature assuming *isentropic* compression from the forecourt Dewar with LH_2 saturated at 3 bar and 24.6 K. While real pumps will not reach this level of performance, final vessel density may be reasonably well approximated due to the low exergetic cost of LH_2 pumping.

Modeling results are shown in Figure 3, which shows hydrogen density after refueling (when the vehicle drives away from the fueling station) as a function of hydrogen density before refueling (when the vehicle drives into the refueling station), for multiple initial vessel temperatures

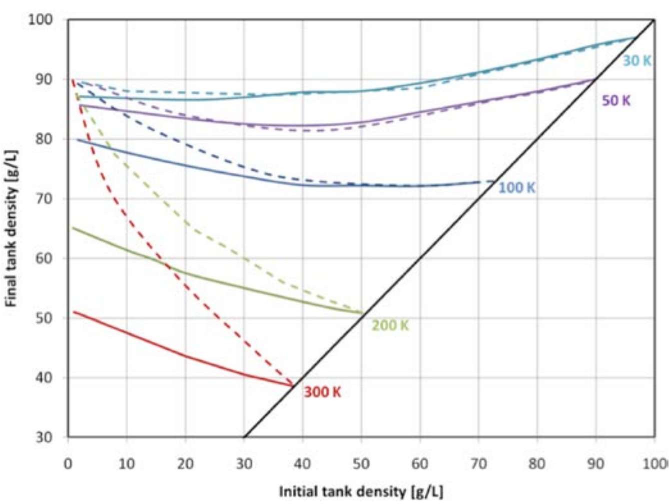

FIGURE 3. Hydrogen density after refueling (when the vehicle drives away from the fueling station) as a function of hydrogen density before refueling (when the vehicle drives into the refueling station), for multiple initial vessel temperatures (30 K, 50 K, 100 K, 200 K, and 300 K). Two sets of lines are shown: *isentropic* pump with negligible pressure vessel thermal mass (dashed); and *isentropic* pump including the vessel thermal mass, and assuming thermal equilibrium between vessel and hydrogen (solid lines).

(30 K, 50 K, 100 K, 200 K, and 300 K). Two sets of lines are shown: isentropic pump with negligible pressure vessel thermal mass (dashed); and isentropic pump including the vessel thermal mass, and assuming thermal equilibrium between vessel and hydrogen (solid lines).

Comparing dashed lines vs. solid lines in Figure 3 shows that vessel thermal mass plays a large role in fill density for warm, empty vessels. At very low temperatures (30-50 K), vessel thermal mass becomes very small, enabling high density refueling regardless of the initial fill level. An isentropic pump filling an initially cold and empty vessel may therefore enable ultimate densities beyond 85 g/L. Final densities beyond 90 g/L are obtained with very cold (30 K) nearly full vessels where the pump is essentially compressing low entropy H_2 already in the vessel.

The black diagonal line in the right of Figure 3 corresponds to a fully pressurized vessel at 700 bar. At this condition, no refueling is possible, and density after refueling equals density before refueling. Driving is necessary before refueling to reduce pressure and cool down the vessel.

In summary, the low exergetic cost of pumping LH_2 may lead to rapid and efficient refueling at high densities. Flow work is also lowest near the liquid phase (Figure 2) minimizing heating and density losses during vessel fill. Future experiments will reveal how closely real pump performance compares with the isentropic pump model.

Conclusions and Future Directions

- Rapid, low loss refueling of cryogenic vessels is possible through pressurized LH_2 dispensing.
- Modeling has revealed potential for high density refueling (85 g/L) for initially cold vessels.
- Model results need to be validated vs. future experimental results.

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FY 2011 Publications/Presentations

1. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, University of Castilla la Mancha, Spain, March 2010.

2. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, International Conference on Hydrogen Production and Storage, Istanbul, Turkey, June 2010.

3. High-density automotive hydrogen storage with cryogenic capable pressure vessels, Salvador M. Aceves, Francisco Espinosa-Loza, Elias Ledesma-Orozco, Timothy O. Ross, Andrew H. Weisberg, Tobias C. Brunner, Oliver Kircher, International Journal of Hydrogen Energy, Vol. 35, pp. 1219-1226, 2010.

4. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, AICHE Topical Symposium on Hydrogen Production and Storage, Salt Lake City, October 2010.

5. Compact (L)H2 Storage with Extended Dormancy in Cryogenic Pressure Vessels, Salvador Aceves, Invited Presentation, International Conference on Sustainable Energy Storage, Belfast, Northern Ireland, UK, February 2011.

6. Cryogenic Hydrogen Storage, Delivery, and Safety, Salvador Aceves, Invited Presentation, Annual Congress of the Mexican Society of Mechanical Engineers, San Luis Potosi, Mexico, September 2011.