

2011 DOE Hydrogen Program



Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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May 13, 2011

Project ID #
MN008

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Overview

Timeline

- Project start date: 09/2008
- Project end date: 03/2012
- Percent complete: 66%

Budget

- Total Budget: \$5,486,848
DOE Share: \$2,566,451
QT/Boeing Share: \$1,920,397
FFRDC Share: \$1,000,000
- Funding received in FY10:
\$400,000
- Funding for FY11: \$650,000

Barriers

- High-Cost Carbon Fiber
- Lack of Carbon Fiber Fabrication Techniques for Conformable Tanks

Partners

- Quantum Technologies, Inc. (QT)
- The Boeing Company (Boeing)
- Pacific Northwest National Laboratory (PNNL)
- Lawrence Livermore National Laboratory (LLNL)

Objectives - Relevance

To manufacture Type IV H₂ storage pressure vessels, utilizing a new hybrid process with the following features:

- Optimize elements of advanced fiber placement (AFP) & commercial filament winding (FW)
- Improve understanding of polymer liner H₂ degradation

With the aim of addressing the barriers by achieving a manufacturing process with:

1. lower composite material usage
2. lower cost fiber
3. higher manufacturing efficiency

Background on Advanced Fiber Placement (AFP) and Why It is Important

- Advanced fiber placement is a computer numerical control (CNC) process that adds multiple strips of composite material on demand
- Reinforce dome without adding weight to cylinder
- Maximum weight efficiency – places material where needed
- AFP can help reduce cost on the compressed gas storage technology



Why not Reduce Cost through Using Alternative (Non Carbon) Fibers?

| Fiber | Cost (\$/lb) | Reason for not Using |
|-----------------|--------------|------------------------------------|
| Basalt | 1.6 | Strength does not meet requirement |
| Ceramic | 274 | High cost |
| Boron | 1,308 | High cost |
| Silicon Carbide | 4,000 | High cost |
| Saffil | No Quote | No continuous tow available |
| T700 | 14 - 15 | - |

Background on Hybrid Vessel Manufacturing



1. Highly-accurate foam mandrels. Three 1/4-inch tows are placed on mandrel.



2. AFP dome caps (forward and aft) are then removed from foam tooling and brought to wind cell.



3. Both forward and aft dome caps are then transferred and installed to the hydrogen storage liner.



4. The final stage is to filament wound over the forward and aft dome caps.

Technical Accomplishments on Hybrid Vessel

- Vessel 7 passed burst test at 22,925 psi (EC-79 requirement is 22,843 psi)
- Accomplished mid cylinder burst predicted by stress analysis
- Saved 17.37 kg of composite from baseline (all FW) vessel (22.9% savings)
- Saved additional 6.27 kg of composite from last successful hybrid vessel (additional 9.7% savings)



Hybrid design vessels can dramatically reduce the amount of carbon fiber used, thus cost.

Approaches

| Vessel # | Weight (kg) | % Wt. Down from BL | Burst Press. (psi) | % Under Std. | Burst Location |
|----------|---|--------------------|--------------------|--------------|-----------------------------|
| 0 (BL) | 76 | - | - | - | - |
| 1 | 64.9 | 14.61 | 23,771 | - | Mid cylinder |
| 2 | Not available | - | 18,666 | 18.29 | Aft (AFP & FW interface) |
| 3 | 67.11 | 11.70 | 21,658 | 5.19 | Aft (AFP & FW interface) |
| 4 | 65.04 | 14.42 | 21,719 | 4.92 | Aft (AFP & FW interface) |
| 5 | 54.44 | 28.37 | 20,500 | 10.26 | Aft (AFP & FW interlaminar) |
| 6 | Built identically to Vessel 5 for analysis only | | | | |
| 7 | 58.63 | 22.86 | 22,925 | - | Mid cylinder |

- Material study
- Composite analysis
- Composite design and stress analysis
- Strain measurements
- Cost model update
- Hydrogen compatibility study on polymer liner

04/10-03/11

Manufacturing process development, manufacture & test best effort tank: built & tested five tanks
Revised cost model: complete, Polymer Liner Hydrogen Compatibility Study: on going
Go/NoGo decision→ demonstrate process can reduce material usage and cost: satisfied

Material Compatibility Study

Boeing Technical Accomplishments

- Determine if the shear strength of materials (BMS 8-276 and QT T700 Wet Wind) was being compromised due to the lower cure temperature (250°F) than that of the Boeing BMS 8-276 resin/matrix system (355°F) through Mode II Fracture Toughness (Shearing, G_{IIC})
- Material study results:

| Laminate | Cure Temp (°F) | Interface | G_{IIC} |
|----------|----------------|-----------|-----------|
| A | 250 | BMS / BMS | 21.4 |
| B | 355 | BMS / BMS | 12.7 |
| C | 250 | BMS / QT | 8.9 |
| D | 250 | QT / QT | 8.1 |

- Laminate A produced a significantly higher fracture toughness than the fully cured case (Laminate B) surprisingly
- The shear strength of the interfaces are at acceptable levels

Boeing BMS 8-276 and Quantum T700 Wet Wind resin systems are compatible with no reduction in performance even at a lower curing temperature.

Advances in AFP

Boeing Technical Accomplishments

- Modification of Programming on Path Steering
 - Benefits include the capabilities to:
 1. Steer fibers off the geodesic path more than is possible with traditional filament winding, due to the tack of prepreg
 2. Allow additional design optimization
 3. Program steering as a function of the polar opening and fiber angle
- New 6 Tow Quarter Inch Head Design
 - New head design/development was driven by:
 1. Highly accurate tow placement with min. tow wandering
 2. Achieve smaller polar openings and tighter turning radius
 - Old design: min polar opening = 2.56 inch diameter
 - New design: min polar opening = <2 inch diameter
 3. Individual Cut / Add / Clamp mechanisms
 4. Ease of maintenance for operators to clear jams and reduce downtime caused by failures/jams



- Vessel design on AFP layers is optimized to take advantage of the option of not following geodesic path.
- The new head design provides the capability to place fiber directly onto a liner to a smaller polar opening, thus increasing design options.

Composite Analysis

Approaches

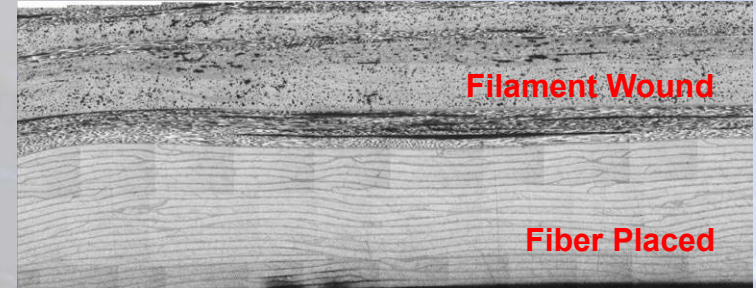
- Cross Sectional Photomicrograph by Boeing
 - Photographed samples from a vessel that did not pass burst test in both longitudinal and circumferential directions
- Short Beam Shear Testing by Quantum
 - Performed tests according to ASTM D 2344/D 2344M with samples from a vessel that was manufactured for analysis only (no burst test prior)
- Composite Build up Analysis by Quantum
 - Measured and compared the actual vs. assumed necking value on both the fore and aft ends

Composite Analysis

Accomplishments

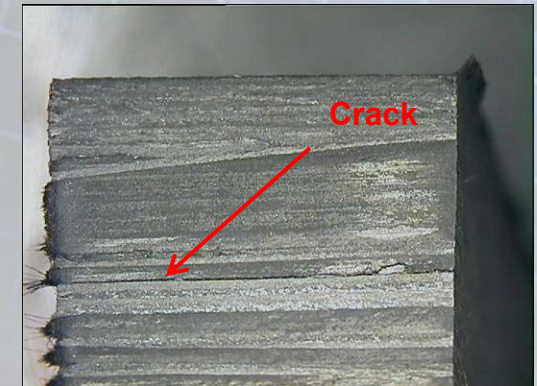
- Cross Sectional Photomicrograph by Boeing

- Results showed that filament winding has more porosity than fiber placement



- Short Beam Shear Testing by Quantum

- 2 samples cracked above the tow placed layer
- 2 samples cracked between a hoop layer and a helical layer
- Reduced porosity with continuous wound (vs. multi-day wound)



- Composite Build up Analysis by Quantum

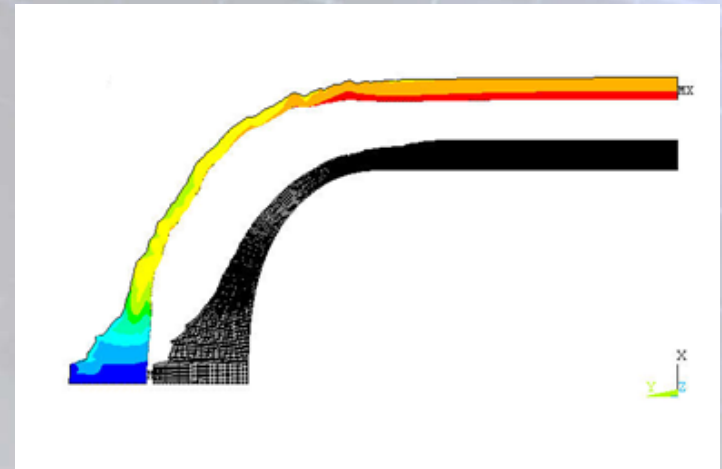
- Calculated necking value showed that composite build up was more significant than assumed value (design adjustments made accordingly)

Design adjustments were made to overcome porosity and bridging, thus reducing the stress and chance of cracking above the tow placed layer.

Composite Design and Stress Analysis

Quantum's Approach

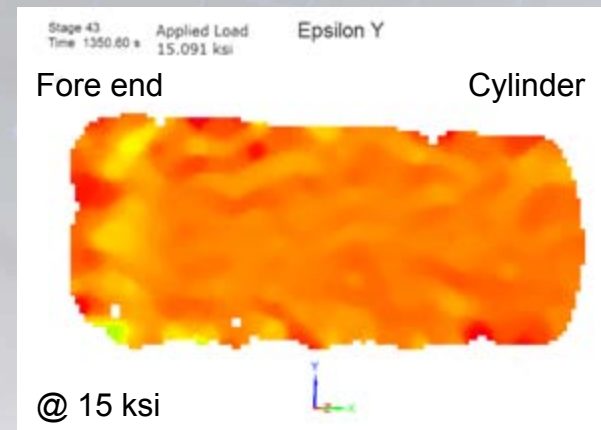
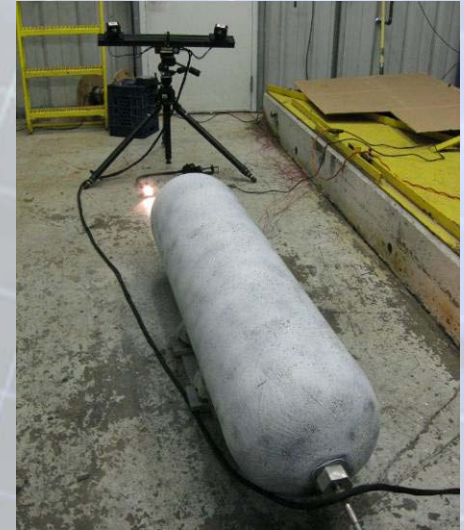
- Composite Design
 - Design for mid cylinder burst with a safety factor of 2.25
 - Minimize bridging and voids
- Stress Analysis
 - Manually replace element type to achieve accuracy
 - Minimize bending
 - Deformed model at 20X magnification follows the shape of un-deformed model well
 - Achieve uniform displacement



Strain Measurements

Approaches

- Strain measurements were taken with two different methods (strain gages and digital image correlation – ARAMIS[®]) between 0 and 105 MPa (15,229 psi), along with pressure measurements
- Strain Gage Measurements by Quantum
 - Eight strain gages on the aft end for correlation with ARAMIS measurements
- Strain Measurements with ARAMIS by Boeing
 - ARAMIS optically measures strains (equal many strain gages on the vessel)
 - Eight videos were taken on the cylinder section at frame rate of 30 seconds
 - Six videos were taken on the domes at frame rate of 30 seconds



Tank Cost Analysis

PNNL's Approach

- Quantum and Boeing's experience provided \$/kg of FW and AFP composites
- Hybrid composite design provided the mass of FW and AFP composites
- Cost model included materials, labor, overhead, balance of system, manufacturing equipment, and factory space costs
- Baseline and two bounding manufacturing scenarios were investigated:
 1. Baseline = Quantum Filament Wound 129 Liter, Type IV Tank
 2. Fully Integrated FW and AFP – Composite layup optimized for high strength, but inefficient machine usage
 3. Fully Separate FW and AFP – 100% machine usage, and able to meet design requirements by success of Vessel 7

FY11 - Cost Model updated to compare Vessel 1 and 7 layup designs with the baseline FW vessel

Tank Cost Analysis

PNNL's Technical Progress

500,000/yr, \$11/lb Carbon Fiber

| | | Baseline 129L | Tank 1 Layup | | Tank 7 Layup | |
|---|-----|----------------|---------------------------|-----------|---------------------------|-----------|
| | | Type IV Tank | Hybrid FW+ AFP Reinforced | | Hybrid FW+ AFP Reinforced | |
| Summary Table | | Filament Wound | Fully Integrated | Separate | Fully Integrated | Separate |
| | | | FWand AFP | FWand AFP | FWand AFP | FWand AFP |
| Composite Mass, kg | FW | 76 | 63.4 | 63.4 | 56.23 | 56.23 |
| | AFP | | 1.5 | 1.5 | 2.4 | 2.4 |
| Total Composite Mass, kg | | 76 | 64.9 | 64.9 | 58.63 | 58.63 |
| Total Place Time, hr/tank | | 5.75 | 7.27 | 4.80 | 8.21 | 4.25 |
| # Manuf. Cells for 500K/yr | FW | 191 | 242 | 159 | 273 | 142 |
| | AFP | | 484 | 165 | 546 | 264 |
| Tank Costs | | | | | | |
| FW Composite | | \$2,290 | \$1,910 | \$1,910 | \$1,694 | \$1,694 |
| AFP Composite | | | \$90 | \$90 | \$145 | \$145 |
| End Boss | | \$250 | \$250 | \$250 | \$250 | \$250 |
| Manuf. Equipment | | \$36 | \$66 | \$41 | \$72 | \$45 |
| Factory Space | | \$7 | \$10 | \$7 | \$11 | \$8 |
| Total Tank Cost | | \$2,583 | \$2,326 | \$2,299 | \$2,171 | \$2,141 |
| % Tank Cost Savings | | 0% | 10% | 11% | 16% | 17% |
| DOE Measures | | | | | | |
| Specific Energy, kWh/kg ¹ | | 1.50 | 1.67 | 1.67 | 1.78 | 1.78 |
| Cost Efficiency, \$/kWh ² | | \$23.45 | \$21.91 | \$21.75 | \$20.98 | \$20.80 |
| ¹ 5 kg H2 * 33.31 kWh/kgH2 / (Tank+OtherComponents+H2 mass, kg) Other CompMass=30kg ² (Tank+OtherComponents \$\$) / (5 kg H2 * 33.31 kWh/kgH2) | | | | | | |

Overall Accomplishments: Material & Cost Saving

| | Baseline 129L | Vessel 1 | Vessel 7 |
|------------------------------------|----------------|-----------------|-----------------|
| Summary Table | | FY-2010 | FY-2011 |
| | Filament Wound | Hybrid FW + AFP | Hybrid FW + AFP |
| Total Composite Mass, kg | 76 | 64.9 | 58.63 |
| Mass Savings, kg | | 11.1 | 17.4 |
| Mass Savings, % | | 14.6 | 22.9 |
| Specific Energy, kWh/kg | 1.50 | 1.67 | 1.78 |
| \$11/lb Carbon, Cost Effic, \$/kWh | \$23.45 | \$21.75 | \$20.80 |
| \$6/lb Carbon, Cost Effic, \$/kWh | \$18.74 | \$17.63 | \$17.01 |

Improvements made between Baseline and Vessel 7:

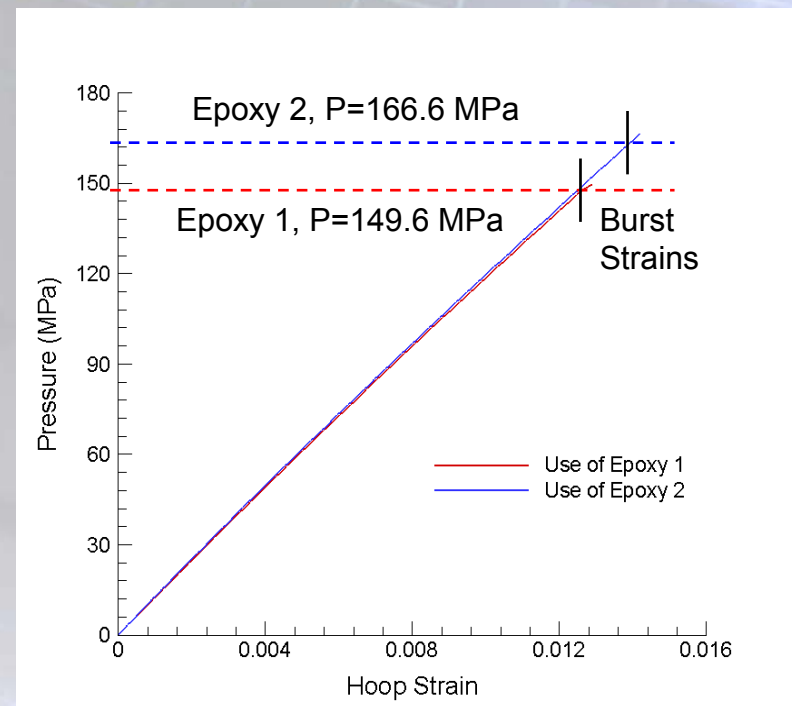
- Composite mass reduced from 76 kg to 58.63 kg (22.9% reduction)
- Specific energy increased from 1.5 to 1.78 kWh/kg
- Cost efficiency reduced from \$23.45 to \$20.80/kWh for \$11/lb carbon fiber
- Cost efficiency would reduce from \$18.74 to \$17.01/kWh for \$6/lb carbon fiber

High Modulus Resin

PNNL's Approach and Technical Progress

- Predicted vessel burst pressure by comparing two different resin systems
- Modeled cylindrical part of the vessel with ABAQUS and multiscale composites model, EMTA-NLA (Eshelby-Mori-Tanaka Approach for Non-Linear Analyses)
- Predicted burst pressure is higher with high modulus resin (Epoxy 2)

| Epoxy | Predicted Burst Pressure, MPa (ksi) |
|-------|-------------------------------------|
| 1 | 149.6 (21.7) |
| 2 | 166.6 (24.2) |



Polymer Liner Hydrogen Compatibility

PNNL's Approach

- Motivation: Polymers absorb relatively large amounts of H₂. This can have detrimental effects on polymer properties; similar to blistering and embrittlement in metals
- Issue: Degradation could affect leak rate, durability and lifetime
- Tested commercial HDPE and QT samples up to 4,500 psi H₂
 - Ex-situ testing
 - ASTM type 3 tensile test
 - 20-30 samples each run for statistics
 - Multiple pressures

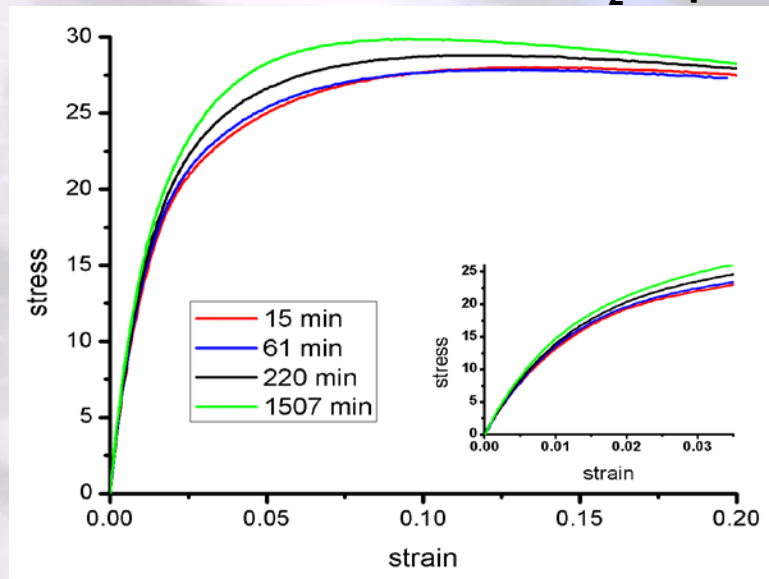


Polymer Liner Hydrogen Compatibility

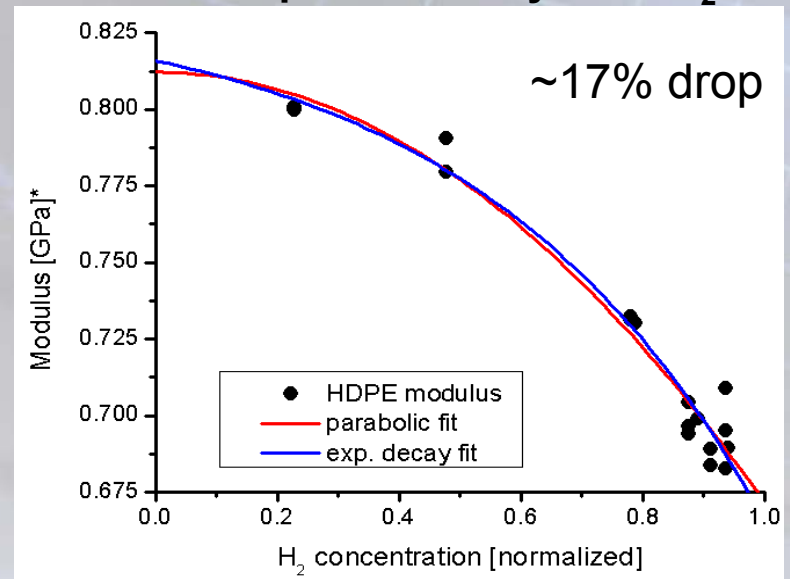
PNNL's Technical Accomplishments

- HDPE modulus & yield strength drop significantly when exposed to high pressure H₂
 - Highly dependent on amount of absorbed H₂ (high pressure = higher effect)
 - Ductility increases with amount of absorbed H₂
 - Modulus reverses as a function of time after exposure

Stress-Strain Curves HDPE H₂ Exposed



Modulus Drop & Recovery from H₂



HDPE modulus is reduced as a function of H₂ absorption, but reversible.
No permanent effect and secondary reactions.

Collaborations

| Partner | Prime | Sub | Industry | Fed Lab | Within DOE H ₂ and FC Program | Collaboration |
|--|-------|-----|----------|---------|--|--|
| Quantum Technologies, Inc. | X | | X | | X | Design and test hybrid pressure vessels manufactured with combination of FW and AFP |
| Boeing Research and Technology | | X | X | | | Develop AFP process for vessel manufacturing and provide material testing capabilities |
| Pacific Northwest National Laboratory | | X | | X | X | Develop cost model for hybrid vessel manufacturing and study the impact of H ₂ absorption in polymer liners |
| Lawrence Livermore National Laboratory | | X | | X | X | Develop dry tape technology |

Proposed Future Work: Strategies for Program Goals

FY11

- Evaluate the application of lower cost carbon fiber on the outer layers of filament winding to further reduce cost
- Test vessels with lower cost fiber per EC-79
 - Ambient temperature burst test
 - Ambient temperature cycle test
- Complete H₂ tensile tests on HDPE & other relevant materials

FY12

- Testing to national standards on critical tests that might be affected by AFP/FW hybrid process
 - Extreme temperature cycle test
 - Accelerated stress rupture
- Developing in-situ tensile test rig for high pressure H₂
- Build and test a tank with higher modulus resin
- Update cost model to include the consideration of lower performance carbon fiber

Project Summary

- A Boeing/Quantum Composite Vessel has been Produced Using a Hybrid AFP/FW Process:
 - Significant step towards DOE's efficiency goals
 - The latest hybrid vessel exceeded the required burst pressure and saved 17.4 kg off the 76 kg baseline vessel (22.9% saving)
 - Reduced tank mass improves:

| | Baseline 129L | Vessel 1 | Vessel 7 |
|---|----------------|-----------------|-----------------|
| | Filament Wound | Hybrid FW + AFP | Hybrid FW + AFP |
| Specific Energy, kWh/kg | 1.50 | 1.67 | 1.78 |
| \$11/lb Carbon, Cost Effic, \$/kWh | \$23.45 | \$21.75 | \$20.80 |
| \$6/lb Carbon, Cost Effic, \$/kWh | \$18.74 | \$17.63 | \$17.01 |

- PNNL Hybrid Process Cost Model Development and Polymer Liner Hydrogen Compatibility:
 - Equipment and Factory costs for hybrid process are small (\$43-\$83/tank) compared to cost saving from reduced fiber usage
 - Absorption of H₂ by HDPE reduces the material's modulus and yield strength, but these properties reverse as H₂ desorbs

Technical Back-Up Slides

Baseline Tank Costs

129 L, Type IV, Filament Wound Tank

Assumptions

| | | | | |
|----------------------|---------|------------------------------|----|---|
| Production volume | 500,000 | DOE requirement | | |
| Direct Labor rate | \$25 | US Dept. of Labor Statistics | | http://data.bls.gov/cgi-bin/dsdrv |
| Labor Overhead | 120% | | | PNNL best estimate |
| Material Overhead | 20% | | | average rate taken from several sources |
| G&A | 10% | | | average rate taken from several sources |
| Labor hours per tank | 6 | hours | | total production time |
| Carbon fiber mass | 119 | lbs | 54 | kg current requirements |
| Carbon fiber cost | \$11 | per pound | | T-700 material cost at 500K/year |
| Composite Weight | 167 | lbs | 76 | kg |

System consists of a single valve, one single stage regulator, a bracket, single line and fitting a pressure sensor and a ground strap
 Capital expenditures for machines, fixtures, etc not included (significant cost driver for 500K parts)- provided separately

Tank Cost

| | | | | | | |
|--------------------------------------|----------------|--------------------|----------------|---------|------------|-------|
| Metal fitting cost | \$250 | estimate @ 500K | Total material | \$1,979 | | |
| Carbon fiber cost | \$1,309 | | | | | |
| Other filament winding material cost | \$65 | | | | | |
| Rotomold material cost (Liner) | \$10 | | | | Material % | 77.9% |
| Bulk material | \$10 | | | | | |
| Misc soft goods | \$5 | | | | | |
| Indirect material cost | 330 | | | | | |
| Direct labor cost | \$150 | | Total labor | \$330 | Labor % | 13.0% |
| Indirect labor cost | \$180 | | | | | |
| G&A cost | \$231 | | | | | |
| Total cost= | \$2,540 | burdened tank cost | | | | |

Cost of Other System Components

| Other Component Costs | | | | |
|--|-------|---|--------------------------------|-------------------------------|
| On-Tank Valve ASM | \$120 | } | Total Component Material Cost= | \$957 |
| Regulator ASM- single stage | \$665 | | Material Overhead= | \$191 |
| Bracket | \$48 | | Direct Assembly Labor= | \$25 |
| Plumbing (line and fitting) | \$48 | | Indirect Labor= | \$30 |
| Pressure Sensor | \$72 | | G&A Cost= | \$120 |
| Ground Strap | \$5 | | Total cost= | \$1,323 |
| TOTAL | | | | |
| (Assembly= components+tank) | | | TOTAL SYSTEM COST= | \$3,863 fully burdened |
| Estimated energy usage per tank (based on 75% rated power of equipment): | | | | |
| - Electrical power is 58.96 KW-Hr | | | | |
| - Heat energy is 325,500 BTU | | | | |

Equipment and Factory Costs for the Filament Winding Process

| Equipment Type | Price | Square Feet | Quantity |
|---|----------------------|----------------|----------|
| Direct Process | \$87,034,452.00 | 161,502 | |
| Liner production | \$29,578,452.00 | 79,098 | 36 |
| Shell production | \$57,456,000.00 | 82,404 | 189 |
| | | | |
| Supporting equipment | \$22,115,071.54 | 80599 | |
| | | | |
| | | | |
| Transport equipment | \$41,500.00 | N/A | |
| Sub Total | \$109,191,023.54 | 242,101 | |
| Total + Misc (Total plant space) | \$125,569,677 | 302,626 | |

Assumptions in calculating equipment and factory costs per tank:

- Production Year = 233 days x 24hrs x 0.9
(Continuous production = 350 days x 24 hr x 0.9 could further reduce factory and equipment costs)
- Manufacturing Equipment: 20 yr economic life, 10 yr depreciable life,
Fixed Charge Rate = .1414
- Factory Space: 30 yr economic life, 20 yr depreciable life, Fixed Charge Rate = .1442
- Factory Construction Cost = \$80 / sq.ft.

Material and Factory Costs for the AFP Process

- Boeing Estimates
 - AFP Material = \$28/lb, assuming the high volume cost is twice the as-formed cost of FW composite, \$14/lb
 - AFP Factory Space = 203 sq.ft. per machine