

IV.F.1 System Level Analysis of Hydrogen Storage Options

Rajesh K. Ahluwalia (Primary Contact),
J-C Peng, T. Q. Hua and Romesh Kumar
Argonne National Laboratory (ANL)
9700 South Cass Avenue
Argonne, IL 60439
Phone: (630) 252-5979; Fax: (630) 252-5287
E-mail: walia@anl.gov

DOE Technology Development Manager:
Sunita Satyapal
Phone: (202) 586-2336; Fax: (202) 586-9811
E-mail: Sunita.Satyapal@ee.doe.gov

Start Date: October 1, 2004
Projected End Date: September 30, 2009

Objectives

The overall objective of this effort is to support DOE with independent system level analyses of various H₂ storage approaches, to help to assess and down-select options, and to determine the feasibility of meeting DOE targets. Specific objectives in FY 2007 included:

- Model various developmental hydrogen storage systems.
- Analyze hybrid systems that combine features of more than one concept.
- Develop models to “reverse-engineer” particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Technical Barriers

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

- (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 2007 and 2010 technical targets for on-board hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg in 2007, 2 kWh/kg in 2010
- System volumetric capacity: 1.2 kWh/L in 2007, 1.5 kWh/L in 2010
- Minimum H₂ delivery pressure: 8 atm in 2007, 4 atm in 2010
- Refueling time: 10 min in 2007, 3 min in 2010 (for 5 kg H₂)
- Minimum full flow rate of H₂: 0.02 g/s/kW (2007 and 2010)

Accomplishments

- Determined the storage capacity of Lawrence Livermore National Laboratory’s (LLNL’s) cryo-compressed Gen-2 system and the dynamics of liquid H₂ refueling, discharge, and dormancy; completed report and provided input to DOE and independent Systems Integrator on assessment of LLNL’s cryo-compressed tank technology.
- Completed system analysis and issued a status report on the storage capacity of systems with activated carbons at low temperatures and high pressures.
- Issued a joint ANL-United Technologies Research Center (UTRC) status report on the gravimetric and volumetric capacities of metal-hydride storage systems and intrinsic capacities needed to meet 2010 and 2015 targets.
- Evaluated energy consumed in regenerating sodium borohydride using Millennium Cell’s flowsheet input and the overall fuel cycle efficiency; provided input to DOE and independent Systems Integrator on go/no-go decision for sodium borohydride.
- Conducted systems analysis to determine the intrinsic capacities, thermodynamics, and kinetics needed to satisfy storage targets with liquid hydrogen carriers. Completed preliminary analysis of organic liquid carrier system and evaluated storage capacity against 2007 targets.



Introduction

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting DOE targets for light-duty vehicular applications. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the

materials and energy interfaces between the storage system and the fuel supply system on the one hand, and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on these approaches and to evaluate their potential to meet the DOE targets for on-board applications.

Approach

Our approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. We will establish performance criteria that may be used, for example, in developing storage system cost models. The models will be refined and validated as data become available from the various developers. We have formed a Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other DOE analysis projects (such as those of TIAX, Gas Technology Institute [GTI], and the Hydrogen Storage Centers of Excellence) to assure consistency and to avoid duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the hydrogen user (fuel cell system or internal combustion engine [ICE] for on-board systems, on-board hydrogen storage subsystem for the off-board systems, etc.).

Results

Assessment of Cryo-Compressed Tank Approach

We developed dynamic models for refueling, discharge, and dormancy to examine the storage capacity of LLNL's Gen 2 cryo-compressed tank [1] and the associated issue of energy requirements for refueling it. The cryogenic approach allows considerable flexibility in how to fill the tank and use it, such as, for example, as a low pressure liquid hydrogen tank, a high pressure liquid hydrogen tank, a compressed gas tank at cryogenic or ambient temperatures, or combinations of these options. The storage capacity is the smallest, 3.5 kg, if the tank is refueled with compressed hydrogen at 350 bar and ambient temperature. In this case, the energy consumed in storing the hydrogen corresponds to the electrical energy required to compress it. This amounts to 1.985 kWh/kg-H₂ or 6% of the lower heating value of hydrogen, assuming that H₂ is compressed off-board to 125% of the storage pressure [2]. The storage capacity

is the highest, 10.7 kg, if the tank is refueled with liquid hydrogen and the initial tank temperature is less than 180 K. In this case, the energy consumed in storing the hydrogen corresponds to the electrical energy needed to liquefy it at the central plant plus the electrical energy needed to pump it at the refueling station. This total energy amounts to 8 kWh/kg-H₂ or 24% of the lower heating value of hydrogen, assuming a liquefaction plant of 200-tons/day capacity [3]. In both cases, the energy required is for the most optimistic case. For example, the liquefaction energy penalty is more commonly about 30 to 35% of the lower heating value of hydrogen.

The cryo-tank will contain between 6.2 kg and 10.7 kg of hydrogen if the tank is refueled with liquid hydrogen but the initial tank (liner and carbon fiber) temperature is between 180 K and 300 K (see Figure 1). In this case, hydrogen is stored not in a liquid state but, depending on the tank temperature at the beginning of the refueling operation, as compressed cryo-gas or a two-phase mixture of liquid and gaseous hydrogen. Regardless of the initial tank temperature, 10.7 kg of liquid hydrogen can always be stored if the tank is equipped with a vent valve and refueled using a feed and bleed procedure. In this case, more than 10.7 kg of liquid hydrogen must be fed to the tank; the amount in excess of 10.7 kg boils off to cool the tank to 180 K. The amount that boils off and discharges through the vent valve to be collected (and re-liquefied) off-board depends on the initial tank temperature: it is >10.7 kg at 300 K initial temperature, 5.4 kg at 200 K initial temperature, and zero at <180 K initial temperature.

Results from the dynamic discharge simulations indicate that an in-tank heater is needed to maintain H₂ above the minimum discharge pressure. The stored hydrogen may undergo complex phase transitions during charging and discharging. For example, subcooled liquid H₂ changes to a liquid-gas mixture as H₂ is withdrawn

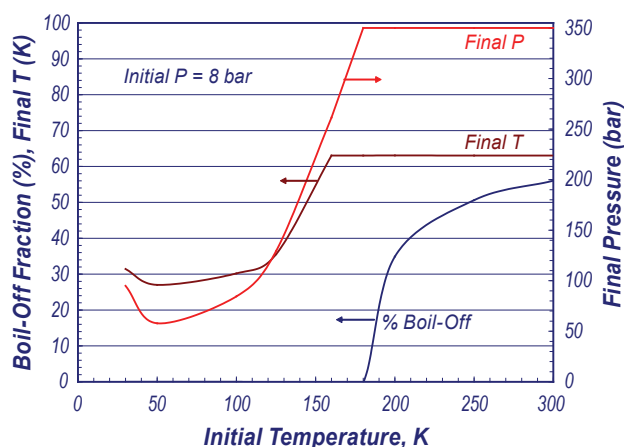


FIGURE 1. High Pressure Refueling of Cryo-Tank With liquid H₂

and then to superheated gas. Conversely, H_2 stored as compressed cryo-gas may liquefy upon expansion as H_2 is withdrawn and further transform to superheated gas as it is heated to maintain the minimum delivery pressure.

One of the key advantages of LLNL's approach is improved dormancy compared to standard liquid hydrogen technology. Dormancy depends on the initial state of stored H_2 and the relief pressure. Assuming that H_2 is vented if the pressure exceeds 425 bar, we estimate a dormancy of 10 Wd (watt-days) for cryo-gas at 350 bar and 63 K and 40 Wd if H_2 is stored as a liquid at 58 bar and 27 K (note that 1 Wd is equivalent to the heat gained at a rate of 1 W over 24 hours). For the latter case, this amounts to more than ten times improved dormancy as compared to standard cryogenic storage systems which vent at about 10 bar [4].

The recoverable storage capacity, which depends on the minimum delivery pressure and the rating of the in-tank heater, of the LLNL's Gen 2 system is estimated to be about 94%. We estimate that the system has 4.7 wt% recoverable gravimetric capacity and $\sim 30 \text{ kg/m}^3$ volumetric capacity. As shown in Figure 2, it may be possible to increase the gravimetric capacity to 5.7 wt% (close to the 2010 target of 6 wt%) by using a lighter-weight aluminum alloy in place of stainless steel for the outer shell of the cryo tank. Similarly, it may be possible to increase the volumetric capacity to $\sim 33 \text{ kg/m}^3$ with improved packaging and thinner insulation. Changes that are more significant will be needed to satisfy the 2010 target of 45 kg/m^3 . Throughout this work, discussions were held with industry developers, DOE's independent Systems Integrator and LLNL. Details were also provided to analysts at TIAX who conducted a cost analysis as part of a separate DOE-funded project.

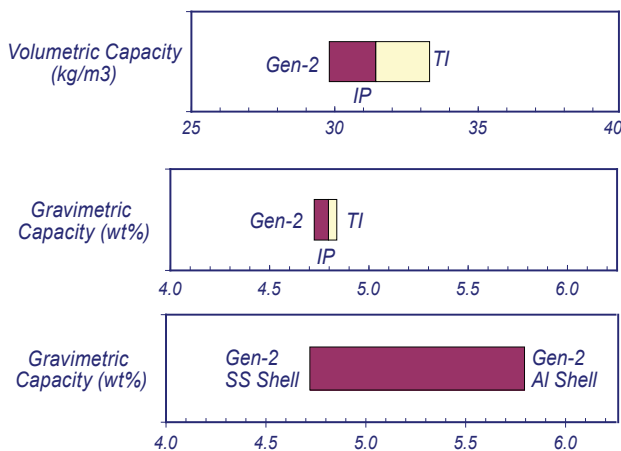


FIGURE 2. Summary of Sensitivity Analyses: Recoverable Storage Capacity of System

Hydrogen Storage in a Liquid Carrier

We analyzed the potential performance of an on-board liquid carrier hydrogen storage system with respect to its available capacity and energy efficiency. Figure 3 shows a method of integrating the storage system with the fuel cell system by controlling the hydrogen utilization such that the thermal energy needed for the dehydrogenation reaction comes from burning the remaining hydrogen with the spent cathode air. The burner exhaust is expanded in a gas turbine to recover additional energy in this pressurized system.

The dehydrogenation reactor in Figure 3 is a critical component of this system. We developed a model to study its performance by incorporating dehydrogenation kinetics into a hydrodynamics model of a trickle bed reactor (TBR). The kinetic constants were determined by analyzing the data from the conversion of N-ethylcarbazole in a batch reactor with 4% Pd on lithium aluminate as the powdered catalyst [5]. The overall model was validated by comparing its results with data from a small TBR with palletized catalyst [5]. The validated model was then used to assess the performance of a TBR in an automotive system using 3-mm-pelletized catalyst with a bulk density of 800 kg/m^3 and in-bed heat exchange tubes. We found that the conversion of N-ethylcarbazole was constrained by mass transfer limitations. For a compact TBR, it is desirable to operate at a liquid hourly space velocity (LHSV) of 20 h^{-1} , but at that rate, conversion of the liquid carrier was unacceptably low. We also developed a concept for dispersing the catalyst on a foam which led to much improved performance. It appears possible to reach the target LHSV with a 50- μm -thick washcoat of the catalyst on a 92% porous 40-ppi Al-6101 foam (bulk density 224 kg/m^3). It should be noted, however, that a trickle flow reactor with foam has not yet been tested experimentally. These results were shared with one of the developers of liquid carriers within the DOE program (Air Products and Chemicals, Inc. [APCI]) and subsequent tests with and without catalyst washcoats are now underway. We will continue to interact with APCI to develop and refine the analyses as required.

Figure 4 presents the modeling results for the on-board storage system efficiency, reactor heat duty, and the reactor temperature, each as a function of the enthalpy of the dehydrogenation reaction. Here, the storage system efficiency is defined as the fraction of hydrogen released in the dehydrogenation reactor that is available for use in the fuel cell stack (the balance being directed to the burner to provide the heat for the dehydrogenation reaction). The storage system efficiency is $<68\%$ for N-ethylcarbazole ($\Delta H=51 \text{ kJ/mol}$) but could be $>82\%$ if an alternative carrier is found that has a ΔH of 35 kJ/mol . The corresponding reactor heat duty would decrease from 83 kW to 44 kW (at the maximum 2 g/s rate of H_2 delivery to a 100-kW

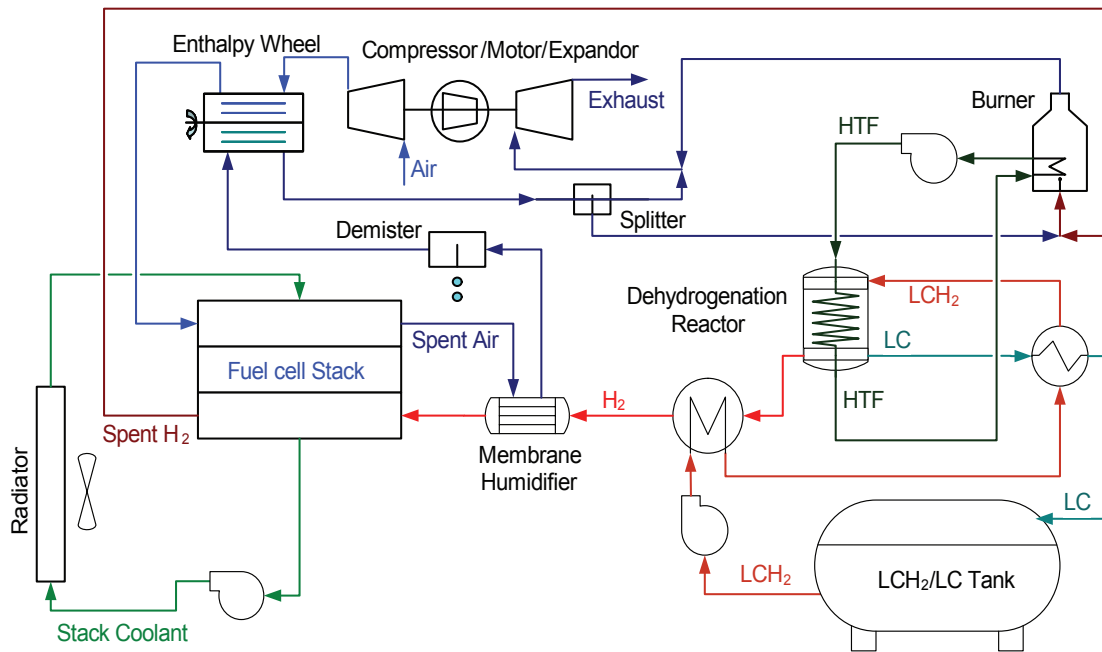


FIGURE 3. Fuel Cell System With H₂ Stored in a Liquid Carrier

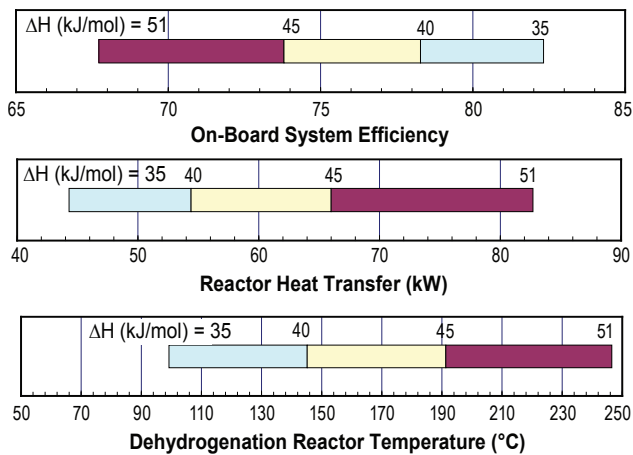


FIGURE 4. On-Board Storage System Efficiency, Reactor Heat Transfer, and Reactor Temperature

fuel cell system) and the reactor temperature would decrease from 246°C to 98°C (assuming that the reactor temperature is 50°C higher than the equilibrium liquid carrier decomposition temperature). The storage system efficiency can be nearly 100% if $\Delta H < 40$ kJ/mol, and the catalyst is sufficiently active so that the reactor temperature can be less than the fuel cell operating temperature (i.e., the fuel cell waste heat can be used for the liquid carrier dehydrogenation reaction).

We also conducted analyses to “reverse engineer” a liquid hydrogen carrier system to determine the intrinsic material properties that would be needed to meet the

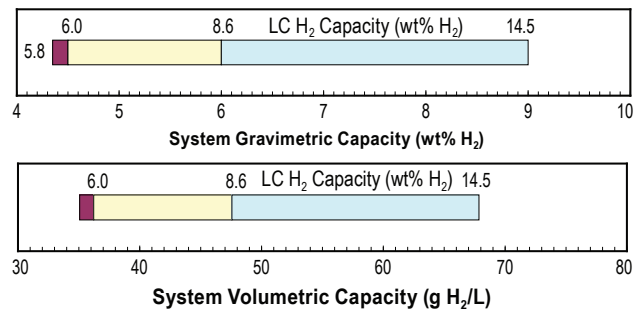


FIGURE 5. Reverse Engineering Analysis Results for H₂ Storage Capacity

system-level targets for gravimetric and volumetric capacities. Figure 5 summarizes the calculated system capacities expressed on the basis of stored H₂, assuming a 20-g H₂ buffer to provide for power transients. As such, the values in Figure 5 should be first multiplied by the conversion in the reactor to estimate the recoverable capacity, and then by the storage system efficiency to determine the usable capacity. For example, the system capacity based on stored H₂ is 4.4 wt% or 35 g-H₂/L for N-ethylcarbazole, which has an intrinsic material capacity of 5.8 wt% H₂. Assuming 95% conversion in the dehydrogenation reactor and 68% storage system efficiency for N-ethylcarbazole, this translates to 2.8 wt% and 23 g/L system capacity based on usable H₂. These analyses show that as long as the temperature required to dehydrogenate the liquid carrier is higher than the waste heat from the fuel cell (<80°C), there is

a significant penalty in total system capacity due to the need for burning hydrogen. Either the material-based capacity must be increased significantly (in this example only 5.8 wt% was used) or the enthalpy of reaction and dehydrogenation temperature must be reduced.

Conclusions and Future Directions

- A detailed analysis was completed on LLNL's cryo-compressed tank design for input to DOE's independent assessment. Results show that the system can achieve 4.7 wt% (exceeding the 2007 target) and 30 kg/m³ (approaching the 2007 target of 36 kg/m³). The cryo-compressed option may achieve reversible capacities of 5.6 wt% and 33 kg/m³ with improved packaging and thinner insulation, but meeting the 2010 volumetric target is a challenge with the current design.
- The storage capacity during refueling of a pressure-capable cryo-tank depends on its initial temperature. It is possible to refuel the tank to its maximum capacity regardless of the initial temperature by using a feed and bleed arrangement, but at the expense of additional energy expended in cooling the tank.
- Depending on the initial state of stored H₂, 10-40 Wd of extended dormancy is possible with a cryo-tank designed for service at 350 bar.
- The first systems-level analysis for liquid/organic hydrogen carriers was completed for DOE. Developing a compact reactor for dehydrogenation of liquid hydrogen carriers will likely require dispersing the catalyst on a high surface area support. The system capacity based on stored H₂ was found to be 4.4 wt% or 35 g-H₂/L for N-ethylcarbazole, which has an intrinsic material capacity of 5.8 wt% H₂. However, due to the hydrogen that must be burned to achieve the required performance, the actual net system capacity is 2.8 wt% and 23 g/L based on usable H₂ (assuming 95% conversion in the dehydrogenation reactor and 68% storage system efficiency).
- Achieving >90% storage efficiency will require a liquid carrier with $\Delta H < 40$ kJ/mol.
- Preliminary results from our systems analyses suggest that we need a liquid carrier with an intrinsic capacity of 8.6 wt% H₂ to satisfy the 2010 system-level targets of 6 wt% and 45 kg/m³. The intrinsic material capacity has to be ~15 wt% H₂ to satisfy the 2015 system target of 9 wt%; also, the buffer storage has to be reduced to meet the volumetric target of 81 kg/m³.

Future plans include:

- Work with APCI in analyzing advanced options for liquid carriers, catalysts, reactors, and system configurations.

- Analyze a metal-hydride hydrogen storage system using the material identified as most promising by Metal Hydride Center of Excellence and conduct reverse engineering to determine the material properties needed to satisfy the capacity targets.
- Continue to conduct independent analyses in FY 2008 to support DOE's go/no-go decisions and to collaborate with TIAX in cost analyses of viable hydrogen storage options.

FY 2007 Publications/Presentations

1. R. K. Ahluwalia, "Sodium Alanate Hydrogen Storage System for Automotive Fuel Cells," accepted for publication in the *Int. J. Hydrogen Energy*, 2006.
2. R. K. Ahluwalia, T. Q. Hua, and J-K Peng, "Fuel Cycle Efficiencies of Different Automotive On-Board Hydrogen Storage Options," accepted for publication in the *Int. J. Hydrogen Energy*, 2007.
3. R. K. Ahluwalia, J-K Peng, and G. Thomas, "Performance of On-Board Metal-Hydride Hydrogen Storage Systems," *Materials Research Society (MRS) Meeting, Symposium Z: Hydrogen Storage Technologies*, Boston, MA, November 27-30, 2006.
4. T. Q. Hua and R. K. Ahluwalia, "SBH Regeneration Analysis: Energy Requirements and Efficiency," *Storage Systems Analysis Working Group Meeting*, Washington, D.C., 12 December 2006.
5. R. K. Ahluwalia, T. Q. Hua, and J-K Peng, "On-Board Hydrogen Storage System Using a Liquid Carrier," *FreedomCAR and Fuels Partnership Analysis Workshop*, Columbia, MD, May 8-9, 2007.

References

1. S. Aceves, G. Berry, F. Espinosa, T. Ross and A. Weisberg, "Insulated Pressure Vessels for Vehicular Hydrogen Storage," 2006 *DOE Hydrogen Program Review*, Arlington, VA, May 16-19, 2006.
2. R. K. Ahluwalia, T. Q. Hua and J. K. Peng, "Fuel Cycle Efficiencies of Different Automotive On-Board Hydrogen Storage Options," *Int. J. Hydrogen Energy*, in press, 2007.
3. B. Kelly, "Liquefaction and Pipeline Costs," *Hydrogen Delivery Analysis Meeting*, Columbia, MD, May 8-9, 2007.
4. S. M. Aceves, G. D. Berry, J. Martinez-Frias and F. Espinosa-Loza, "Vehicular Storage of Hydrogen in Insulated Pressure Vessels," *Int. J. Hydrogen Energy*, 31, 2274-2283, 2006.
5. G. P. Pez, A. R. Scott, A. C. Cooper, and H. Cheng, "Hydrogen Storage by Reversible Hydrogenation of Pi-Conjugated Substrates," *Patent US 200402239071A1*, Nov. 11, 2004.