Autothermal Cyclic Reforming and $H_2$ Refueling System

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DOE Project Review
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This presentation does not include any proprietary or confidential information
Outline

• Objectives
• Project Timeline & Budget
• DOE Targets
• Accomplishments over last year
• Safety Status
• Project Plan for Next Year
• Summary
Objectives

• Overall
  > Design a reformer based refueling system that can meet the DOE cost (<$2.50/kg) target
  > Fabricate and operate an integrated 60 kg of H₂/day reforming and refueling system

• Last Year
  > Design, fabricate and operate reformer and pressure swing adsorber pilot-scale sub-systems
  > Design the prototype reformer and pressure swing adsorber
  > Design the compression, storage and dispensing system and collect data on sub-systems
Project Timeline – Major Milestones

- **Phase I – Design and Analysis**
  1. Completed conceptual design
  2. Completed economic analysis
- **Phase II – Subsystem Development**
  3. Operated pilot-scale reformer and PSA
  4. Completed prototype reformer and PSA design
  5. Fabrication and shakedown of prototype reformer and PSA
- **Phase III – Integrated System Operation**
  6. Integration of ACR with PSA
  7. Complete bench-scale catalyst durability testing
  8. Integration of H₂ generator with H₂ compressor and dispenser
  9. Operation of ACR based hydrogen refueling system
Budget

- Total: $4.8 Million
- Industry: $2.1 Million
- DOE: $2.7 Million
- FY04 Funding: $0.6 Million
Technical Barriers and Targets

- Distributed H₂ Production from Natural Gas Barriers
  - A. Fuel Processor Capital Costs
  - B. Operation & Maintenance Issues
  - D. Carbon Dioxide Emissions
  - E. Control & Safety
  - Z. Catalysts
  - AB. H₂ Separation & Purification

- Targets

<table>
<thead>
<tr>
<th></th>
<th>2003</th>
<th>2005</th>
<th>2010</th>
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</thead>
<tbody>
<tr>
<td>Cost ($/kg)</td>
<td>5.0</td>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Efficiency (LHV)</td>
<td>62</td>
<td>68</td>
<td>75</td>
</tr>
</tbody>
</table>
Prototype Hydrogen Generating & Dispensing System

Autothermal Cyclic Reforming & H₂ Refueling
Exergy of Reformers for H₂ Generation

SMR/ACR

ATR

Exergy Destruction in Vent + Misc.

Exergy Destruction in Reformer + HX + Shift

H₂ Production Exergy

SMR – Steam Methane Reforming
ACR – Autothermal Cyclic Reforming
ATR – Conventional Autothermal Reforming
# Reformers Choice Depends on Application

<table>
<thead>
<tr>
<th></th>
<th>Conv. SMR</th>
<th>Conv. ATR</th>
<th>ACR</th>
</tr>
</thead>
<tbody>
<tr>
<td>%H₂ from reformer</td>
<td>70%</td>
<td>40-50%</td>
<td>70%</td>
</tr>
<tr>
<td>Efficiency</td>
<td>75%</td>
<td>65%</td>
<td>75%</td>
</tr>
<tr>
<td>Capital Cost</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Fuel Flexibility</td>
<td>Natural Gas, Propane</td>
<td>Natural Gas, Propane, Diesel Fuel, Biogas</td>
<td>Natural Gas, Propane, Diesel Fuel, Biogas</td>
</tr>
<tr>
<td>Sulfur Tolerance</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Turndown</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>
Stable Operation of Low-Pressure Pilot-Scale ACR

Autothermal Cyclic Reforming & H₂ Refueling
Stable Operation of Low-Pressure Pilot-Scale ACR

ACR Reactor Temp

Time, minutes

Temp, °C
Shift Reactor Testing

Specification: %CO < 1%

Time, minutes

Shift Temperature

Shift Outlet CO%
Reformer Testing Accomplishments

- Operated system with about 30 start-stop cycles
- Operated system continuously for up to 30 hours using automated controls several times.
- Demonstrated less than 0.5% CO at exit of shift reactor
- Operated system from 55 kg/day to 15 kg/day (3.5:1 load change)
- Lab scale tests for 2,000 hrs
High Pressure Reformer Reactor: 3-D Stress & Thermal Modeling

<table>
<thead>
<tr>
<th>Reformer Zones</th>
<th>Heat Loss, kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>0.4</td>
</tr>
<tr>
<td>Side</td>
<td>2.7</td>
</tr>
<tr>
<td>Bottom</td>
<td>0.3</td>
</tr>
<tr>
<td>Total</td>
<td>3.4</td>
</tr>
<tr>
<td>Specification</td>
<td>&lt; 5.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Critical welds</th>
<th>Cold-Start Cycles to failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hottest Internal</td>
<td>&gt; 90,000</td>
</tr>
<tr>
<td>Outer Shell</td>
<td>&gt; 1,000,000</td>
</tr>
<tr>
<td>Specification</td>
<td>&gt; 1,000</td>
</tr>
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</table>
Praxair PSA Pilot Plant Meets Requirements

Design Goals: 60 kg/day, 99.99% H₂ purity, 75% recovery

4 bed design
> Shortened bed height
> Reduced amount of sieve required
> Improved recovery

3 bed design
> Advanced sieve material
> Proprietary 12-step cycle
> Lowered feed pressure requirements
Praxair PSA Prototype Skid Status

• Skid design 75% complete
• Adsorbent - on order
• Logged 300,000 cycles on valves
  > No detectable leaks using He @ 150 psig
## H₂ Purity Status

<table>
<thead>
<tr>
<th>Component in the Product</th>
<th>DOE Targets</th>
<th>Current Status</th>
<th>Status with Future Development</th>
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</thead>
<tbody>
<tr>
<td>H₂</td>
<td>98% dry basis</td>
<td>99.99% dry basis</td>
<td>~ 99.9999% dry basis</td>
</tr>
<tr>
<td>CO</td>
<td>&lt; 1 ppm</td>
<td>&lt; 5 ppm</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt; 100 ppm</td>
<td>&lt; 10 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Sulfur</td>
<td>&lt; 10 ppb</td>
<td>&lt; 50 ppb</td>
<td>&lt; 10 ppb</td>
</tr>
<tr>
<td>Ammonia</td>
<td>&lt; 1 ppm</td>
<td>&lt; 10 ppm</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>&lt; 100 ppm</td>
<td>&lt; 10 ppm</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>O₂, N₂ &amp; Ar</td>
<td>&lt; 2%</td>
<td>~ 100 ppm</td>
<td>~ 100 ppm</td>
</tr>
</tbody>
</table>
Hydro-Pac Hydraulic H₂ Compressor

- Praxair’s LAX project provided an opportunity to gain experience needed for the ACR program
- Measured incoming power and calculated the compressor efficiency during factory run test on helium

\[ \eta_{\text{adiabatic}} = 67.8\% \]
Fill Pump Dispensing with Added Low Pressure Bank (Patent Pending)

- Requires 1/3 the amount of storage than cascade dispensing
- Added low pressure storage bank to maximize utilization
- Requires only one “modified” packaged compressor by separating functionality of each intensifier during fill
  > Stages 1 & 2 fill low pressure bank
  > Stage 3 acts as fill pump
- Small scale testing to begin in 2nd quarter of 2004

Diagram:
- 150 psig H₂ from Reformer
- Stage 1 & 2 Intensifier
- Stage 3/ Filling Intensifier
- Hydraulic fluid reservoir
- 400-700 psig low P storage bank
- 1000-6500 psig mid-high P storage bank
- Dispenser
- 6500 psig H₂ to FC vehicle
- 1/3 the amount of storage than cascade dispensing
- Added low pressure storage bank to maximize utilization
- Requires only one “modified” packaged compressor by separating functionality of each intensifier during fill
  > Stages 1 & 2 fill low pressure bank
  > Stage 3 acts as fill pump
- Small scale testing to begin in 2nd quarter of 2004
Stationary Storage

- Plan to use ASME Section VIII, Division 1 Coded seamless steel cylinders
  - Designed with a safety factor of 3.0
  - Praxair has a perfect safety record when employing these vessels for H₂ service
- Work with ASME to develop new rules for composite vessels
  - Praxair working with ASME and is actively participating in the H₂ Steering Committee for storage and transport of H₂
Praxair is working with Fueling Technologies on Dispenser

- Safety
- Additions
  - A vibration switch terminates the fill operation in the event of vehicle contact and remains locked out until reactivated
  - A shear frame assembly and automatic shutoff valves as a safeguard against a more severe vehicular collision
  - FTI provided new connections to allow the use of N₂ for purging both the enclosure in an LEL shut-down event and for continuously purging the dispenser H₂ vent header
Project Safety

- System Component FMEA’s
- Preliminary Hazard Assessment
- Haz Op (with independent review)
- Accident Scenario Review (performed review on any medium scoring item on Haz Op)
ACR Project Plan for 2004-5

<table>
<thead>
<tr>
<th>#</th>
<th>Task Name</th>
<th>2004</th>
<th>2005</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Q4</td>
<td>Q1</td>
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<tr>
<td>1</td>
<td>Low pressure reformer operation</td>
<td></td>
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<tr>
<td>2</td>
<td>High pressure reformer design and fabrication</td>
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<td></td>
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<tr>
<td>3</td>
<td>Catalyst durability testing</td>
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<tr>
<td>4</td>
<td>PSA design and fabrication</td>
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<td></td>
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<tr>
<td>5</td>
<td>Installation in UCI</td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td>Design of H2 compressor, storage and dispenser</td>
<td></td>
<td></td>
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<tr>
<td>7</td>
<td>High pressure ACR reactor shakedown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>High pressure reformer start-up and operation</td>
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<tr>
<td>9</td>
<td>Integration with PSA</td>
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<tr>
<td>10</td>
<td>Integration with PEM fuel cell</td>
<td></td>
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</tr>
<tr>
<td>11</td>
<td>Integration with H2 compressor, storage and dispenser</td>
<td></td>
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</tbody>
</table>

- Increased Reliability in Startups
- Extended Operation
- ASME Codes
- Modeling Stress due to Reformer Cycles
- Catalyst Durability test for 3000 hrs
- Codes & Standards
- Safety Reviews
Significant Reviewer Comments

• Excellent implementation of economics; Economic analysis should include reformers from other manufacturers
  > Working on DOE H₂ A panel
  > Supporting DOE on an apples-to-apples comparison of different reforming technologies

• Little innovation outside of GE reformer evident
  > Praxair submitted patents on PSA and refueling system recently
  > Novel 3-bed and 4-bed designs
  > Some of the innovation is confidential and will be presented to DOE

• Excellent component developed and test plans; Future plans are weak
  > Included a detailed project plan for next year
Summary

• Low-pressure pilot-scale ACR operation
  > Stabilized for extended periods of time
  > 30 start-stop cycles

• High pressure prototype reformer design is complete

• Prototype reformer and PSA will be fabricated and operated this year

• Reformer will be integrated with PSA, compressor and storage tanks

• Operation of integrated system in 2005
Acknowledgements

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• California Air Resources Board
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