Hydrogen Regional Infrastructure Program in Pennsylvania

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Concurrent Technologies Corporation
May 15, 2007

PDP19

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Overview

Timeline

• Start - September 1, 2004
• Finish - March 31, 2008
• 59% Complete

Budget

• Total project funding
  – DOE share - $5,917K
  – Contractor share - $1,183K
• Funding received in FY06
  – $990K
• Funding for FY07
  – $0

Barriers

<table>
<thead>
<tr>
<th>Barriers</th>
<th>Task</th>
<th>MYRDDP Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lack of Hydrogen/Carrier and Infrastructure System Analysis</td>
<td>HD</td>
<td>3.2.4.2 A, 3.1.1</td>
</tr>
<tr>
<td>Hydrogen Embrittlement of Pipelines</td>
<td>SM</td>
<td>3.2.4.2 D</td>
</tr>
<tr>
<td>Gaseous Hydrogen Storage Costs Storage Tank Materials and Costs</td>
<td>CM</td>
<td>3.2.4.2 F, 3.2.4.2 G</td>
</tr>
<tr>
<td>Lack of Hydrogen/Carrier and Infrastructure Hydrogen Embrittlement of Pipelines</td>
<td>SP</td>
<td>3.2.4.2 A, 3.2.4.2 D</td>
</tr>
<tr>
<td>Hydrogen Embrittlement of Pipelines Hydrogen Leakage and Sensors</td>
<td>SN</td>
<td>3.2.4.2 D, 3.2.4.2 I</td>
</tr>
</tbody>
</table>

HD – Hydrogen Delivery, SM – Steel Materials, CM – Composite Materials, SP - Separations, SN - Sensors

Partners

• Air Products and Chemicals, Inc.
• Resource Dynamics Corporation
• Electric Power Research Institute
• HyPerComp Engineering, Inc.
• American Society of Mechanical Engineers
• Savannah River National Laboratory
Barriers, Objectives and Approach
Pennsylvania Hydrogen Delivery Studies and I-95 Corridor

• Barriers Addressed
  – Lack of Hydrogen/Carrier and Infrastructure (MYRDDP 3.2.4.2 A)
  – DOE’s 2015 target of $2.00-$3.00/gge (delivered, untaxed) at the pump for hydrogen (H₂) (MYRDDP 3.1.1)

• Subtask Objectives
  – Analyze tradeoffs between alternative H₂ production and delivery approaches using commercial and near commercial options
  – Evaluate economic delivery scenarios for the I-95 Corridor. Assess the feasibility of hydrogen infrastructure along I-95 Corridor
  – Determine Pennsylvania’s economic delivery scenarios using regional cost of indigenous energy resources (i.e., coal, landfill methane, biofuels, wind, water, municipal waste, anaerobic digestion and nuclear) using the DOE H2A model

• Approach
  – Build upon work completed under Phase I of Project’s Infrastructure Analysis
  – Work with Resource Dynamics Corporation (RDC) to apply the DOE’s H2A model and other analytic methods to the State of Pennsylvania and the I-95 Corridor
  – Capitalize on the Pennsylvania indigenous energy resources to identify the pathway for the lowest cost delivered hydrogen
Technical Accomplishments

Why Investigate Hydrogen Infrastructure for Pennsylvania?

- Air quality is not just a California issue; Pennsylvania has similar problems
- Philadelphia Co. is one of the 10 worst ozone attainment counties in the US
- Allegheny Co. is one of the 10 worst particulate attainment counties in the US
- Transportation is a major contributor to both pollutants
- Pennsylvania transportation statistics are approximately 1/3 of California
- Pennsylvania adopted California’s vehicle emissions standards in December 2006 to combat these pollutants
- Pennsylvania is rich with indigenous energy resources, which contribute to a lower cost solution for delivered hydrogen throughout the State

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Source</th>
<th>CA</th>
<th>PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline Sales (gal/d)</td>
<td>EIA, 2004</td>
<td>40,645,000</td>
<td>13,111,000</td>
</tr>
<tr>
<td>Gasoline Stations</td>
<td>Dept of Census, 2003</td>
<td>8,228</td>
<td>4,356</td>
</tr>
<tr>
<td>Area (sq. mi.)</td>
<td>Dept of Census, 2000</td>
<td>155,959</td>
<td>44,817</td>
</tr>
<tr>
<td>Vehicle Registrations (LDVs)</td>
<td>Federal Highway Administration, 2003</td>
<td>28,600,000</td>
<td>9,259,000</td>
</tr>
<tr>
<td>LDV per Capita</td>
<td>Calculated</td>
<td>0.80</td>
<td>0.75</td>
</tr>
</tbody>
</table>

LDV – light duty vehicle

Heaviest concentration of CO₂ in the northeast United States, including Pennsylvania and along the I-95 Corridor
Technical Accomplishments
Pennsylvania Case Study - Phase I Results Summary

Approach
• Applied an innovative approach in conjunction with the DOE’s H2A model; a combination of regional and county specific data applied to optimize delivered cost
• Pennsylvania coal as a feedstock for hydrogen was a critical aspect of the study. Multiple feedstocks (based on statewide averages), plant sizes, and delivery methods considered
• Determine the lowest delivered hydrogen cost based on life cycle cost analysis

Results
• Coal is the best feedstock to fuel the hydrogen economy in the State at higher demand levels
• Lowest delivered cost for 1% LDV penetration is $4.08/kg using distributed production and natural gas as the feedstock; applicable for entire state. Eliminates the cost of delivery
• Lowest delivered cost for 30% LDV penetration is $3.28/kg using central production, coal gasification, and a combination of pipeline and liquid truck delivery
• Generally, if carbon is sequestered, an increased cost is realized

30% Demand Scenario with Two Central Plants
Technical Accomplishments
Pennsylvania Indigenous Energy Options

Approach
- Consider various indigenous energy resources within State boundaries as hydrogen feedstock options to reduce delivered hydrogen cost
- Apply DOE’s H2A model using regional pricing in lieu of state average pricing

Results
- Feedstocks considered for Pennsylvania case study included coal, coalbed methane, forestry and wood resources, municipal waste, livestock manure, landfills, wastewater, electricity (renewable and nuclear)
- Bituminous coal is prevalent in western Pennsylvania and could easily provide 100% LDV demand
- Coal could provide 19 times more hydrogen compared to the next resource (manure) considered
- Preliminary results indicate the cost of hydrogen, using coal as a feedstock, has increased from the Phase I results. However, the delivered hydrogen cost is due to an increase in the coal feedstock price.
Technical Accomplishments
Establishing a Hydrogen Economy along the I-95 Corridor

Approach
• Apply DOE H2A model leveraging knowledge gained assessing Pennsylvania
• Serve combined urban areas to build hydrogen volume
• Reach out to stakeholders to explore critical steps

Results
• I-95 Corridor worst concentrated carbon dioxide source on east coast and includes many ozone non-attainment areas
• I-95 Corridor contains densely populated areas, 13% of US population in less than 1% of land and 22 million light duty vehicles (15 % of US)
• Includes 1st, 7th, 11th, and 19th largest metropolitan statistical areas (MSA) in US
• Total delivery cost for MSAs along I-95 Corridor are less than $3.00/kg
• Lower delivery costs are realized with increased demand scenarios. Largest MSA approaches $2.25/kg at 30% demand level
Future Work
Pennsylvania Indigenous Energy and I-95 Corridor Studies

• Pennsylvania Indigenous Energy Options
  – Continue to investigate Pennsylvania indigenous energy resources. Apply current coal price to pertinent Phase I analyses for a useful comparison with Phase II results
  – Continue scenario evaluations to include optimum production and delivery options for other indigenous resources
  – Meet with stakeholders for their input to possible impacts and their value added review
  – Work with EPRI to assess current industrial hydrogen markets

• Establishing a Hydrogen Economy along the I-95 Corridor
  – Investigate multiple plants closer to demand centers to offer lower delivery cost and investigate potential locations
  – Assess the impact of production economies of scale
  – Evaluate the impact of production volume increases on initial capital investments
  – Establish criteria for when dedicated pipelines replace liquid truck delivery
  – Determine the impact of carbon sequestration on production costs from a coal feedstock
  – Meeting with stakeholders for their input as to how the I-95 Hydrogen Corridor should develop
Barriers, Objective and Approach
Steel Pipeline Material

• Barrier Addressed
  – Hydrogen Embrittlement of Pipelines (MYRDDP 3.2.4.2 D)

• Subtask Objective
  – Aid characterization of pipeline material performance in H₂ by:
    • Conducting mechanical testing of pipeline materials in 1,500 psi H₂
    • Ensure that critical data requirements are being met while minimizing duplication of effort

• Approach
  – Participate in DOE Pipeline Working Group and interface with American Society of Mechanical Engineers (ASME) to assess data and test needs, test methods and quality control, and documentation needs
  – Facilitate and coordinate mechanical testing in hydrogen with Savannah River National Laboratory (SRNL)
  – Distribute generated test data to H₂ community
Technical Accomplishments
Steel Pipeline Material

Tensile Test Conditions
- ASTM A-106 Grade B Carbon Steel
- Base Metal, Weld and Heat Affected Zone (HAZ)
- Crack 90 degrees to rolling direction (L-C orientation)
- Atmosphere: 100 ATM (H₂), 1 ATM (Air)
- Strain Rate: 10^-4 /sec

Results
- Confirmed HAZ and weld metal demonstrate largest effect in the presence of H₂
- Confirmed HAZ as potential region of concern
- Demonstrated need to conduct fracture testing
- Accumulated tensile data for ferritic pipeline steel
Ongoing and Future Work
Steel Pipeline Material

- Collaborating with SRNL to conduct mechanical testing (threshold stress intensity and fracture toughness) in 1,500 psi H₂
- Coordinating with ASME and DOE Pipeline Working Group (Testing Standards & Sample Standardization Working Team) to pursue other high-priority data capture
- Organizing workshop with ASME to create a prioritized material test matrix to facilitate code and standard development

<table>
<thead>
<tr>
<th>Specimen Geometry</th>
<th>Specimen Location</th>
<th>Number of Tests</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Threshold stress intensity testing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base</td>
<td>2</td>
<td>Air</td>
<td></td>
</tr>
<tr>
<td>Base</td>
<td>2</td>
<td>H₂</td>
<td></td>
</tr>
<tr>
<td>HAZ</td>
<td>2</td>
<td>H₂</td>
<td></td>
</tr>
<tr>
<td>Weld</td>
<td>2</td>
<td>H₂</td>
<td></td>
</tr>
</tbody>
</table>

Note: Specimen will contain notch to be pin loaded

<table>
<thead>
<tr>
<th>Fracture toughness testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
</tr>
<tr>
<td>HAZ</td>
</tr>
<tr>
<td>Weld</td>
</tr>
<tr>
<td>Base</td>
</tr>
<tr>
<td>HAZ</td>
</tr>
<tr>
<td>Weld</td>
</tr>
</tbody>
</table>

All specimens C-R orientation, extracted from ASTM A-106 (Grade B) 4” O.D., 0.5”- thick pipe
Barriers, Objective and Approach
Composite Overwrapped Pressure Vessels

• Barriers Addressed
  – Gaseous Hydrogen Storage Costs (MYRDDP 3.2.4.2 F)
  – Storage Tank Materials and Costs (MYRDDP 3.2.4.2 G)

• Subtask Objective
  – Advance gaseous hydrogen storage by:
    • Selecting appropriate constituent materials and improving Composite Overwrapped Pressure Vessels (COPV) design and fabrication to simultaneously target DOE cost and volumetric efficiency goals\textsuperscript{1} for off-board gaseous hydrogen storage
    • Monitor progress of U.S. COPV standards development and support data acquisition through mechanical testing of relevant composite materials

• Approach
  – Team with HyPerComp Engineering, Inc. (HEI) to model, design, construct and test COPVs
  – Interface with American Society of Mechanical Engineers (ASME) to support and benefit from evolving COPV standards activity

\textsuperscript{1} See “Ongoing and Future Work” slide for specific goals
Technical Accomplishments
Composite Overwrapped Pressure Vessels

- Fabricated, burst tested and fatigue tested twelve Type III COPVs
  - 7.75 liter water volume aluminum liner; 10,000 psi design pressure
  - Hoop and helical wrapped with carbon fiber
  - Designed to fail in sidewall
- Weight efficiency primary target – based on DOE goals at start of project \(^2\)
  - 5.2% weight efficiency achieved with non-optimized design
  - 0.035 kg of hydrogen per liter of storage volume
  - Tank cost $4,700/kg of stored hydrogen (note that cost reduction is primary focus of ongoing work)

<table>
<thead>
<tr>
<th>COPV #</th>
<th>Burst Pressure (psi)</th>
<th>COPV #</th>
<th>Cycles Achieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>03280604</td>
<td>25.880</td>
<td>03230601</td>
<td>3,161</td>
</tr>
<tr>
<td>03080601</td>
<td>25.770</td>
<td>03240601</td>
<td>3,466</td>
</tr>
<tr>
<td>03220602</td>
<td>25.001</td>
<td>03270602</td>
<td>3,047</td>
</tr>
<tr>
<td>03270601</td>
<td>25.020</td>
<td>03270601</td>
<td>3,747</td>
</tr>
<tr>
<td>03280603</td>
<td>25.496</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

 Avg. Burst Pressure: 25.433
 Standard Deviation: 410.65
 Coefficient of Variation: 1.61%

<table>
<thead>
<tr>
<th>COPV #</th>
<th>Cycles Achieved after Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>03270603</td>
<td>2,760</td>
</tr>
<tr>
<td>03280601</td>
<td>2,436</td>
</tr>
<tr>
<td>03280605</td>
<td>2,921</td>
</tr>
<tr>
<td>03290602</td>
<td>2,184</td>
</tr>
</tbody>
</table>

 Avg. Cycles Achieved: 2,575
 Standard Deviation: 329.72
 Coefficient of Variation: 12.80%
Ongoing and Future Work
Composite Overwrapped Pressure Vessels

- Focus on revised DOE goals for off-board gaseous hydrogen storage\(^3\)
  - Construction and testing of improved COPVs
- Exploration of COPV serviceability modeling
  - To include mechanical testing of COPV constituent materials as input to component lifetime prediction

<table>
<thead>
<tr>
<th>Off-Board Gaseous Hydrogen Storage Tanks (for forecourts, terminals, or other off-board storage needs)</th>
<th>2005 Status</th>
<th>FY2010</th>
<th>FY2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage Tank Purchased Capital Cost ($/kg of H(_2) stored)*</td>
<td>$820</td>
<td>$500</td>
<td>$300</td>
</tr>
<tr>
<td>Volumetric Capacity (kg H(_2)/liter of storage volume)**</td>
<td>0.023</td>
<td>0.030</td>
<td>&gt;0.035</td>
</tr>
</tbody>
</table>

* Storage Tank Capital Cost: These costs are based on the H2A Components Model V1.1. The model uses a current cost of $820 per kg of hydrogen stored for a 1,500 kg/day Forecourt station. This is based on quotes from vendors for steel tanks capable of 6,250 psi working pressure. The 2015 target cost is set to achieve the overall delivery cost objectives.

** Forecourt Storage Volumetric Capacity: The 2005 value is based on the specific volume of hydrogen at room temperature and 6,250 psi. The 2015 target is based on the specific volume of hydrogen at room temperature and approximately 12,000 psi. Off-board storage tank technology could use carriers as opposed to or in addition to compressed hydrogen as a means to store hydrogen. The most important target is system capital cost. However, the footprint for the storage must also be taken into consideration where space is limited such as at forecourts. For this reason, it is assumed that the hydrogen volumetric content of the storage volume should be at least as high as for 10,000 psi hydrogen gas.

\(^3\) DOE Multi-Year Research, Development and Demonstration Plan—Hydrogen Delivery (Revision February 6, 2007; Table 3.2.2)
## Barriers, Objectives and Approach

### SEPARATIONS

#### Subtask Objective
- Create a low cost Rapid Pressure Swing Adsorption (RPSA) system with the capability of achieving 99.995% purity hydrogen, which is required for the hydrogen economy
  - Range of Production:
    - 10 to 300 (normal cubic meters) Nm³/hour at purity, 150 psig pressure
    - Focus on 50 – 100 Nm³/hour (75 as basis)
  - Low capital, compact system
  - 99.995% hydrogen purity

#### Approach
- Conduct patent and technical literature search
- Structured adsorbent vendor search
- Demonstrate applicability of modeling software for packed bed RPSA
- Refurbish/start-up experimental RPSA Test Unit
- Contact select adsorbent vendors and conduct material evaluations
- Determine availability and suitability of RPSA components and investigate process packaging concepts

### SENSORS

#### Subtask Objective
- Advance current hydrogen-specific sensors and sensor technologies to ensure reliable operation and performance in hydrogen applications

#### Approach
- Assess current commercial and pre-commercial hydrogen sensor technologies
- Down select sensor technologies that meet defined performance requirements
- Test selected sensors according to defined protocols with custom designed test process/setup
  - Evaluate hydrogen sensor performance in air, nitrogen, and natural gas environments
  - Study the affects of contaminants, temperature, and humidity
- Control or eliminate the effects contaminants have on hydrogen-specific sensors to extend their useable life
- Communicate results with sensor manufacturers so modifications can be implemented
- Help expedite commercialization of reliable H₂ sensors

### Barriers

<table>
<thead>
<tr>
<th>Barriers</th>
<th>Separations</th>
<th>Sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lack of Hydrogen/Carrier and Infrastructure Options Analysis (3.2.4.2 A)</td>
<td>High Capital Cost and Hydrogen Embrittlement of Pipelines (3.2.4.2 D)</td>
<td>High Capital Cost and Hydrogen Embrittlement of Pipelines (3.2.4.2 D)</td>
</tr>
<tr>
<td>Hydrogen Leakage and Sensors (3.2.4.2 I)</td>
<td></td>
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</tr>
</tbody>
</table>
Technical Accomplishments

RPSA Test Unit

RPSA Final Design:
• PLC-controlled
• No adsorbent hold-down units used
• Mass Spectrometer used to analyze feed and effluent compositions
• Assembly of the unit has been completed and adsorbent testing is now underway

Test Conditions for Adsorbent Evaluations:
• Helium (He) used in place of Hydrogen during evaluations due to cost and safety reasons
• Process Steps:
  1) Feed gas  2) De-pressurize  3) Purge  4) Pressurize
• Pressure: 100 psig
• Temperature: Ambient
• Feed time range: 1-20 seconds
• Bed thickness range: 0.6 – 1.7mm
• Feed Gas Composition: 20% CO₂/He
• Purge/Feed Flow Ratio (P/F) Range: 0.25 – 2.50

Adsorbent Performance Ranked by Evaluating:
• The percent He recovery using several binary feed gases:
  – He + Carbon Dioxide (CO₂)
  – He + Nitrogen (N₂)
  – He + Carbon Monoxide (CO)
• Bed Size Factor (BSF) productivity – which is the ratio of the column volume to the He produced per hour

*Where MFC = Mass Flow Controller; CYL = Cylinder; PR = Pressure Valve; NV = Needle Valve
Technical Accomplishments
1st Adsorbent Evaluation (Gen2 Adsorbent)

Results:
- The optimal P/F ratio for this adsorbent is 1.0 based on the He recovery and BSF results.
- Lower cycle times do not appear to affect the BSF; however, the He recovery is reduced when cycle times are dropped.
- Fig. 3 shows that recovery can be maximized at a specific BSF value.
- Goal of development work is to find adsorbent materials that yield data in the upper left hand corner of the plot in Fig. 3.
Technical Accomplishments
Selected Sensor Testing

Sensor Reliability Test Protocols

<table>
<thead>
<tr>
<th>Performance Testing</th>
<th>Durability Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Hydrogen concentration correlations – random sequence</td>
<td>• Operate sensors in a natural gas environment for extended times and record effects</td>
</tr>
<tr>
<td>• Statistics ($R^2$ of linearity, standard deviation)</td>
<td></td>
</tr>
<tr>
<td>• Hysteresis testing</td>
<td></td>
</tr>
<tr>
<td>• Repeatability</td>
<td></td>
</tr>
<tr>
<td>• Humidity and temperature effects</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interference Testing</td>
</tr>
<tr>
<td></td>
<td>• Test the effects of natural gas components (i.e. CH$_4$, H$_2$S, H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>• Test the effects of ambient air contaminants (i.e. CO, CO$_2$, motor fumes, field air)</td>
</tr>
<tr>
<td></td>
<td>• Hysteresis testing (repeated exposure to interferent, ex: H$_2$S)</td>
</tr>
</tbody>
</table>

Reliability Test Results

• Three sensors were selected for reliability testing: sensors A, B, and C
• Sensor B was eliminated from the test exercise due to humidity affects and initially low hydrogen measurements when the hydrogen levels were suddenly increased
• Performance testing showed that sensors technologies A and C gave good responses when compared to the manufacturers’ claims and described data
• Although the interference testing showed some encouraging results, H$_2$S has been shown by other investigators to cause degradation of palladium-based sensors at high concentrations
• After completion of the sensor reliability testing, the manufacturers of sensors A and C were consulted to modify both sensors as follows in an attempt to reduce palladium degradation due to H$_2$S composition:
  – Sensor A (palladium capacitor) – additional coating added to reduce degradation
  – Sensor C (palladium field effect transistor) – designed-in degradation resistance
• Testing was then conducted on the modified sensors using 100 PPMv H$_2$S in N$_2$ for extended times and at increased pressures to determine the resistance to the degradation
Technical Accomplishments

Modified Sensor Test Results

Test Results

- Testing showed that the modifications to both sensors A and C do prevent degradation of palladium by H₂S (the most aggressive sulfur contaminant in natural gas)

- Sensor C is an order of magnitude faster in response time than coated Sensor A

- Sensor A saw a drop in the H₂ result from 4% down to 3.3% - This is attributed to an electronic problem with this specific prototype sensor, which the manufacturer has corrected in a second generation; the fault was not due to the palladium sensor but to another electronic component which degraded with time in all of the prototypes used

Modified Sensor Testing Results
## Future Work

### Separations and Sensors

<table>
<thead>
<tr>
<th>SEPARATIONS</th>
<th>SENSORS</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Continue limit of technology study on beaded and structured adsorbents</td>
<td>• Identify existing and emerging technologies from universities and national laboratories that could potentially mitigate the effects of contamination on H₂ sensor technologies</td>
</tr>
<tr>
<td>• Determine availability and suitability of RPSA components</td>
<td>• Develop prototype units for laboratory and field testing. As time allows, modifications will be made to the prototype designs based on the initial test results and additional testing completed</td>
</tr>
<tr>
<td>• Develop and characterize structured adsorbent material and optimize adsorbent properties</td>
<td>• Design and construct an intrinsically safe package to contain a safety hydrogen leak monitoring sensor system</td>
</tr>
<tr>
<td>• Develop methodology to package the adsorbent to ensure good gas-adsorbent contacting, to eliminate any channeling of the gas, and to minimize the pressure drop</td>
<td>• Establish an intrinsically safe guideline and with independent testing facilities define safety performance criteria</td>
</tr>
<tr>
<td>• Optimize new process through modeling and experimental work</td>
<td>• Determine methodology required for bi-directional (wired/wireless) communications in hydrogen production, transport, and storage environments</td>
</tr>
<tr>
<td>• Create guidelines for scaling up the device to higher flow rates will created</td>
<td></td>
</tr>
<tr>
<td>• Develop preliminary design for a 5 Nm³/hour device</td>
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</tbody>
</table>