VI.3 Development of Advanced Manufacturing Technologies for Low-Cost Hydrogen Storage Vessels

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Subcontractors
- Boeing Research and Technology, Seattle, WA
- Pacific Northwest National Laboratory (PNNL), Richland, WA

Project Start Date: September 26, 2008
Project End Date: March 31, 2014

Overall 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 lower-strength, higher-modulus fibers on the outer layers of FW.
- 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 to optimize storage volume.

Fiscal Year (FY) 2014 Objectives

- Design hybrid vessel with the latest version of mWind software.
- Pass all critical tests to the hybrid design per EC79/2009 standard.
- Improve manufacturing quality of AFP dome caps.
- Complete cost model for hybrid vessel manufacturing.
- Perform polymer liner material testing with in situ tensile rig and compare results.

Technical Barriers

The project addresses the following technical barriers from the Manufacturing R&D section (3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(M) Lack of Low-Cost Carbon Fiber

(N) Lack of Low-Cost Fabrication Techniques for Storage Tanks

Contribution to Achievement of DOE Manufacturing R&D Milestones

This project will contribute to achievement of the following DOE milestone from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- Milestone 7.2: Develop fabrication and assembly processes for high pressure hydrogen storage technologies that can achieve a reduction of 10% off the baseline cost of $18/kWh for Type IV, 700 bar tanks. (4Q, 2015)

FY 2014 Accomplishments

- Passed burst test with latest vessel design at 162.5 MPa, exceeding the minimum requirement by more than 3%.
- Passed ambient cycle, accelerated stress rupture and impact damage tests, which are critical to the hybrid design.
- Upgraded fiber creel system by Boeing to manufacture higher quality AFP dome caps.
- Saved 32% in mass and 27% in cost with latest design compared to baseline (all FW) vessel resulting in $20.7/kWh and 1.93 kWh/kg.
- Revealed high-density poly-ethylene (HDPE) ultimate tensile strength (UTS) decreases with increasing hydrogen pressure up to tested pressure of 5,000 psi.

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 manufacturing costs. The development is to integrate the features of high-precision AFP and commercial FW while satisfying design requirements.

APPROACH

Based on the latest in-house software developed for generating finite element analysis models of composite shells with option of using AFP methods, vessel design was completed for Boeing to build the AFP dome caps and Quantum to complete the vessel with FW. The design was tested in five different tests that are critical to the hybrid design. This project serves as a proof of concept that hybrid vessels can significantly reduce mass and save cost.

RESULTS

Vessel Build and Testing

Vessel 14: At the time of writing the 2013 annual report, Vessel 14 was being built with the latest design from the mWind software. During winding, a convex surface was observed between two layers of the AFP aft dome cap that would result in bridging of fiber. Chopped fiber with resin was used to fill in the gap. To ensure sufficient compaction to minimize the amount of voids, computed tomography (CT) scan on the vessel was planned before the burst test, but the equipment was not available. Nevertheless, a high-speed camera was utilized to help understand the burst mode for future design improvements if necessary.

The vessel achieved a burst pressure of 141.3 MPa (20,499 psi), short of the 157.5 MPa (22,844 psi) burst requirement. The rupture initiated from the aft dome area, which is consistent with the location that chopped fiber was applied. Although the dome cap was filled to avoid fiber bridging across the convex surface, the amount of void content in chopped fiber is unknown and may have contributed to lower translation efficiency at those locations.

Vessels 15 and 16: From observing the failure mode of Vessel 14, there was sufficient confidence that the vessel would have passed the test if there were no convex surface in the dome cap. Due to project timing, no extra time was available to redesign the aft dome cap to eliminate the convex surface. Carbon fiber woven rings of various sizes were used to fill in the convex surface for the next winds. Further, both Vessels 15 and 16 were wound on the winding machine at the same time because there was no need to develop new winding patterns.

Upon installing the woven rings, a very small amount of chopped fiber with resin was still necessary to eliminate all fiber bridging. A CT scanner was available this time. Figure 1 shows the CT scan result of Vessel 15, which indicates minimal voids at locations where woven rings and chopped fiber were used.

One of the two vessels was designated for burst test, and the other was for ambient cycle test. From previous experience in this project, a release film is necessary to be placed between the liner and composite, so they do not bond physically during composite cure.

A burst pressure of 162.5 MPa (23,572 psi), exceeding the minimum burst requirement of 157.5 MPa was achieved on Vessel 15. The composite mass was 51.5 kg, which translates to a 32% mass savings from the baseline vessel (composite mass of 76 kg). The failure mode was mid cylinder, as shown in Figure 2. Vessel 16 completed 15,000 cycles between 10% and 125% of service pressure without developing a leak or rupture.

Vessels 17 and 18: From the positive results on the previous two tests, two additional vessels were manufactured at the same time again using the same design. Vessel 17 was built for the accelerated stress rupture test, which evaluates the compatibility of the filament wound and advanced fiber placement resin systems (QT and Boeing) to transfer load between AFP and FW layers and determine if there

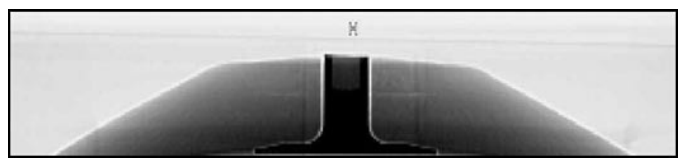

FIGURE 1. CT Scan of Vessel 15 Aft Dome

FIGURE 2. Vessel 15 Post Burst Test

is a resin creep issue with discontinuous winding. The test was performed at 125% of service pressure (87.5 MPa or 12,691 psi) at 85°C (185°F), which is the upper design limit temperature of the vessel, for 1,000 hours. The vessel was kept inside an environmental chamber, which was then placed inside a pit to protect personnel from injuries in case of rupture during test. Burst test was then performed after the 1,000-hour hold to evaluate the vessel's residual strength. The minimum requirement is 85% of the nominal working pressure times the burst pressure ratio (85% x 70 MPa x 2.25), which is equivalent to 133.9 MPa (19,421 psi).

After the 1,000-hr hold, the vessel successfully passed the test by rupturing at 153.0 MPa (22,191 psi), exceeding the minimum requirement. When compared with the virgin burst result (162.5 MPa or 23,572 psi) of Vessel 16, there is a 5.8% reduction in burst pressure.

The results showed that the vessel design was capable of resisting creep degradation at the test conditions even though

1) two different resin systems were used on the hybrid design and
2) the Boeing resin using in AFP was under-cured due to liner processing temperature limitation.

Vessel 18 was built for the impact damage test. The purpose of the test was to evaluate the vessel's resistance to impact damage even with a 32% reduction of composite in mass. The foam domes and foam rings designed for the baseline (all FW) vessel were used on this particular vessel to prepare for the test. Since the hybrid design reduced the vessel diameter significantly, the foam domes were modified to fit onto the vessel. Foam dome material was removed to fit them over the smaller composite domes, as shown in Figure 3. In addition, the inside curvatures of the two halves of the foam dome had to be forced to conform to the composite dome profile. However, a perfect conformance was

FIGURE 3. Vessel 18 with Foam Domes Modified from Baseline Vessel

not possible due to the stiffness of the foam domes. Some air gaps were present as a result. In addition to the less-than-ideal foam domes, the composite domes were much thinner as a result of the hybrid design. This further affected the outcome of the impact damage test.

Upon impact, deformations and cracks were observed on the foam domes. They were most likely caused by air gap between the foam domes and composite. This was inevitable when complete conformance was not achievable. During post impact cycle testing, the vessel developed a leak after 11,658 cycles, exceeding the requirement of 3,000 cycles.

Vessel 19: The last vessel built was for extreme temperature pressure cycle testing, which evaluates the compatibility of two resin systems to transfer load between AFP and FW layers effectively.

After conditioning the vessel for 48 hours at 85°C, the vessel completed 3,679 fill cycles before rupturing on the aft end. The pre-mature rupture showed that the load transfer mechanism could have been compromised with higher operating temperature and pressure cycling. With only a few inches of AFP and FW overlapping on both ends of the vessel for load transfer, this location could have been weakened under cycling by the under-cured AFP resin. The cure temperature was limited due to the liner processing temperature restrictions. Because of the rupture, the low extreme temperature portion of the test could not be performed.

Upgrading Fiber Creel System

The final control logic was integrated into the upgraded creel system at Boeing. This controller allows the linear potentiometers that are associated with each individual dancer arm to send information back to the motor that it is affixed to, creating a more-refined tension control system. Each motor controls an individual tow; thus, each of the six tows is controlled independently of each other. Each motor will output the correct torque for its particular lane so that tension across all six tows is consistent, regardless of differences in drag from lane to lane.

The motors also allow the material to be wound back up or re-spooled when the head articulates in a manner which creates slack. Having this function keeps the material from coming into contact with any unwanted or foreign materials, while keeping consistent tension on the tows at all times.

Vessel Manufacturing Cost Modeling

The vessel manufacturing cost model was updated to evaluate the mass and cost savings of the Vessel 15 design. Cost comparison between the baseline vessel and the hybrid vessel designs 1, 7 and 15 was completed. Each of these vessel designs exceeded the burst pressure requirement during testing. The calculations assume a carbon fiber price at $13/lb. The improvement of Vessel 15's design was significant—32% mass savings and 27% cost savings compared to the baseline filament wound vessel. In comparison, Vessel 7 only achieved 23% mass savings and 17% cost savings compared to the baseline vessel.

Hydrogen Testing of Polymer Liner Materials

After completion of the build and debugging the in situ tensile rig in 2013 by PNNL, the in situ frame was tested in air numerous times, and the stress/strain curves were cross-correlated with identical samples and strain rates in a standard tensile test frame equipped with a strain gauge. This allowed PNNL to obtain the "effective" gauge length of the polymer samples. Samples used were miniature tensile "dog-bone" geometry from ASTM International standards with the tabs reduced for the miniature grips. A procedure for reproducibly mounting the samples and setting the solenoid initial displacement was developed during this air testing to ensure high reproducibility. Even so, some tests showed either minor, or major jumps in the stress/strain curves at low strain within the elastic limit that are likely caused by "sticking" somewhere in the system and indicates some minor design modifications are needed. Due to limited funding, a larger number of samples was tested instead, and tests with major jumps in the stress/strain curve that indicated sticking were disregarded. After analysis, minor inflections in the stress strain curve in the elastic limit were considered acceptable for analysis of the UTS degradation in high-pressure hydrogen.

Testing occurred in a high-pressure hydrogen autoclave at pressures of 4,000 psi, 4,500 psi, and 5,000 psi. This represents the upper safe working limit of the autoclave. Multiple tests were carried out at each pressure. Tests exhibiting no inflections (signs of mechanical sticking) in the stress/strain curve are shown in Figure 4. From simple

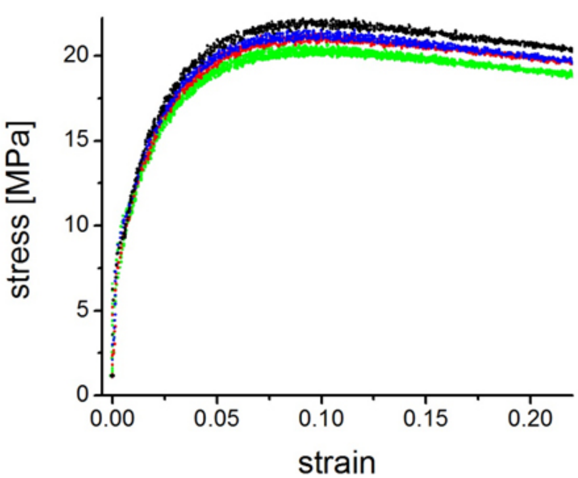

FIGURE 4. Stress/Strain Curves for HDPE Samples Tested in Air (black) and in High-Pressure Hydrogen at 4,000 psi (blue), 4,500 psi (red) and 5,000 psi (green)

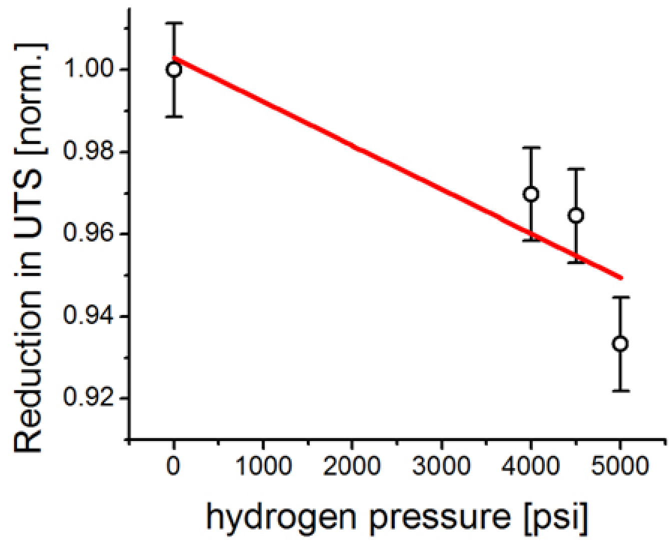

FIGURE 5. UTS Data Showing Marked Decrease with Increasing Hydrogen Pressure

examination of these curves, it appears that changes in the modulus are minimal, but there is a clear decrease in the UTS with increasing hydrogen pressure.

The data around the UTS demonstrating a clear decrease in the UTS of up to nearly 10% as compared to in air at 5,000 psi hydrogen. This marked decrease is similar to what was seen in ex situ measurements previously performed by PNNL. Again, these data are only those with no inflections in the elastic region. Figure 5 shows the average UTS as a function of hydrogen pressure. There appears to be a potentially non-linear behavior to the data with the UTS decreasing at more after 4,500 psi, but that cannot be confirmed without further testing at higher pressures not attainable with the current autoclave system.

CONCLUSIONS AND FUTURE DIRECTIONS

- Achieved significant mass (32%) and cost (27%) savings with hybrid design, comparing to all FW baseline vessel.
- The latest vessel design passed 80% of all tests that are critical to the hybrid design.
- Improved AFP dome caps achieved high consistency from part to part.
- mWind software is sufficiently accurate for hybrid vessel development based on test results.
- Modify AFP layup to avoid using woven fiber rings and chopped fiber as filler.
- Improve fit between AFP dome caps and boss/liner to improve fatigue performance.

- Extend the FW and AFP load transfer interface to improve cycle durability in the extreme temperature pressure cycle test.
- Investigate the potential non-linear UTS behavior of HDPE in hydrogen at pressures higher than 4,500 psi.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels, Annual Merit Review and Peer Evaluation Meeting, Department of Energy, June 16–20, 2014, Washington, D.C.