IV.A.1 System Analysis of Physical and Materials-Based Hydrogen Storage

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

Overall Objectives

- Model various developmental hydrogen storage systems
- Provide results to Hydrogen Storage Engineering Center of Excellence (HSECoE) 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) 2015 Objectives

- Performed ABAQUS analysis of improved Type 4 tank design that has the potential to reduce carbon fiber (CF) requirement
- Determine relationship between high-density polyethylene (HDPE) liner properties and liner failure at cryogenic temperatures to support cryo/cold H_2 storage
- Determined well-to-wheel energy consumption and fuel cost for cold hydrogen storage
- Establish chemical hydrogen material properties needed to satisfy onboard and off-board storage system targets

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:

(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 2017 technical targets for onboard hydrogen storage systems:

- System gravimetric capacity: 1.8 kWh/kg
- System volumetric capacity: 1.3 kWh/L
- Minimum H_2 delivery pressure: 5 bar
- Refueling rate: 1.5 kg/min
- Minimum full flow rate of H_2: 0.02 g/s/kW

FY 2015 Accomplishments

- ABAQUS analysis was conducted to determine HDPE liner behavior at cryogenic temperatures. The analysis predicted liner failure at -190°C for a liner with stiffness of 6 GPa and liner separation from the composite if tank pressure is below 3.2 MPa. ABAQUS analysis revealed high stress concentration at the liner/boss interface corners with peak stress approaching the liner tensile strength if the tank is kept at -190°C and 63 MPa internal pressure.
- Off-board analysis was performed for the cold gas storage option and determined that fuel cost is about 5% higher than baseline (700 bar compressed H_2) but onboard cost is ~20% lower. The well-to-wheel energy efficiency is about six percentage points lower than baseline.
- We formulated models and performed reverse engineering to determine thermodynamic properties of chemical hydrogen materials needed to meet onboard system and off-board well-to-engine efficiency targets.

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INTRODUCTION

Several different approaches are being pursued to develop onboard hydrogen storage systems with the goal of meeting the DOE targets for light duty vehicle 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 the various approaches and to evaluate their potential to meet the DOE targets for onboard applications, including the off-board targets for energy efficiency.

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 establish performance criteria that may be used, for example, in developing storage system cost models. We refine and validate the models as data become available from the various developers. We work with the Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other analysis projects 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 fuel cell.

RESULTS

Physical Storage

We conducted ABAQUS analysis of HDPE liner in Type 4 tanks for cold gas storage. We obtained the tensile stress strain data for HDPE from Pacific Northwest National Laboratory (PNNL) for two different temperatures, 25°C and -190°C [1]. The samples were prepared by injection, extrusion, or cut from a sheet. Two types of sheet samples were used, differing in the Young's modulus (2 GPa and 6 GPa). The data were fitted for input to ABAQUS for our analysis. We analyzed a typical Type 4 tank (length to diameter ratio = 3) which holds 5.6 kg recoverable hydrogen. The hoop and helical thicknesses of the carbon fiber composite were determined for nominal 500 bar storage pressure with a 2.25 safety factor. The HDPE liner is assumed to be 5 mm thick.

Figure 1 shows the calculated stresses in the liner with different Young's modulus. Initially the tank has an inner pressure of 2 MPa and is at room temperature. The small inner pressure does not cause the tank to deform; as a result the liner experiences a small compressive stress (black lines). As the tank cools down to -190°C, the inner pressure acts to oppose liner shrinkage causing the liner to be under tension. The axial and hoop tensile stresses (blue curves) are higher for the stiffer liner (6 GPa) but remain below the tensile strength. Increasing the inner pressure from 2 MPa to 63 MPa introduces compressive stress in the "soft" liner (E = 2 GPa). This is due to the larger deformation in the liner than the deformation of the tank in both the axial and

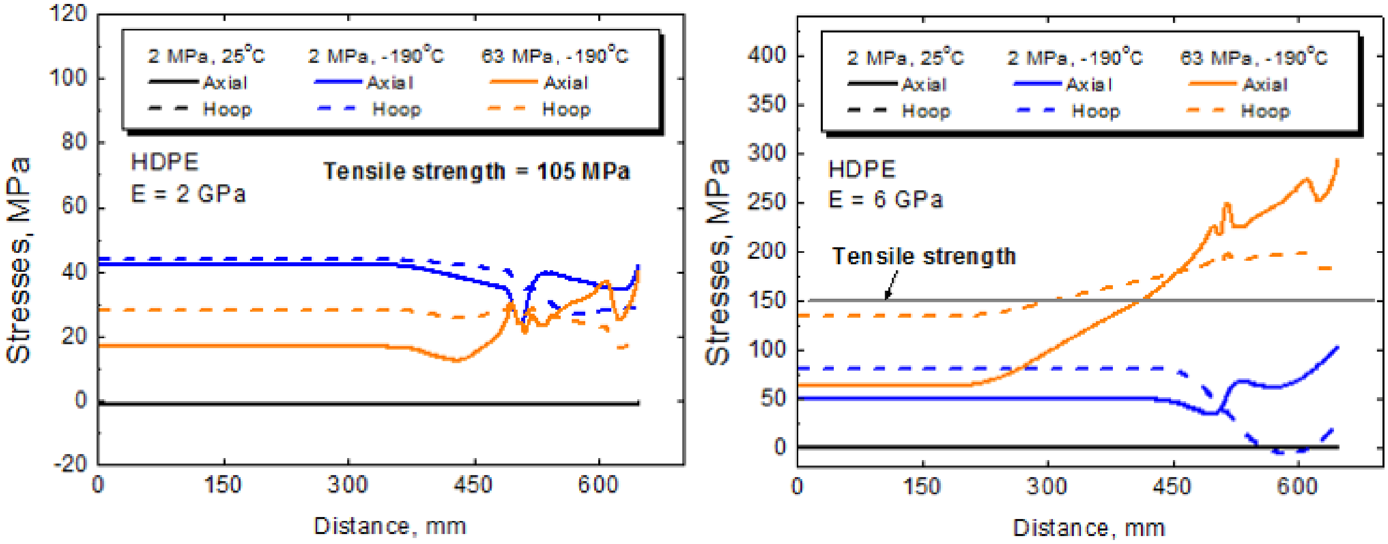


FIGURE 1. Axial and circumferential stresses in the HDPE liner for E = 2 and 6 GPa

hoop directions. The compressive stress has the net effect of reducing the tensile axial stress to 17 MPa and the hoop stress to 28 MPa. In the "stiff" liner (E = 6 GPa), increasing the inner pressure from 2 MPa to 63 MPa results in an increase in the tensile stress which exceeds the tensile strength of the liner. Under this scenario, liner failure is predicted.

Figure 2 shows that at -190°C, there is a minimum inner pressure needed to avoid liner separation as a result of the difference in the coefficients of thermal expansion (CTE) between liner and the composite. The gap can be as large as 6.4 mm in the dome and 2.8 mm in the cylinder if the tank is empty. The gap in the cylinder is eliminated and reduces to 1.3 mm in the dome if the tank has an inner pressure of 2 MPa. No gap exists when the pressure exceeds 3 MPa.

Additionally, ABAQUS simulations of the full-sized tank reveal high stress concentration region at the interface corners between the liner and the aluminum boss. At room temperature and inner pressure of 2 MPa, the peak stress at the interface is 1.9 MPa and increases 25-fold to 48 MPa when the tank is cooled to -190°C due to CTE mismatch between the HDPE liner and Al-6061 boss. The peak stress approaches the tensile strength of the liner (105 MPa) when the tank is further pressurized to 63 MPa at -190°C. For comparison, testing of two Type 4 tanks at liquid nitrogen (LN_2) temperature by Hexagon Lincoln showed that both tanks leaked at <28 MPa and cracks occurred at the liner–boss interface [2].

We analyzed an off-board delivery pathway for cold gas. Hydrogen is produced by steam methane reforming, transmitted via pipeline to the gas terminal at city gate. At the gas terminal, H_2 is compressed to 340 bar, then cooled to 83 K using LN_2 for storage in trailer tubes which are transported to the forecourt by tube trailers. Liquid nitrogen production plant is assumed to co-locate with the gas terminal. At the forecourt, the cold gas is compressed to 1.35x the nominal onboard storage pressure and stored in insulated Type 3 tube banks for cascade refueling. We conducted netting analysis (calibrated with ABAQUS model) to determine the weight, volume, and hydrogen capacity for the trailer tubes constrained by the International Organization for Standardization container dimensions and trailer payload for both baseline (700 bar, 300 K onboard) and cold gas storage (400 bar, 200 K onboard). Similar analysis was also carried out for the cascade storage tubes at the forecourt. As presented in Table 1, the amount of carbon fiber composite required for baseline is ~2.6x the requirement for cold gas. While the cost of CF is lower, the cold trailer tubes incur added cost for vacuum insulation. We estimated that the cold gas trailer tubes were ~38% lower in total cost due to the substantial reduction in CF requirement.

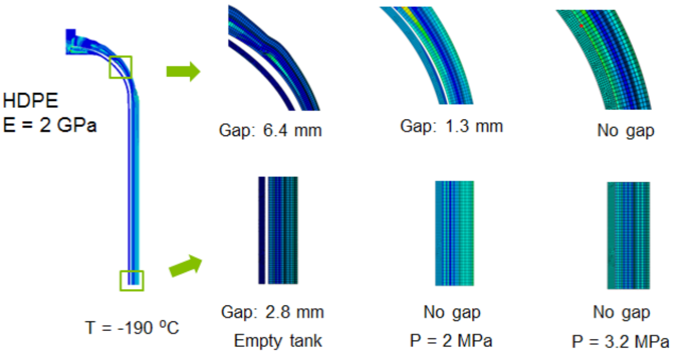


FIGURE 2. Gaps between the HDPE liner and the composite at -190°C

The off-board primary energy consumption for cold gas option is equivalent to ~ 60% of the lower heating value of hydrogen, and is ~73% higher than for baseline. The well-to-tank efficiency for cold gas storage was less than 50%, approximately six percentage points lower than baseline (Figure 3). The reduction is due primarily to the significant amount of electricity consumed to produce liquid nitrogen (7 kg LN_2/kg H_2) for cooling H_2 to 83 K at the gas terminal. We estimated that the off-board cost for cold gas is \$0.18–\$0.31/kg H_2 higher than baseline due to significantly higher costs at the gas terminal partially offset by lower costs at the forecourt and lower tube trailer costs.

Hydrogen Storage in Chemical Hydrogen Materials

We conducted a reverse engineering analysis to determine the minimal material requirements for a chemical hydrogen storage system to meet the DOE 2017 performance targets. Materials with negative free energy of decomposition (ΔG) are thermodynamically unstable at room temperature and are stabilized by extremely slow kinetics (e.g., alane, AB) or by other chemical means (addition of 3% NaOH to aqueous $NaBH_4$). Materials with positive ΔG (e.g., n-ethylcarbazole) are stable at room temperature. They can be decomposed at elevated temperatures or require a catalyst for sufficient kinetics at low temperatures. Results from our previous

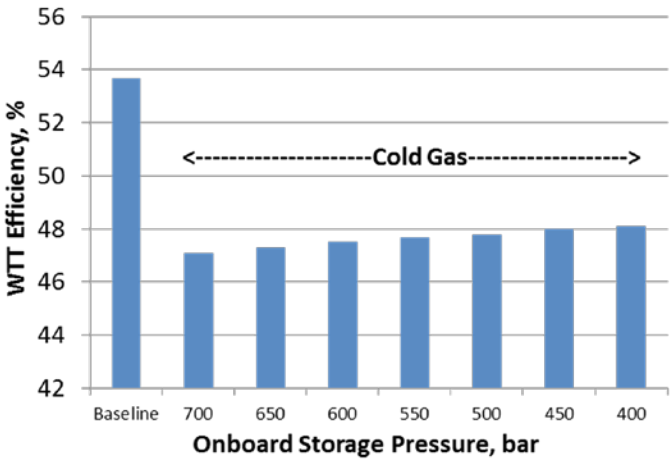


FIGURE 3. Well-to-tank (WTT) efficiency for ambient and cold gas storage

TABLE 1. Physical Parameters and CF Requirements for Storage Tubes

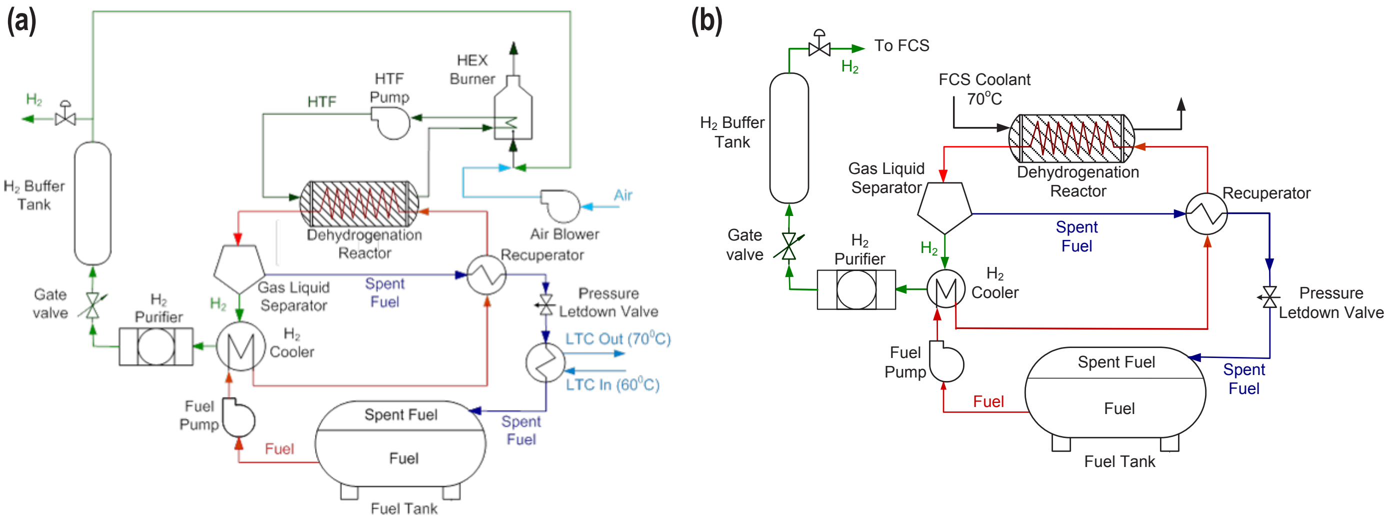
	Unit	Trailer Tube		Cascade Storage Tube	
		Baseline	Cold Gas	Baseline	Cold Gas
Type		4	3	3	3
Nominal Storage Pressure	bar	340	340	945	534
Minimum Pressure	bar	15	15	varies	varies
Nominal Storage Temperature	K	300	83	300	116
H_2 Stored	kg	116	137	46	45.3
H_2 Volume	m^3	5.1	2.25	0.96	0.77
Outside Length	m	12.1	11.1	5.8	5.1
Outside Diameter	m	0.79	0.56	0.58	0.51
Carbon Fiber Composite Weight	kg	1,148	425	712	278
Liner (Al or HDPE) Weight	kg	138	402	190	189
Shell Weight	kg	-	487	-	329
Total Tube Weight	kg	1,421	1,483	958	856

regeneration analyses for $NaBH_4$, AlH_3, AB, CBN, and LCH_2 were used to develop correlations between regeneration primary energy and free energy of decomposition. Three sets of correlations were obtained for low, medium, and high regeneration efficiencies. It was found that materials with large positive ΔG require elaborate regeneration processes with high demand for primary energy while materials with negative ΔG (rehydrogenation reaction is exothermic) or small positive ΔG require significantly less primary energy for regeneration. To achieve well-to-tank regeneration efficiencies of 50–60%, the free energy of decomposition should exceed 1.6 kJ/mol if ΔG(298 K) is positive and >-6.4 kJ/mol if ΔG(298 K) is negative. Over this narrow range of the desired ΔG(298 K) and for the expected material entropy in the range of 80–130 J/mol K, the enthalpy of reaction ΔH needs to be between 20 kJ/mol H_2 and 40 kJ/mol H_2, therefore exothermic materials are unsuitable. It was also noted that materials that decompose above the fuel cell system (FCS) coolant temperature (a burner is needed to provide the heat for decomposition) may not be acceptable since the onboard system efficiency is <70% for ΔH = 40 kJ/mol-H_2. It is desirable to have a class of materials that can decompose at 60–80°C using the FCS waste heat, mostly likely as a catalytic process in the reactor, otherwise the material would have short shelf life. Additionally, the desired decomposition kinetics should be independent of back pressure because the equilibrium hydrogen partial pressure at these conditions are too low, and as a result, the onboard buffer tank would have to be refueled with high pressure gaseous H_2 at the forecourt, a scenario that is unlikely to be acceptable.

Two onboard systems were analyzed, one with a burner and one without. The main system components include a volume exchange fuel tank, a hydrogen buffer tank for start-up and to accommodate fast transients, a reactor that operates at elevated pressure, reaction kinetics that are independent of back pressure, and heat exchangers (Figure 4). The fuel may be liquid, slurry, or in solution. For systems with a burner, a 50-kW microchannel HEX burner is used. For a reactor that operates at 150°C and ΔH = 40 kJ/mol H_2, the target usable gravimetric capacity of the material is 21 wt% H_2 with a volumetric capacity of 114 g H_2/L. The material capacity targets are strong functions of reactor temperature and ΔH. It was difficult to meet the 90% onboard system efficiency if a burner is needed. For systems without a burner, the reactor is thermally integrated with the FCS and provides an advantage of mitigating the FCS heat rejection problem. For a reactor that operates at 70–80°C with 100-bar back pressure, the target material capacity is 9.6 wt% H_2 with a material volumetric capacity of 68.5 g H_2/L. The baseline material targets for a system without a burner are summarized in Table 2.

CONCLUSIONS AND FUTURE DIRECTIONS

- The analysis results of HDPE liner behavior at cryogenic temperatures indicated that the tank fails at -190°C and 63 MPa internal pressure, and there is a minimum required internal pressure of 3 MPa to avoid liner separation at near LN_2 temperature. At -190°C, the peak stress at the liner/boss interface corners exceeds the tensile stress and could result in tank leakage
- The analysis results for cold gas storage showed that it has the potential to meet the gravimetric capacity target but is unlikely to meet the volumetric capacity target. The fuel cost is ~5% higher than baseline, off-



LTC – Low temperature coolant

FIGURE 4. Schematics of onboard system for chemical hydrogen storage material (a) with a burner and (b) without a burner

TABLE 2. Baseline Material Targets for a System with a Burner

		Units	Reference	Range of	Comments and Relevant
			Values	Values	Targets
Chemical Storage Material	Free Energy of Decomposition	kJ/mol	-1.6	-6.4 to 1.6	60% WTE efficiency
	Enthalpy of Decomposition	kJ/mol	40	20 to 40	90% on-board system efficiency
	Fuel Hydrogen Capacity	wt% H_2	TBD	TBD	5.5 wt% system gravimetric capacity
	Fuel Volumetric Capacity	g-H_2/L	TBD	TBD	40 g/L system volumetric capacity
	Decomposition Kinetcs		TBD	TBD	Avrami kinetics, 0.05 g/s/kg H_2 loss rate
Operating	Dehydrogenation Reactor	°C	150	150 - 250	1.6 g/s minimum full flow of H_2
Temperatures	Heat Transfer Fluid (HTF)	°C	200	200 - 300	
	Recuperator	°C	100	100 - 200	
Operating	Storage Pressure	bar	100	50 - 200	
Pressures	Minimum Delivery Pressure	bar	5		DOE target
H_2 Flow	Refueling Rate	kg/min	1.5		Not relevant for liquid fuels
Rates	Minimum Full Flow Rate	g/s	1.6		DOE target
Buffer H_2	Storage Pressure	bar	100	50 - 200	Start-up from -40°C
Storage	Buffer Storage Capacity	g-H_2	TBD	TBD	

WTE – Well-to-engine; TBD – to be determined

board cost for cold gas is \$0.18–\$0.31/kg H_2 higher, but onboard system cost is ~20% lower than baseline. The well-to-tank efficiency for cold gas is approximately six percentage points lower than baseline and is unlikely to meet DOE targets.

- The results from reverse engineering analysis of a chemical hydrogen material showed that to achieve well-to-tank regeneration efficiencies of 50–60%, the free energy of decomposition should exceed 1.6 kJ/mol if ΔG(298 K) is positive and >-6.4 kJ/mol if ΔG(298 K) is negative. Over this narrow range of the desired ΔG(298 K) and for the expected material entropy in the range of 80–130 J/mol K, ΔH needs to be between 20 kJ/mol H_2 and 40 kJ/mol H_2; therefore, exothermic materials are unsuitable.
- In FY 2016, we will conduct ABAQUS simulations to determine the CF requirements for Type 4 700-bar hydrogen storage tanks incorporating recent improvements in liner design, hoop and helical winding methods, boss design, graded carbon fiber construction, alternate fibers, and alternate resins. We will use the model to perform sensitivity analysis with respect to fiber variability, tank length-to-diameter ratio, tank capacity, and on-board packaging restrictions.
- In FY 2016, we will determine the potential and attributes of unstable metal hydrides that can improve the performance of high pressure hydrogen storage tanks. We will conduct reverse engineering analysis to map the desired material physical, transport, thermodynamic ,and kinetic properties needed for the hybrid high pressure metal hydride tank system to approach the near term system cost and performance targets.
- In FY 2016, we will update the sorption model to analyze the performance of the best-of-class metal organic frameworks (e.g., M_2(m-dobdc), M = Mg, Mn, Fe, Co, Ni series of frameworks), developed at Lawrence Berkeley National Laboratory, in a representative on-board storage system under realistic operating conditions. Conduct system analyses to determine the resulting improvements in cost and performance relative to MOF-5 metal organic framework material that is considered the current standard.

FY 2015 PUBLICATIONS/PRESENTATIONS

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8. R.K. Ahluwalia, T.Q. Hua, J.K. Peng, and H.S. Roh, "System Level Analysis of Hydrogen Storage Options," Hydrogen Storage Tech Team Meeting, Southfield, MI, February 19, 2015.

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1. David Gotthold, PNNL, personal communication.

2. Norm Newhouse, "Development of Improved Composite Pressure Vessels for Hydrogen Storage," DOE Annual Merit Review, May 14, 2013.