

## VI.9 Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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Contract Number: DE-FG36-08GO18055

Subcontractors:

- Boeing Research and Technology, Seattle, WA
- Lawrence Livermore National Laboratory (LLNL), Livermore, CA
- Pacific Northwest National Laboratory (PNNL), Richland, WA

Project Start Date: September 26, 2008

Project End Date: March 31, 2012

Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) High-Cost Carbon Fiber
- (H) Lack of Carbon Fiber Fabrication Techniques for Conformable Tanks

### Contribution to Achievement of DOE Manufacturing R&D Milestones

This project will contribute to achieving Milestone 24 from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Develop fabrication and assembly processes for high-pressure hydrogen storage technologies that can achieve a cost of \$/kWh. (4Q, 2015)

### FY 2011 Accomplishments

- Passed burst test with Vessel 7 and reduced 22.9% of carbon fiber from baseline vessel.
- Completed cost model for hybrid process according to the latest vessel design.
- Characterized polymer materials in high-pressure hydrogen environment.
- Completed the design, build, and integration of the next-generation AFP head.
- Down-selected a lower-cost and lower-strength carbon fiber suitable for vessel outer layers.



### Fiscal Year (FY) 2011 Objectives

Develop new methods for manufacturing Type IV pressure vessels for hydrogen storage with the objective of lowering the overall product cost by:

- Optimizing composite usage through combining traditional filament winding (FW) and advanced fiber placement (AFP) techniques.
- Exploring the usage of alternative fibers on the outer layers of the FW process.
- Building economic and analytical models capable of evaluating FW and AFP processes including manufacturing process variables and their impact on vessel mass savings, material cost savings, processing time, manufacturing energy consumption, labor and structural benefits.
- Studying polymer material degradation under high-pressure hydrogen environment.

### Technical Barriers

The project addresses the following technical barriers from the Manufacturing R&D section (3.5) of the Fuel Cell

### Introduction

The goal of this project is to develop an innovative manufacturing process for Type IV high-pressure hydrogen storage vessels, with the intent to significantly lower costs. Part of the development is to integrate the features of high precision AFP and commercial FW.

In this project period, a vessel was designed that passed the burst test successfully. Boeing's improvements included re-machining the foam mandrels to resolve the wrinkling issues due to poor fit-up between the end caps and the liner, refining the AFP processes, and developing a new AFP head to reduce downtime and increase productivity for processing of pressure vessels. Energy and cost targets were improved significantly in the cost model developed by PNNL after the success of Vessel 7. PNNL also characterized polymer materials in high-pressure hydrogen environments.

## Approach

The hybrid vessel designs were based on finite element analysis results to optimize strain distribution and achieve uniform displacement in the domes of the vessel.

## Results

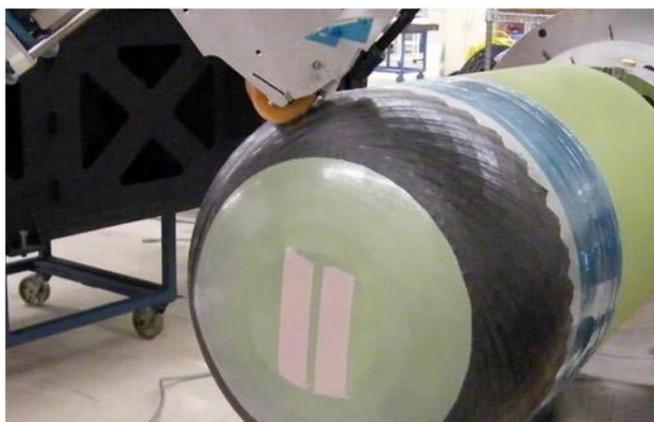
### Vessel Designs

**Vessel 3:** At the time of writing the 2010 annual report, Vessel 3 was in the process of being manufactured. It achieved a burst pressure of 21,658 psi, which is lower than the requirement of current CSA America Hydrogen Gas Vehicle (HGV) standard of 22,843 psi. However, it was an improvement over Vessel 2 by almost 3,000 psi. (See Table 1 for test result summary.) Since the burst pressure was 95% of the standard's minimum burst requirement, the plan was to lower the peak strain of design 3 by 7%.

**Vessel 4:** The peak strain location of Vessel 4 was relocated to the cylinder section by adding localized hoops at the transitions between AFP and FW. The outer layers of FW composite were reordered to have a hoop as the outer layer (vs. helical). This was done to keep tension in the last helical circuit and reduce voids. Vessel 4 reached a burst pressure of 21,719 psi, below the design requirements (Table 1) and slightly lower than the burst value for Vessel 3, even though strains were reduced by 7% as planned. In post test analysis a 1" X 2" block was cut from the aft end and inspected under a microscope. The inspection showed that the second group of AFP layers had waviness on top of the FW surface, but the first AFP did not show any sign of waviness. It was concluded that the waviness of the second AFP layer was due to the non-uniform surface of the FW base layers that they were built on. When a layer of fiber is wavy, it does not carry the portion of the load that those layers are designed for.

**Vessel 5:** Vessel 5 was essentially completely redesigned while keeping certain key design characteristics of Vessel 1 (passed burst test) and applying the lessons learned from previous vessels: 1) use single AFP to avoid fiber waviness and streamline manufacturing process, 2) maintain or reduce strain values of Vessel 1, and 3) manufacture AFP end caps on rigid foam tool. The design was much improved from that of Vessel 1 in terms of fiber usage, stress distribution, and strain values. It achieved a burst pressure of 20,500 psi, which was lower than Vessel 4 but had a fiber reduction of 10.6 kg from Vessel 4 (Table 1).

Earlier installation of the AFP end caps (Figure 1) on Vessels 3 and 4 revealed that they did not adequately fit the contour of the liner. The caps required significant manipulation to align them onto the dome, ultimately resulting in wrinkled tows and lower strength. Therefore, the foam mandrels were re-machined to a new and more accurate surface according to the liner contour data defined and measured by a laser tracking system. The newly cut surfaces also included higher-fidelity features for the boss



**FIGURE 1.** Fiber Placement of the End Cap (Older Generation Head)

**TABLE 1.** Vessel Test Result Summary

Vessel #	Weight (kg)	% Wt. Down from Baseline	Burst Pressure (psi)	% Under Std. <sup>1</sup>	Burst Area
0 (Baseline)	76.0	-	-	-	-
1	64.9	14.61	23,771	-	Mid Cylinder
2	N/A	-	18,666	18.29	Aft
3	67.11	11.70	21,658	5.19	Aft
4	65.04	14.42	21,719	4.92	Aft
5	54.44	29.37	20,500	10.26	Aft
6	Built identically to Vessel 5 for analysis only				
7	58.63	22.86	22,925	-	Mid Cylinder
8	57.29 <sup>2</sup>	24.62	- <sup>3</sup>	-	-

<sup>1</sup> Current HGV standard burst pressure requirement is 22,843 psi.

<sup>2</sup> Continuous winding and additional squeegeeing contribute to even lower weight.

<sup>3</sup> Cycle test ended after 13,500 cycles, thus no burst test afterward.

detail; further reducing wrinkling in the key polar regions. The better fit of the AFP end caps to the liner successfully eliminated wrinkling at each end of Vessel 5.

**Vessel 6:** Due to the inconsistencies seen in burst performance vs. fiber strains, Vessel 6 was built identically to Vessel 5 for destructive analyses. Half of the forward and aft ends of the vessel were sent to Boeing. At Boeing, computed tomography-scanning and photo-microscopy were performed to quantify porosity and resin rich areas within the structure, along with FW fiber waviness. At Quantum, after polishing the remaining ends, excessive voids were found in the aft end due to bridging (Figure 2). Bridging was caused by incorrect assumption of the "necking factor" value used in the design input file. Necking factor is defined as the ratio of fiber bandwidth at the polar opening vs. bandwidth in the cylinder section.



**FIGURE 2.** Voids are Shown in the Sectioned Aft Dome of Vessel 6



**FIGURE 3.** Vessel 7 Burst Test Result Showing Rupture in Mid Cylinder

Vessel 7: It was believed that the bridging issue was causing separation and reduction of load translation between the FW layers, which led to Vessel 5 failure. After entering the new necking factor, the models on both fwd and aft ends showed multiple opportunities to reduce bridging in the design. The excessive bridging locations were resolved by adjusting the fiber angles and polar openings. The total weight savings on Vessel 7 was 17.37 kg or 22.9% from the baseline (all FW) vessel (Table 1). Vessel 7 passed the burst test at 22,925 psi. The burst location was in the mid cylinder as designed (Figure 3).

Vessel 8: Vessel 8 was built identically to Vessel 7 for cycle test, but it developed a leak after 13,500 cycles, 1,500 cycles short of the requirement. Root cause of the leak will be determined in Phase III.

#### New Six-Tow Quarter Inch AFP Head Development

Boeing has built a prototype tow-placed head designed specifically for processing of pressure vessels. The ¼-inch, 6-tow machine has improved infrared heating capabilities and a more compact size enabled by the use of stainless

steel (vs. aluminum). Boeing's new head is able to apply fiber ½-inch closer to the polar boss. This enables a more-efficient, lower-weight pressure vessel design. Boeing has incorporated the ability to cut each individual tow, as well as a reverse-style cutter, allowing for higher speed cutting on the fly. Overall, Boeing has decreased downtime and increased productivity by improving the ease of operation and maintenance. The entire head opens up with only one tool allowing the operator to quickly clear jams. This increases the production of pressure vessels and reduces touch labor.

The head has been integrated onto a robotic cell, which will utilize a rail and a KUKA KR240 long arm system to provide more control and flexibility during lay-up. The system will allow the optimal placement of the robot base to minimize wasted motion and be capable of fiber placing a vessel with one tooling setup. An important characteristics of this cell is the significantly lower cost of the overall system compared to what is available in the industry.

#### Cost Model

Meeting the burst requirement with Vessel 7 showed that the AFP end caps can be successfully made in a parallel manufacturing line. This allows optimization of machine usage. Parallel AFP and FW processing lines reduce the vessel manufacturing time from 8.2 hr to 4.3 hr. This reduces the required number of FW cells by 48% and the number of AFP cells by 52% (for 500,000 units/year). This equals a \$30 per vessel savings in manufacturing cost. The reduced composite weight of Vessel 7 increased the specific energy from 1.5 to 1.78 kWhr/kgH<sub>2</sub> and reduced the vessel cost from \$23.45 to \$20.80/kW-hr.

#### Polymer Materials Characterization

PNNL has quantified the impact of high-pressure hydrogen environments on the mechanical properties of high density poly-ethylene (HDPE). Over 100 tensile specimens (ASTM D638 type 3) were tested after exposure to 4,000 psi H<sub>2</sub> to quantify the impact of H<sub>2</sub> concentration on the mechanical properties of polymers. Samples were soaked in the high pressure H<sub>2</sub> for at least 7 days per batch to ensure full H<sub>2</sub> saturation based on simple diffusion limited rate calculations.

Preliminary analysis of the standard HDPE H<sub>2</sub> exposed data shows reproducible trends. First, there is a nearly 20% decrease in elastic modulus that recovers as hydrogen diffuses from the material with time. Second, a nearly 10% decrease is seen in the tensile strength with a corresponding increase in ultimate strain (these are the peak values before the material necks), these also recover with time and escape of hydrogen from the HDPE. Recovery time scales were measured to be on the order of 1 day. Tests were also performed on a lower crystallinity material – low density poly-ethylene (LDPE). LDPE exposed to the same high pressure H<sub>2</sub> conditions demonstrates markedly different

behavior, with strong evidence of internal blistering and non-recoverable changes to the material. It appears that higher crystallinity and cross-linking densities are beneficial for reduced permeation and material durability under H<sub>2</sub> exposure.

#### Assessment of Alternate Composite Resins

Nonlinear stress analysis of the vessel composite layup was performed to estimate the increase in burst pressure that may be achieved by transitioning to a particle-reinforced resin with higher strength and stiffness. The ABAQUS finite element code was enhanced to include the Eshelby-Mori-Tanaka Approach for NonLinear Analysis model, which is a nonlinear composites material model that incorporates progressive damage and lamina failure criteria. The model with the standard epoxy closely predicted the actual burst pressure from testing, and the model with high performance filled epoxy predicted a 12% increase in burst pressure with the same composite lay-up.

#### Conclusions and Future Directions

- The hybrid manufacturing method is able to produce pressure vessels that achieve the required burst pressure and save carbon fiber (22.9% in Vessel 7) at the same time.
- Equipment and factory costs for hybrid process are small relative to fiber cost reduction.
- Absorption of H<sub>2</sub> by HDPE reduces the material's modulus and yield strength, but is reversible.
- Design vessel with lower-cost and lower-strength fiber to replace T700S for vessel outer layers.
- Perform testing on latest vessel design according to the latest automotive standards.
- Shake down improved AFP head design hardware for production.
- Update cost model.

#### FY 2011 Publications/Presentations

1. Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels, Annual Merit Review, Department of Energy, May 9–13, 2011, Washington, D.C.