

VI.10 Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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Contract Number: DE-FG36-08GO18055

Working Partners:

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

Cost-Sharing Partner:

Boeing Research and Technology, Seattle, WA

Project Start Date: September 26, 2008

Project End Date: March 31, 2012

Project Objective

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 automated fiber placement (AFP) techniques,
- Exploring the usage of alternative fibers on the outer layers of the FW process,
- Investigating dry-tape technology which could drastically shorten the manufacturing time,
- Building economic and analytical models capable of evaluating FW, AFP, and tape fabrication processes including manufacturing process variables and their impact on tank mass savings, material cost savings, processing time, manufacturing energy consumption, labor and structural benefits, and
- Studying polymer material degradation under hydrogen environment.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

This study will contribute to achieving milestone 24 of the Manufacturing R&D section of Multi-Year Research, Development and Demonstration Plan: Develop fabrication and assembly processes for high-pressure hydrogen storage technologies that can achieve a cost of \$2/kWh.

Accomplishments

- Refined the stress analysis approach to predict stresses in the transition areas between the domes and the cylinder section.
- Designed new AFP and FW patterns to create better transition between the two fibers, thus further reducing stresses.
- Improved programming of the tow-placed system to reduce the cycle time for off-part motion by about 50%.
- Designed the geometry of the liner and boss at each end of the layup mandrels as the surfaces for fiber placement, forming the tow-placed end-caps in a stand-alone operation.
- Fitted end-caps onto liner well using a heat gun and a filament-wind helical.
- Identified that there are no cost-competitive alternative fibers other than carbon fibers at this time.
- Tape fabrication processes, mechanisms, equipment schematics, and micrographs were documented for presentation to team members and DOE reviewers. Tape development was advanced by new diagnostic capabilities applied to the first generation of prototype tapes. Remedies for bubble defects found in first generation tapes were developed.



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 the costs. Part of the development is to integrate the features of high precision AFP and commercial FW with the potential of using alternative fibers on the outer layers of FW. As a potential, dry-tape technology is being investigated by LLNL, which could shorten production cycle time.

In this project period, stress analysis approach has been refined after the second vessel failed burst test unexpectedly. Boeing has improved programming of the tow-placed system to reduce the cycle time for off part motion. The first set of AFP is no longer directly placed onto the liner, instead the end-caps are formed on the layup mandrels that have the geometry of the liner and boss at each end. These end-caps fitted well on the liner with the aid of a heat gun and a FW helical. Alternative fibers are being investigated for outer layers of FW. Quantum and Boeing supplied manufacturing cost information to PNNL to refine the cost model, which has been used to assess the cost sensitivities of this manufacturing technique compared to the baseline FW process. LLNL continues to develop an advanced composites manufacturing process that should be particular well suited to the production of pressure vessels. PNNL and LLNL will expand on their activities in separate reports.

Approach

The approach on stress analyses has been improved by taking the transition areas between the domes and the cylinder section into account. The original method analyzed the domes and the cylinder section separately, which contributed to not realizing the failure mode of the second vessel in the model.

Since manufacturing tow placed end-caps became a stand-alone process, different winding sequences have been investigated to prevent the end-caps from wrinkling upon laying down the first FW helical.

Results

Stress Analyses

The first vessel tested in October of 2009 passed the burst test at 23,771 psi, exceeding the requirement of European Commission (EC) 79-2009 standard of 22,804 psi. After passing the burst test, the composite design was refined to further reduce fiber usage on the next vessel. The overall design of second vessel required two layups of AFP. Instead of having fiber directly placed onto the liner for the first AFP layup, end-caps formed on foam tools were delivered to Quantum for installation. The completed vessel was burst-tested in December of 2009, but it failed at 18,666 psi, which is below the EC 79 standard. Since the second vessel failed unexpectedly, the approach on stress analyses was

revisited to understand why the failure was not realized in the model.

Stress analyses on each of the first and second vessels were based on three individual analyses on forward dome, aft dome, and cylinder section. However, this analysis method failed to evaluate the stresses in the transition areas between the domes and the cylinder section. Instead, two integrated analyses are necessary. One is for the forward dome and the cylinder section, and the other is for the aft dome and the cylinder section. On the forward dome, the patterns from AFP and FW are fed into the stress analysis model, but the material placed in the cylinder section by AFP is manually replaced with material of the hoops. This simulates the real-world situation, where hoops make up for the fiber that is missing between the domes wrapped by AFP. The same methodology also applies for the aft dome.

With this improved approach, stress analyses were performed on the AFP and FW patterns from the second vessel. The results confirmed that maximum stress was observed at the transition areas between the domes and the cylinder section. It is consistent with the actual burst location, which is between the aft dome and the cylinder section. As a result, the AFP and FW patterns have been modified to reduce stresses at the transitions to levels below those seen in the cylinder section of the vessel.

Third Vessel Development

The Boeing team continues to build tow-placed layups for the latest iteration of storage vessel design. Boeing uses the current delivery head design with improved heating capabilities. In these recent efforts, improvements to the programming of the system allow for the acceleration of the off-part motion between the end of one course and the start of another course. This improvement reduces the cycle time for off-part motion by about 50%.

In the build process for the current, third vessel, layup mandrels having the geometry of the liner and boss at each end are used as surfaces for fiber placement. This forms the tow-placed end-caps in a stand-alone operation. A picture of the end-caps for the most recent vessel-design iteration is shown in Figure 1.

The first set of APF end-caps made by Boeing according to the modified patterns from stress analyses was received in May for developing the third vessel. The liner with end-caps was installed onto a winding machine. FW patterns were laid down according to the design. All hoop layers went onto the liner smoothly. As soon as the first helical layer was laid down, the end-caps wrinkled. The wrinkles were caused by air gaps between the AFP end-caps and the liner. The tension from the FW carbon fiber compressed the AFP end-caps toward the cylinder section, but the end-caps were



FIGURE 1. Tow-Placed End-Cap on Foam Layout Mandrel Prior to Release

constrained from movement in the axial direction due to FW hoop layers already placed over the edge of the AFP end-caps. This resulted in the wrinkles in the AFP end-caps. The wrinkles made these end-caps no longer useful.

On the second set of end-caps received from Boeing, it was decided to use a FW low-angle helical to capture the end-caps. The liner with end-caps was placed on a winding machine. Heat was applied to the end-caps using a heat gun. Once both end-caps started to soften and become pliable, a low-angle helical that closed around both forward and aft bosses was applied to hold the end-caps tight. Then the helical was cut off before laying down the first set of FW pattern. Once FW was finished, the vessel was put on B-stage until the surface became tack free. The vessel was then shipped back to Boeing in late June. Boeing now has the task of laying-up the next sequence of tows in this hybrid design. Once this is done, Quantum will finish the vessel with the final courses of filament wound material.

Alternative Fibers

Various alternative fibers are being investigated to further lower the cost of manufacturing fuel storage vessels by utilizing lower tensile strength fibers on the outer layers of FW due to lower stresses in comparison to the inner layers. Possible alternative fibers could include glass, basalt, Saffil, alumina, boron, and silicon carbide.

Glass and basalt fibers were investigated initially, but they have been eliminated at this stage of the research because the tensile moduli are significantly lower than the carbon fiber, which is 33.4 Msi. Quantum expects that unless the tensile modulus of the fibers on the outer layers is equal or higher than those of the inner carbon layers, the outer layers will not carry significant percentage of the pressure load. As a result, Saffil, alumina, boron, and silicon carbide fibers were

further investigated. However, all these fibers have been disqualified for consideration because the fibers either do not have the required tensile modulus, are not available in continuous form, or too expensive.

Without finding an alternative fiber that is cost-effective for the application, the focus shifts back to searching for an alternative carbon fiber. The alternatives include Toray T300, Zoltek Panex35, Toho Tenax HTR40, and Cytec T-300C. After initial review, the most promising candidates are Zoltek and Toho because of their material properties and pricing.

Cost Model

PNNL developed cost models using Quantum and Boeing's manufacturing data to compare the costs of traditional filament wound tanks with the hybrid FW+AFP tanks. Two bounding manufacturing scenarios were considered, one that optimized the composite layup without concern for machine usage and one that considered 100% machine usage. The first hybrid tank produced by Quantum and Boeing exceeded the required burst pressure and saved 11.1 kg of the 76 kg baseline (14.6%). Eliminating 11.1 kg of carbon fiber composite significantly outweighed the added manufacturing cost (for machinery and factory space) of the hybrid process. The cost model estimates that the tank cost is reduced from \$23.45 to \$21.75 per kWh of hydrogen based on \$11/lb of carbon fiber. The gravimetric efficiency is also increased from 1.5 to 1.67 kWh/kg. Further details are provided in PNNL's annual report.

Dry-Tape Development

Although many details of the best dry-tape processes remain proprietary, a broad spectrum of coarse economic analyses quantifies their cost advantages. Among the alternative tape fabrication processes, LLNL has been reducing two to practice. These two have been chosen, not because they will perform best (either structurally or economically), but because their development might be affordable given the limited funding available. Both alternatives LLNL is developing are capable of the speed that underlies tape fabrication economic advantages. However, those advantages degrade rapidly if any structural performance is sacrificed by the microstructure built up by fabrication. This subproject's Phase 2 milestone will achieve full technical proof of concept by demonstrating that at least 90% of the tensile strength and 50% of the shear strength of conventional epoxy matrix composites is preserved in tape fabrication.

The first generation of tape specimens was built by pultrusion in the autumn of 2009. However, the tape specimens possessed a shortage of infused matrix in their acute-angled corners, and have occasional thin bubbles

along the fiber axis. These microscopic defects would make that generation vulnerable to significantly reduced strength in shear. Therefore, second generation tape prototyping is underway, with new materials processing due to begin in July.

Conclusions and Future Direction

- AFP end-caps can be manufactured as a stand-alone process.
- Lower cost carbon fibers with equal tensile modulus to inner fiber and low tensile strength are still the most cost-effective alternative fibers. Down-selection will be based on price and performance.
- The third vessel has gone through the first set of AFP and FW. Boeing will be laying up the next sequence of tows. Quantum will apply the final courses of FW and perform a burst test.
- If the burst test goes well, the next composite design iteration will incorporate an alternative fiber on the outer layers of FW. Two vessels will be built for burst test and ambient cycle test.
- Boeing has started the process for the design and build of an improved head design. The new head will include features that allow fiber placement into tighter locations, such as in the polar radius. Other features will include advanced heating, cutting, and teardown capabilities.
- The cost model will be updated to reflect the improvements in tank manufacturing methods.
- PNNL will continue hydrogen degradation testing of polymer liner materials.
- Continue dry-tape development.

FY 2010 Publications/Presentations

1. Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels, Annual Merit Review, Department of Energy, June 7-11, 2010, Washington, D.C.