System Analysis of Physical and Materials-Based Hydrogen Storage

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Project Start Date: October 1, 2004
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Model various developmental hydrogen storage systems.
- Provide results to DOE for assessment of performance targets and goals.
- Develop models to "reverse engineer" particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Fiscal Year (FY) 2019 Objectives

- Support the H2@Scale initiative by analyzing one-way and two-way liquid hydrogen carrier pathways.
- Investigate scenarios for which hydrogen carriers can be cost competitive with the baseline gaseous hydrogen pathway.
- Perform reverse engineering analysis to establish initial targets for production, transmission, and decomposition of hydrogen carriers for overall $2/kg H_2 production cost.
- Analyze the performance and cost of hydrogen bulk storage in different quantities and durations for various applications of interest.
- Determine the performance of on-board hydrogen storage systems for medium-duty and heavy-duty trucks.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life Cycle Assessments.

Technical Targets

This project is conducting system-level analyses to address the DOE 2020 technical targets for on-board hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg
- System volumetric capacity: 1.0 kWh/L
- Minimum hydrogen delivery pressure: 5 bar
- Refueling rate: 1.5 kg/min
- Minimum full flow rate of hydrogen: 0.02 g/s/kW.

FY 2019 Accomplishments

- Determined the scenario for which methanol as hydrogen carrier can be cost competitive with the incumbent technology.
- Proposed initial targets for production, transmission, and decomposition of hydrogen carriers for overall $2/kg H_2 production cost.
- Established the cost of storing 1–3,000 tonnes of hydrogen in underground tubes, lined rock caverns, and salt caverns.

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

- Determined carbon fiber requirements, gravimetric capacities, volumetric capacities, and dormancy for 350-bar, 700-bar, and cryo-compressed hydrogen storage on-board medium-duty and heavy-duty trucks.

INTRODUCTION

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting the DOE targets for light-duty vehicle applications. Each approach has unique characteristics, such as pressure and temperature, the thermal energy and temperature of charge and discharge, and kinetics of the physical and chemical process steps involved. The approaches take into account the requirements for the materials and energy interfaces between the storage system, the fuel supply system, and the fuel user. Other storage system design and operating parameters influence the projected system costs as well. Models are being developed to understand the characteristics of storage systems based on the various approaches and to evaluate their potential to meet the DOE targets for on-board applications—including the off-board targets for energy efficiency.

APPROACH

The approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. These models are then used to identify significant component and performance issues and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. Performance criteria are established that may be used, for example, in developing storage system cost models. Data is refined and validated as the models become available from the various developers. An important aspect of this work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the fuel cell.

RESULTS

Hydrogen Carriers

We initiated a new task last year to analyze liquid hydrogen carrier (LHC) pathways. To take advantage of the economies of scale and favorable location-specific feedstock prices, we updated our scenario as shown in Figure 1. As in our initial study, the annual average daily use of hydrogen for the city (Sacramento, California) is 50 tonnes per day (tpd). This amount of LHC is siphoned from large central production plants located on the Gulf Coast (Texas). Transmission of LHC occurs by (a) unit-train from Texas to a storage terminal near the city gate (3,250 km), and (b) trucks from the storage facility to the city gate for dehydrogenation (150 km).

Figure 1b presents the levelized hydrogen cost at city gate for 50,000 kg-H_2/d (50 tpd) annualized production rate. The costs are broken down for the various steps in the LHC pathway: hydrogen production, LHC production, LHC transmission, LHC decomposition, hydrogen terminal, and distribution to refueling stations. The following is a brief summary of the sources of the changes in levelized costs for different LHC production plant scales and compared to the gaseous hydrogen (GH_2) scenario.

Methanol:

- Comparing large (10,000 tpd) vs. small (350 tpd) methanol plants, LHC production costs are reduced by 2.13 $/kg-$H_2$.
- Approximately half of the cost reduction (0.97 $/kg-$H_2$) is due to lower feedstock prices ($2.65/MBtu vs. $6.80/MBtu natural gas cost) and utility costs.
- Transmission incurs an additional cost of 0.5 $/kg-$H_2$ (unit train delivery every 10 days, 42 railcars).
- Delivered hydrogen cost is competitive with the baseline GH_2 scenario.

Ammonia:

- LHC production costs are reduced by 2.11 \$/kg-H_2 when comparing large (2,500 tpd) vs. small (370 tpd) ammonia plants.
- Approximately 61% of the cost reduction (1.29 \$/kg-H_2) is due to lower feedstock costs (\$2.65/MBtu vs. \$6.80/MBtu natural gas cost).
- Transmission incurs an additional cost of 1.17 \$/kg-H_2 (increased cost relative to methanol due to the need of pressurized railcars).
- The delivered hydrogen cost is 1.53 \$/kg-H_2 higher for the ammonia pathway than for the baseline GH_2 scenario.
- The advantage of the economy of scale is partially offset by higher transmission cost.
- As a carrier, ammonia is a more expensive option than methanol.

Toluene/methylcyclohexane (MCH):

- LHC production costs are reduced by 1.54 \$/kg-H_2 when comparing large (6,700 tpd) vs. small (890 tpd) MCH production plants.
- The majority of the cost reduction (1.41 \$/kg-H_2) is due to lower hydrogen production cost (\$2.65/MBtu vs. \$6.80/MBtu natural gas cost).
- Transmission incurs an additional cost of 1.73 \$/kg-H_2 (the low volumetric hydrogen capacity for MCH [47 g/L] vs. 149 g/L for methanol increases the frequency and number of railcars needed for transmission).
- The delivered hydrogen cost is 1.70 \$/kg-H_2 higher for the toluene/MCH pathway than for the baseline GH_2 scenario.
- The advantage of producing MCH at large scale is more than completely offset by higher transmission cost.

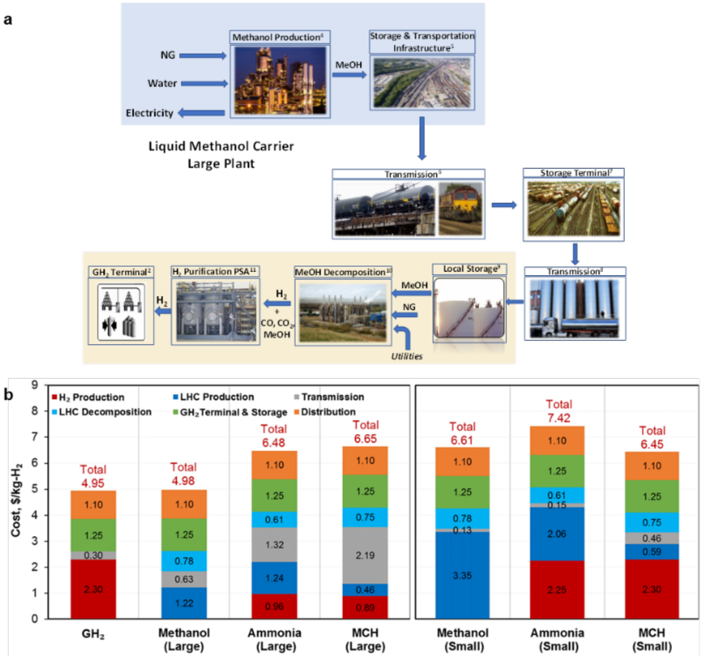

Figure 1. Techno-economic analysis of hydrogen carriers: (a) hydrogen carrier pathway: large production plants; (b) levelized cost of hydrogen distributed to stations (50 tpd-H_2)

We also analyzed the hydrogen production cost at different demands. Figure 2 presents the levelized hydrogen cost at city gate for 10 to 350 tpd annualized production rate. Compared to the GH_2 scenario, methanol may be attractive as hydrogen carrier in the transition phase, at <50 tpd H_2 demand.

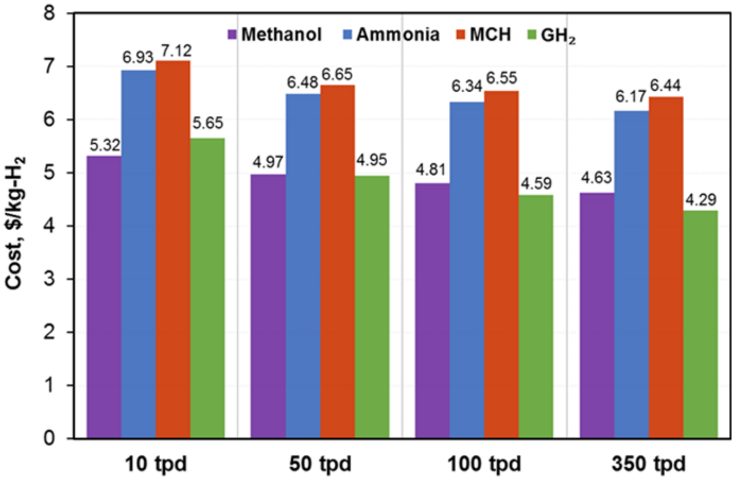

Figure 2. Hydrogen production cost at different demands

Bulk Hydrogen Storage

We initiated a new task to analyze methods for bulk storage of hydrogen. After a literature review, we identified six feasible options for different applications, and to narrow the scope of the study, we considered only large-scale gaseous storage options necessary for outages of hydrogen production plants (10–30 days of daily capacity) and seasonal variations in hydrogen demand. We considered two geological storage options (salt caverns and lined rock caverns) and one geographically agnostic underground pipe storage method. Bottom-up cost analyses were performed for each case and are briefly summarized below.

Underground Pipes

Gas utility companies have installed underground pipe storage facilities since 1980 [1]. This kind of storage vessel is constructed from standard tubes commonly used in trade with a large nominal diameter able to withstand high operating pressures of 64–100 bar. High frequency electric resistance welded pipes are preferred for hydrogen service. As such, electric resistance welded longitudinal seams were assumed in all analyses. API 5L X52 was chosen as the baseline material with different diameter and wall thickness.

We estimated the cost of the underground pipe facility capable of storing 500 tonnes of hydrogen (8 to 100 bar pressure cycle). The lowest capital cost ($516/kg-$H_2$ stored) is achieved when using 24-in. outer diameter, schedule 60 (0.968-in. wall thickness) pipes. As the majority of the cost is due to the manufacturing of the pipes, followed by welding and pressure testing, minimizing the number of pipes and/or pipe mass is important in reducing costs. For example, choosing a pipe with a schedule of less than 60 will increase the number of pipes required to store hydrogen (hydrogen stored at lower pressure) while pipes with a schedule of 60 and greater will incur incremental costs due to additional mass of the pipes and increased welding expenses.

Lined Rock Caverns (LRC)

In regions where salt caverns are absent, rock caverns may provide large storage capacities if locations are available with crystalline and metamorphic strata forming the majority of rocks. Unlined rock caverns have been used to store a wide range of low-vapor-pressure products, mostly liquids such as crude oil, butane, and propane. While there are no commercial storage sites based on the LRC technique, the concept has been successfully demonstrated for natural gas storage in Scandinavia. The reports of the demonstration project have been detailed enough to build a cost model for hydrogen storage and served as a baseline facility [2]. The main cost factors considered in the construction of the LRC storage system consist of two parts: the surface-bound facility and the excavation of the underground facility including the dome enclosure.

We estimated the cost of the LRC facility capable of storing 500 tonnes of hydrogen. The minimum pressure is kept constant at 20 bar while the maximum storage pressure varies from 75 to 300 bar as part of the sensitivity analysis. The lowest capital cost ($56/kg-$H_2$ stored) is achieved when hydrogen is stored at high pressures. The majority of the cost of the LRC is due to the underground facility with the cavern contributing almost half of that cost. The capital cost for LRC is almost 10 times lower compared to the cost of underground pipe storage. However, the applicability of LRC is restricted geographically to finding a suitable rock mass strength that can store hydrogen at high enough pressures.

Salt Caverns

Salt caverns are by far the most important options for natural gas and have been used to store hydrogen at three sites in the United States (Texas) and two sites in the United Kingdom. Low-cost hydrogen storage in salt caverns is especially suitable for very large quantities, but good geological conditions are limited to a few sites [3–4]. In the United States, favorable locations are found in the south (Texas) and the northeast part of the country. As with the LRC storage case, the main cost factors in the construction of the salt cavern storage system consist of two parts: the surface-bound facility and the leached salt cavity.

We estimated the cost of a salt cavern facility capable of storing 500 tonnes of hydrogen. As part of the sensitivity analysis, the cavern depth is varied between 500 and 1,200 m; this affects the maximum pressure at which hydrogen can be stored and the cost of the bore and production tubing. Minimum cushion gas is kept constant at 30% of storage capacity. The main costs are due to the cavern construction followed by aboveground facilities and brine disposal. The capital cost (~$35/kg-$H_2$ stored) is rather insensitive to the maximum storage pressure. As pressure increases, the leaching costs (water and brine disposal) decrease, but the costs of the production tubing and hydrogen compressor increase by almost the same amount.

Figure 3 shows the effect of economy of scale for the three storage options analyzed. LRC and salt caverns exhibit significant cost reductions as the storage amount is increased. Pipe storage facilities, on the other hand, show virtually no cost reduction with scale, as the main cost contribution is due to the manufacturing of the tubes. At large scales (hydrogen stored in excess of 1,000 tonnes), the salt caverns are more economical than lined rock caverns. Underground pipe storage becomes more economical than geological storage for <20 tonnes of usable hydrogen. Even so, the life cycle cost (30 years) of underground pipe facilities is far too high (~$90 kg-$H_2$ stored) to be considered for production plant outages. A suitable application for this storage option would likely be in the smaller scale such as hydrogen storage to meet seasonal and daily peak demands.

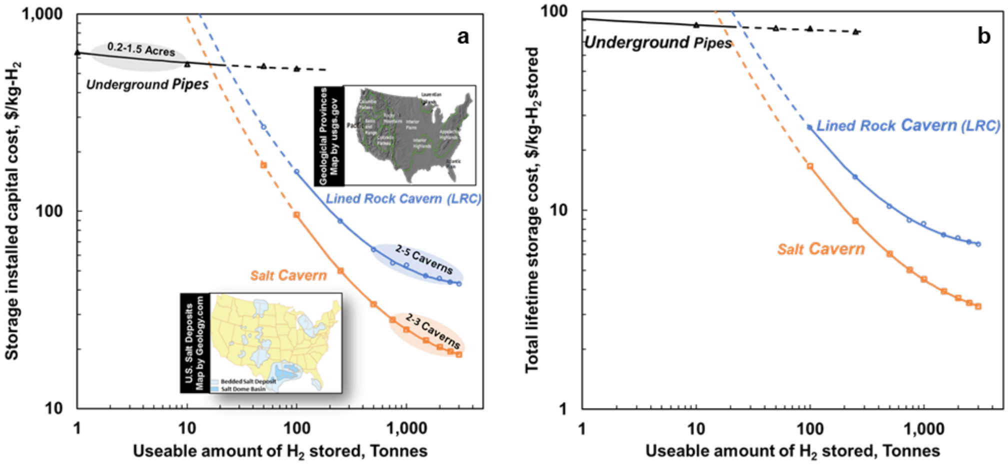

Figure 3. Outlook of bulk hydrogen storage: (a) installed capital cost and (b) yearly storage cost

On-Board Hydrogen Storage Systems for Medium-Duty and Heavy-Duty Trucks

We initiated a new task to analyze the performance of on-board hydrogen storage systems for medium- and heavy-duty trucks using three configurations that are currently offered by A-1 Alternative Fuel Systems for compressed natural gas trucks on different platforms. The available options include two, three, and four Type-

3 or Type-4 tanks for behind-the-cab (BTC) configuration, two Type-3 or Type-4 tanks for frame-mounted (FM) configuration, and four Type-3 tanks for roof-mounted (RM) configuration. The tank volumes range from 246–415 L for BTC configuration, 301–968 L for FM configuration, and 171–298 L for RM configuration. In our study, we consider the same tank sizes for compressed hydrogen (cH_2) storage at 350 bar, cH_2 storage at 700 bar, and cryo-compressed hydrogen (CcH_2) storage at 500 bar.

We conducted ABAQUS/WCM FEA and FE-SAFE simulations to determine the amount of carbon fiber required for 2.25 burst safety factor and 15,000 pressure cycles. As shown in Figure 4a, for the same usable hydrogen, the required amount of carbon fiber composite varies in the following order: CcH_2 << 350-bar Type-3 cH_2 ~ 350-bar Type-4 cH_2 << 700-bar Type-4 cH_2. The future work will collaborate with the Hydrogen Materials Compatibility Consortium to verify fatigue life of stainless steel 316 liner in CcH_2 and Al 6061-T6 alloy liner in cH_2. We will also collaborate with our industrial partners to validate the modeled carbon fiber composite requirements shown in Figure 4a for 700-bar cH_2 tanks.

We conducted storage system simulations to determine the gravimetric and volumetric capacities. As shown in Figure 4b, for the same usable hydrogen, the system gravimetric capacities are aligned in the following order: CcH_2 >> 350-bar Type-4 cH_2 > 700-bar Type-4 cH_2 > 350-bar Type-3 cH_2. The future work will consider mounting of BTC, FM, and RM tanks, structural reinforcement, and safety. We will also update balance-of-plant components and systems for trucks.

Figure 4c indicates that, for the same usable hydrogen, the system volumetric capacities are aligned in the following order: CcH_2 >> 700-bar Type-4 cH_2 > 350-bar Type-4 cH_2 ~ 350-bar Type-3 cH_2. Assuming 10 bar as the minimum or empty tank pressure, the usable amount of hydrogen is 98% for 700-bar storage, 97% for 350-bar storage, and 95% for CcH_2 storage.

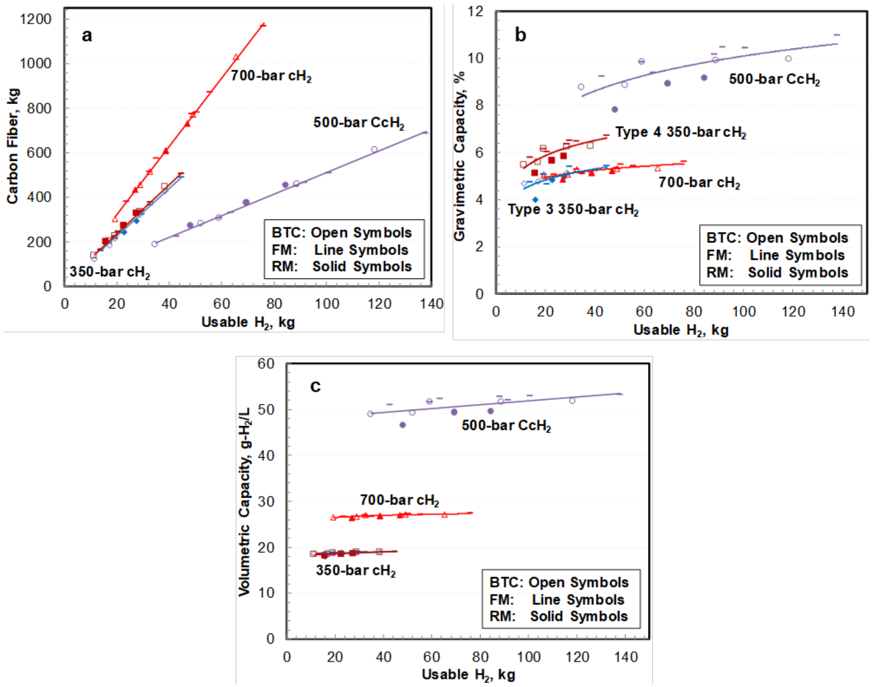

Figure 4. Performance of on-board hydrogen storage systems for trucks using BTC, FM, and RM configurations: (a) carbon fiber requirement; (b) gravimetric capacity; and (c) volumetric capacity

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2019, we:

- Determined the large-scale production and transmission scenario for which methanol as hydrogen carrier can be cost competitive with the baseline gaseous hydrogen pathway at 50-tpd transition stage.

- Proposed initial targets for production, transmission, and decomposition of hydrogen carriers for overall \$2/kg H_2 production cost.
- Established the cost of storing 1–3,000 tonnes of hydrogen in underground tubes, lined rock caverns, and salt caverns.
- Determined carbon fiber requirements, gravimetric capacities, volumetric capacities, and dormancy for 350-bar, 700-bar, and cryo-compressed hydrogen storage on-board medium-duty and heavy-duty trucks.

In FY 2020, we will:

- Investigate scenarios that favor hydrogen carriers, such as byproduct hydrogen, conduct case studies with different demand and supply scenarios, investigate carriers that are particularly suitable for renewable hydrogen production and energy storage, and perform reverse engineering to determine desirable properties of liquid carriers including ease of dehydrogenation and hydrogen purification.

Complete analyses of different storage methods (geological and non-geological), storage capacities (1–10 days), and storage locations (city gate vs. forecourt).

FY 2019 PUBLICATIONS/PRESENTATIONS

1. R.K. Ahluwalia, J.K. Peng, H.S. Roh, T.Q. Hua, C. Houchins, and B.D. James, "Supercritical Cryo-compressed Hydrogen Storage for Fuel Cell Electric Buses," *International Journal of Hydrogen Energy* 43 (2018): 10215–10231.
2. D.D. Papadias, J-K Peng, and R.K Ahluwalia, "Chemical Carrier Concepts for Hydrogen Delivery," International Hydrogen Infrastructure Workshop, Boston, MA, September 11–12, 2018.
3. D.D. Papadias, J-K Peng, and R. K Ahluwalia, "Hydrogen Carrier Analysis," HyMARC Phase 2 Kickoff, Lawrence Livermore National Laboratory, September 26, 2018.
4. T. Autry and R. Ahluwalia, "Hydrogen Carriers for Bulk Storage and Transport of Hydrogen," Fuel Cell Technologies Office Webinar, December 5, 2018.
5. R.K. Ahluwalia, D.D. Papadias, J.K. Peng, and H.S. Roh, "System Level Analysis of Hydrogen Storage Options," Hydrogen Storage Tech Team Meeting, January 17, 2019.
6. R.K. Ahluwalia, J.K. Peng, H.S. Roh, and D. Papadias, "System Analysis of Physical and Materials-Based Hydrogen Storage," FY 2018 Annual Progress Report, DOE Hydrogen and Fuel Cells Program, 2019.

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1. V. Tietze, S. Luhr and D. Stolten, "Bulk Storage Vessels for Compressed and Liquid Hydrogen," *Hydrogen Science and Engineering: Materials, Processes, Systems and Technology* (2016): 659–689.
2. Sofregaz US Inc. *Commercial Potential of Natural Gas Storage in Lined Rock Caverns (LRC)*, Topical Report SZUS-0005 DE-AC26-97FT34348-01 (1999).
3. A. Lord, P.H. Kobos and D.J. Borns, "Geologic storage of hydrogen: Scaling up to meet city transportation demands," *International Journal of Hydrogen Energy* 39 (2014): 15570–15582.
4. A. Liebscher, J. Wackerl and M. Streibel, "Geologic Storage of Hydrogen – Fundamentals, Processing, and Projects," *Hydrogen Science and Engineering: Materials, Processes, Systems and Technology* (2016): 629–658.