Performance and Durability Testing of Volumetrically Efficient Cryogenic Vessels and High-Pressure Liquid Hydrogen Pump

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Subcontractor:
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Project Start Date: January 2014
Project End Date: September 2018

Overall Objectives

- Characterize cryogenic vessel and liquid hydrogen (LH_2) pump performance by modeling important performance parameters including: refuel density, boil-off, hydrogen temperature and pressure during fill, and system (volumetric and gravimetric) storage density.

Fiscal Year (FY) 2018 Objectives

- Characterize LH_2 pump performance by modeling vessel fill experiments.
- Determine vessel fill density, weight and volume storage performance, and vent losses by modeling typical vehicle utilization patterns.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

(C) Hydrogen Storage

(D) Lack of Hydrogen Infrastructure Performance and Availability Data.

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from the Technology Validation section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan: Milestone 3.4: Validate station compression technology provided by delivery team (4Q, 2018).

FY 2018 Accomplishments

- Developed a thermodynamic model to determine fill density for any initial vessel condition.
- Determined vessel fill density for typical vehicle utilization and refueling patterns.
- Demonstrated very low potential for vent losses even under extreme vehicle utilization scenarios.
- Evaluated volumetric and gravimetric cryogenic vessel storage performance for typical utilization conditions.

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

INTRODUCTION

Cryogenic pressure vessels (also known as cryo-compressed vessels) have fundamental thermodynamic advantages enabling high-density hydrogen storage without the boil-off losses typical of cryogenic systems. High density is critical for practical hydrogen-fueled transportation, enabling vehicles with similar driving autonomy and refueling time as today's gasoline vehicles while producing zero regulated and climate-changing emissions. High density enables storage of a large amount of fuel in a small package that occupies less space onboard the vehicle and weighs less, therefore reducing system cost by reducing the need for expensive structural materials (carbon fiber and metals). Low vessel cost combined with effective LH_2 distribution, storage at the station, and dispensing results in minimum cost of ownership among existing approaches for automotive hydrogen storage. Safety is also improved because cryogenic hydrogen has lower internal energy and therefore expands less in case of vessel failure. An outer vacuum jacket provides an extra layer of protection and volume for hydrogen expansion, reducing expansion pressure and thrust.

Cryogenic pressure vessel refueling also is thermodynamically favored. A two-stage LH_2 pump manufactured by Linde enables direct pressurization of dense LH_2, therefore minimizing compression work (hence low electricity consumption) and enabling high throughput (100 kg/h, enough for 5-minute automobile refuels) from a small displacement (0.36 liters) two-stage piston pump. Additionally, refueling at densities higher than LH_2 at the dewar (65 g/L) is possible due to the high compressibility of LH_2.

APPROACH

We developed a thermodynamic model capable of predicting cryogenic vessel fill pressure and temperature (and therefore density) for any initial condition. The model has been validated by comparison with the results of 24 cryogenic pressure vessel fill experiments with a LH_2 pump manufactured by Linde and installed at the Lawrence Livermore National Laboratory campus [1]. The LH_2 piston pump takes LH_2 from the station dewar at near ambient pressure (3 bar) and very low temperature (24.6 K) and pressurizes it to the vessel pressure in two stages of compression, up to 875 bar. Experiments spanned initial vessel temperatures from ambient to 22 K, enabling pump testing over a broad range of conditions.

We also conducted a comprehensive evaluation of all factors affecting cryogenic vessel fill density in an effort to evaluate system performance versus operational parameters over a broad range of conditions. The model considers use patterns, insulation performance, vessel characteristics, liquid hydrogen pump performance, and para-hydrogen to ortho-hydrogen conversion [2].

Lastly, we evaluated cryogenic vessel *system* storage performance, including volumetric (g H_2/L), gravimetric (H_2 weight fraction), and vent losses over a broad range of conditions.

RESULTS

Key results from this year's effort include the following.

- Fill densities are well predicted (RMS error = 0.7 g/L) with a thermodynamic fill model that assumes constant 10 kJ/kg K inlet vessel entropy.
- The thermodynamic fill model has been applied to generate diagrams that can be used for directly reading fill density for any initial vessel condition (Figure 1).
- Fill density increases monotonically with driving distance (Figure 2). The main effect determining this behavior is heat transfer from the environment. Increased driving distance rapidly depletes hydrogen in the vessel, reducing time available for heat transfer, leading to colder vessels that fill to higher density. This is synergistic with hydrogen storage needs of frequently driven vehicles—more capacity in the vehicles that most need it.

- Para-hydrogen to ortho-hydrogen (P-O) conversion absorbs heat and cools down the vessel, leading to significant increases in fill density (up to 5.3%). P-O conversion is most active for vehicles driven 20–60 km/day, and therefore will have a major effect on most personal vehicles (Figure 2).

- Cryogenic vessel system density (defined as hydrogen stored divided by total system volume) is greatest for 700-bar vessels. There is little gain (1 g/L or less) in increasing pressure beyond 500 bar, however, and maximum fill density at 150 km/day driving distance (42 g/L) is equal for 500-bar and 700-bar vessels (Figure 3).

- A 350-bar vessel can store hydrogen at system density up to 40.5 g/L and appears a reasonable alternative with average system density only 2.5 g/L less on average than 700-bar vessels (Figure 3).

- Weight fraction (hydrogen mass divided by total system mass) is greatest (7.4%) for 150 bar and 250 bar, and a 350-bar vessel is nearly as weight efficient (7%). For 500- and 700-bar vessels, the weight fraction drops to 6.4% and 5.6% due to thicker composite walls (Figure 4).

- Results indicate that 250–350 bar appears to be a superior design space for cryo-compressed storage due to lower composite mass (and therefore lower cost) than 500- to 700-bar vessels, while maintaining nearly as high system density (Figure 3, Figure 4). A full economic and functional evaluation is necessary, however, to determine "optimum" design pressure for cryogenic vessels.

- Cryogenic vessels with a working vacuum insulation are unlikely to have any vent losses during normal operation. Venting only occurs when the vehicle is continuously driven for many hours, filled to maximum capacity at the end of the trip, and used infrequently (10 km to 30 km per day) after fill. Vessels 350 bar and stronger do not lose hydrogen if driven 10 km/day or more. Losses can be avoided by educating drivers to not fill the vessel to full capacity after a long drive if they anticipate infrequent use of the vehicle in the following days.

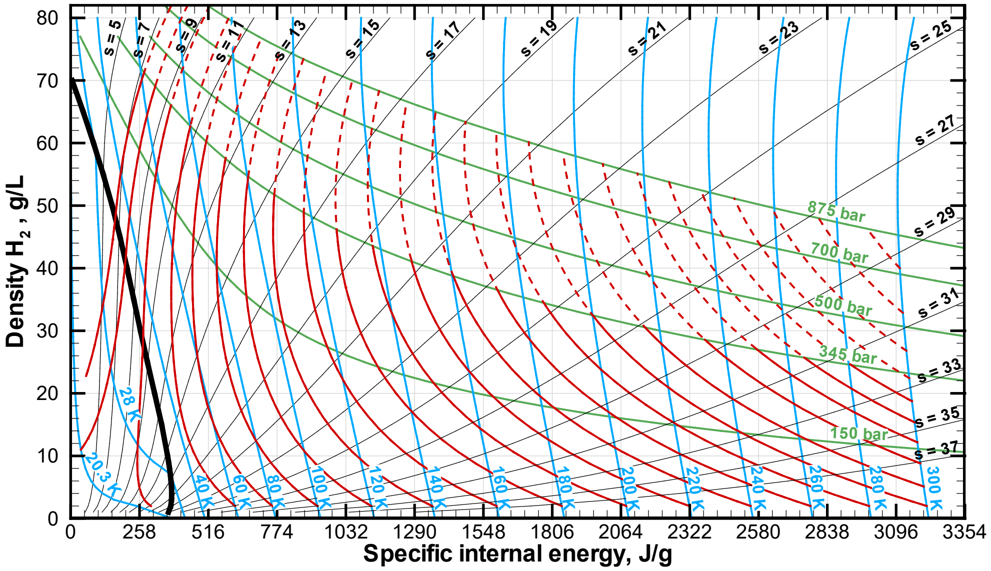

Figure 1. Hydrogen phase diagram showing liquid hydrogen pump fill lines in red. To calculate fill density, identify the initial condition (p_0, T_0) in the diagram, and follow the red line from p_0, T_0 to the final fill pressure. Fill lines assume constant vessel inlet entropy s_{H2} = 10 kJ/kg-K and thermal equilibrium between the experimental vessel and hydrogen inside the vessel.

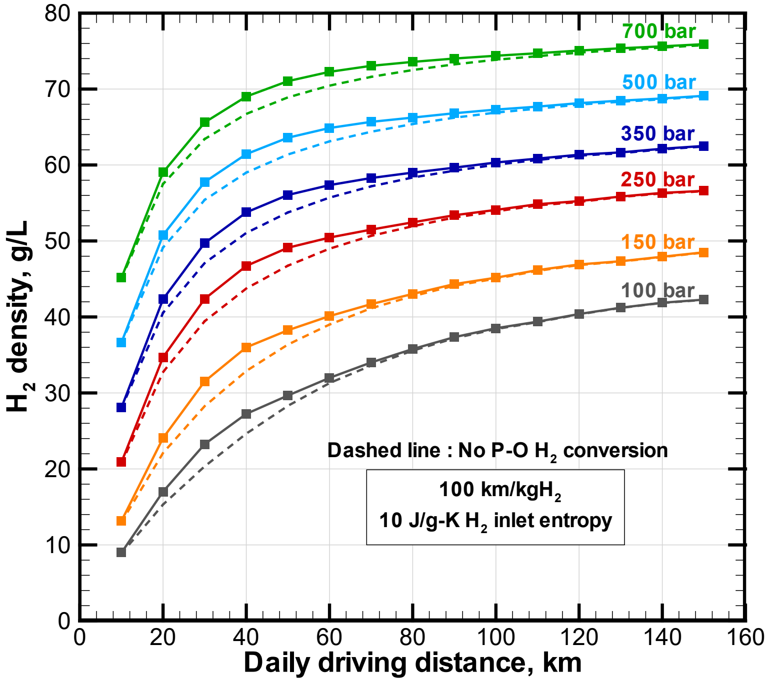

Figure 2. Steady-state fill density for 100-bar to 700-bar vessels continuously driven the same daily distance. In addition to the predicted fill density (solid), the figure shows a dashed line indicating fill density if P-O conversion is absent [2].

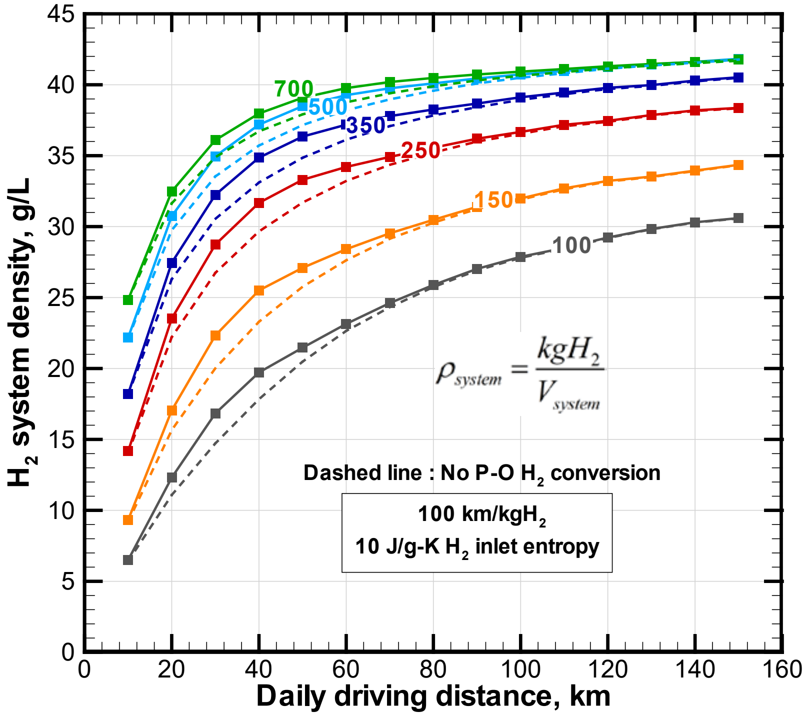

Figure 3. Steady-state system storage density (hydrogen mass divided by total system volume) as a function of daily driving distance and design pressure. Dashed lines indicate system density if P-O conversion is absent.

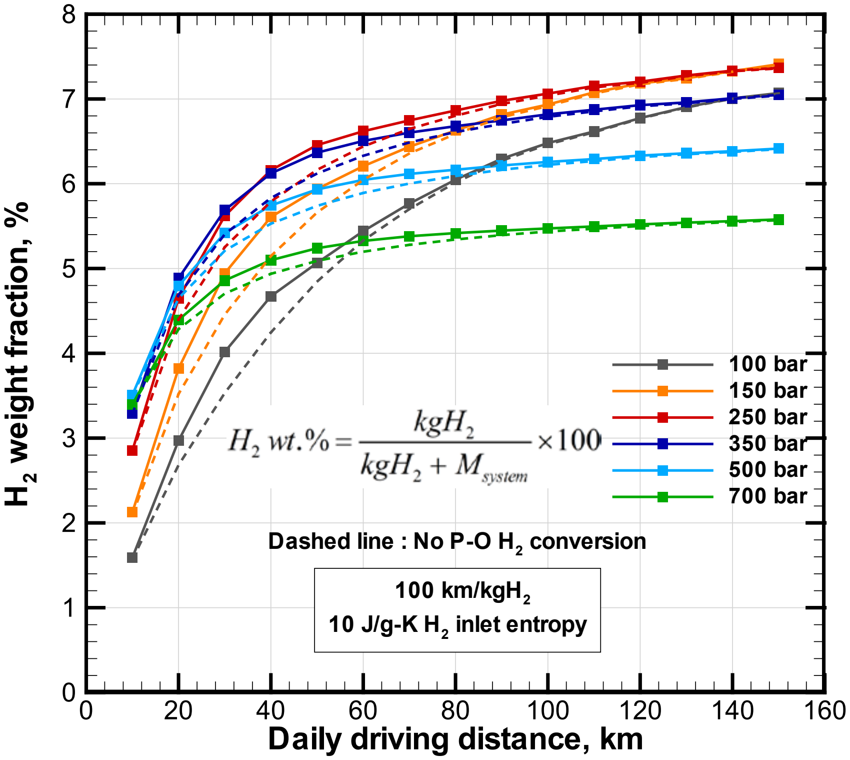

Figure 4. Steady-state system hydrogen weight fraction (hydrogen mass divided by total system weight) as a function of daily driving distance and design pressure. Dashed lines indicate hydrogen weight fraction if P-O conversion is absent.

CONCLUSIONS AND UPCOMING ACTIVITIES

The results confirm previous experiments and models indicating that cryogenic vessels have maximum system density of all available storage technologies and avoid vent losses in all but the most extreme situations. Design pressures in the 250 bar to 350 bar range seem most advantageous due to high system density and low weight and cost, although determining an optimum pressure demands a complete economic and functional analysis.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Cryogenic pressurized storage with hump-reinforced vacuum jacket, Salvador M. Aceves, Francisco Espinosa-Loza, Guillaume Petitpas, Vernon A. Switzer, Elias Rigoberto Ledesma-Orozco, Victor Alfonso Alcantar-Camarena, US Patent 10,082,246, September 25, 2018.

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2. V. Alcántar, S.M. Aceves, E. Ledesma, S. Ledesma, and E. Aguilera. “Optimization of Type 4 Composite Pressure Vessels Using Genetic Algorithms and Simulated Annealing.” *International Journal of Hydrogen Energy* 42 (2017): 15770–15781.

3. J.C. Moreno-Blanco, F. Elizalde-Blancas, A. Gallegos-Muñoz, and S.M. Aceves. “The Potential for Avoiding Hydrogen Release from Cryogenic Pressure Vessels after Vacuum Insulation Failure.” *International Journal of Hydrogen Energy* 43 (2018): 8170–8178.

4. G. Petitpas and S.M. Aceves. “Liquid Hydrogen Pump Performance and Durability Testing Through Repeated Cryogenic Vessel Filling to 700 Bar.” *International Journal of Hydrogen Energy* 43, no. 39 (2018): 18403–18420.
5. Guillaume Petitpas, Julio Moreno-Blanco, Francisco Espinosa-Loza, and Salvador M. Aceves. “Rapid High-Density Cryogenic Pressure Vessel Filling to 345 Bar with a Liquid Hydrogen Pump.” *International Journal of Hydrogen Energy* 43, no. 42 (2018): 19547–19558.

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1. Guillaume Petitpas, Julio Moreno-Blanco, Francisco Espinosa-Loza, and Salvador M. Aceves, “Rapid High-Density Cryogenic Pressure Vessel Filling to 345 Bar with a Liquid Hydrogen Pump,” *International Journal of Hydrogen Energy* 43, no. 42 (2018): 19547–19558.
2. Julio Moreno-Blanco, Guillaume Petitpas, Francisco Espinosa-Loza, Francisco Elizalde-Blancas, Joel Martinez-Frias, and Salvador M. Aceves, “The Fill Density of Automotive Cryo-Compressed Hydrogen Vessels,” *International Journal of Hydrogen Energy* (2018) (in press).
3. Julio Moreno-Blanco, Guillaume Petitpas, Francisco Espinosa-Loza, Francisco Elizalde-Blancas, Joel Martinez-Frias, and Salvador M. Aceves, “The Storage Performance of Automotive Cryo-Compressed Hydrogen Vessels,” *International Journal of Hydrogen Energy* (2018) (submitted for publication).