Advanced Hydrogen Liquefaction Process

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Praxair - Tonawanda, NY

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Introduction

Program Timeline

<table>
<thead>
<tr>
<th>Phase</th>
<th>7/08 - 7/09</th>
<th>7/09-7/10</th>
<th>7/10-7/11</th>
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</thead>
<tbody>
<tr>
<td>Phase I - Feasibility</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Develop Alternative Hydrogen Liquefaction Processes</td>
<td>Validate Ortho-Para Conversion Process Performance</td>
<td></td>
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<tr>
<td>Phase II - Hydrogen Liquefaction Process Development</td>
<td>3</td>
<td>4</td>
<td></td>
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<tr>
<td></td>
<td>Establish Efficiency, Equipment, and Material Performance Targets</td>
<td>Estimate Capital Cost</td>
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<tr>
<td>Phase III – Process Performance Evaluation</td>
<td>5</td>
<td>6</td>
<td></td>
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<tr>
<td></td>
<td>Demonstrate Improved Ortho-Para Conversion Process</td>
<td>Evaluate Potential Cost Reduction and Efficiency Improvement</td>
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</table>

2008 Budget

<table>
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<tr>
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<th>Requested</th>
<th>Spent Through 4/15/08</th>
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<tbody>
<tr>
<td>DOE</td>
<td>$99,712</td>
<td>$0</td>
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<tr>
<td>Praxair</td>
<td>$24,928</td>
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<tr>
<td>TOTAL</td>
<td>$124,640</td>
<td>$0</td>
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</table>

Barriers Addressed

- C. High Cost and Low Energy Efficiency of Hydrogen Liquefaction
  - Reduced capital cost
  - Improved efficiency
  - Improved overall process by integration
Objectives

- Program - Develop a low-cost hydrogen liquefaction system for 30 and 300 tons/day that meets or exceeds DOE targets for 2012
  - Improve liquefaction energy efficiency
  - Reduce liquefier capital cost
  - Integrate improved process equipment invented since last liquefier was designed
  - Continue ortho-para conversion process development
  - Integrate improved ortho-para conversion process
  - Develop optimized new liquefaction process based on new equipment and new ortho-para conversion process

- Phase I – Feasibility
  - Develop conceptual designs for improved processes
  - Validate ortho-para conversion process performance
### Hydrogen Liquefaction Targets

<table>
<thead>
<tr>
<th>Category</th>
<th>2005 Status</th>
<th>2012</th>
<th>2017</th>
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<tbody>
<tr>
<td><strong>Small-Scale Liquefaction (30,000 kg H₂/day)</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Installed Capital Cost ($)</td>
<td>$50M</td>
<td>$40M</td>
<td>$30M</td>
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<tr>
<td>Energy Efficiency (%)</td>
<td>70%</td>
<td>75%</td>
<td>85%</td>
</tr>
<tr>
<td><strong>Large-Scale Liquefaction (300,000 kg H₂/day)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Installed Capital Cost ($)</td>
<td>$170M</td>
<td>$130M</td>
<td>$100M</td>
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<tr>
<td>Energy Efficiency (%)</td>
<td>80%</td>
<td>&gt;80%</td>
<td>87%</td>
</tr>
</tbody>
</table>

Efficiency = \[
\frac{\text{Liquefied Hydrogen LHV}}{\text{Liquefied Hydrogen LHV + Liquefaction Energy}}
\]
Milestones

- **Phase I - Feasibility**
  - Develop Novel Conceptual Process Designs
  - Validate Improved Ortho-Para Performance

- **Phase II - Process Development**
  - Establish Performance Targets
  - Develop Preliminary Capital Cost Estimate

- **Phase III – Performance Evaluation**
  - Demonstrate Ortho-Para Performance
  - Validate Capital Cost and Performance Improvement
Program Approach

- Build on successful high-risk, low-effort program funded through EMTEC
  - $200,000 program that demonstrated potential for improved ortho-para conversion process
  - Enabled Praxair to propose this project to advance hydrogen liquefaction process development

- Incorporate other process improvements beyond improved ortho-para conversion
Phase I Plan

- **Process Optimization, Design, and Economics (45%)**
  - Develop alternative hydrogen liquefaction processes that can optimally integrate new equipment and improved ortho-para process

- **Process Equipment Evaluation (30%)**
  - Evaluate commercially available critical equipment
  - Evaluate novel turbomachinery

- **Ortho-Para Conversion Optimization (25%)**
  - Validate process performance in laboratory-scale test facilities
Liquid Hydrogen

- In the 1960’s, liquid hydrogen plants were built to support the Apollo program
  - Space shuttle capacity is 113 tons (383,000 gallons)
  - Saturn V rocket used 100 tons (339,000 gallons)

- Today, liquid hydrogen is used to reduce the cost of hydrogen distribution
  - Liquid hydrogen can be transported economically in larger quantities for longer distances than compressed gas
  - Liquid hydrogen is used to provide high purity product because impurities condense before hydrogen
Hydrogen Liquefaction
Existing Process Flow Diagram
Hydrogen Liquefaction

- The plants are very capital intensive
  - Infrequent builds make it difficult to reproduce designs
  - Large plants have high capital risk
    - Want to avoid unused capacity
- The process is very energy intensive
  - Typical unit powers are about 12.5 to 15 kWh/kg
  - Hydrogen lower heating value is about 33 kWh/kg
  - Hydrogen boiling point is 20 K = - 253°C = - 423°F
- Capital cost is more than half of the total

![Bar chart showing the share of capital, power, and O&M costs.]

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Hydrogen Distribution

- Both weigh about 80,000 lbs
- Liquid hydrogen might not be the best way to supply the “Hydrogen Economy”, but it will play a significant role in the transition period
Hydrogen Delivery

- **Pipeline (~ 1 billion scfd)**
  - Refineries and other large hydrogen consumers

- **Liquid (~ 10 million scfd)**
  - 1.8 million scf/truck
  - Liquid serves an important market segment

- **Tube Trailers**
  - 125,000 scf/truck

- **Cylinders**
  - 250 scf/cylinder
Forms of Molecular Hydrogen

- **Difference is due to proton spin**
  - Normal Hydrogen is 75% Ortho, 25% Para
  - Equilibrium Liquid Hydrogen is 0.2% Ortho, 99.8% Para

- **Ortho-Para conversion requires 18 - 45% of the minimum work requirement for liquefaction**
  - Depends on the conversion process used

Para fraction increases as temperature approaches liquid range

- Catalyst is used to reach equilibrium composition during cooling
Ortho-Para Enthalpy

- Heat of liquefaction/vaporization is 192 Btu/lb
- Heat of conversion from n-H₂ to e-H₂ in liquid is higher


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Boil-Off Loss

- Heat of conversion from normal to para is higher than the heat of liquefaction
  - Spontaneous conversion in the storage tank can cause vaporization

Calculated values from:
Future Work – Task 1

- Process Optimization, Design, and Economics
  - Develop alternative liquefaction processes
    - 2009 Critical Milestone
  - Incorporate improved ortho-para conversion process
  - Estimate capital cost
    - 2010 Critical Milestone
  - Establish component performance targets
    - 2010 Critical Milestone
  - Develop process simulations for new designs
  - Validate potential cost reduction
    - 2011 Critical Milestone
Future Work – Task 2

Process Equipment Evaluation

- Evaluate commercially available critical equipment
  - Use this to develop new liquefaction processes
- Evaluate novel turbomachinery
  - Use this to develop new liquefaction processes
- Estimate capital cost
  - 2010 Critical Milestone
- Update critical equipment evaluation

Equipment development is beyond the scope of this program
Future Work – Task 3

- Ortho-Para Conversion Process Optimization
  - Validate improved ortho-para performance
    - 2009 Critical Milestone
  - Select best candidate ortho-para process
  - Demonstrate process performance
    - 2011 Critical Milestone
## Hydrogen Liquefier Equipment Design Considerations

<table>
<thead>
<tr>
<th>Component</th>
<th>State of the Art</th>
<th>Near Term</th>
<th>Long Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressors</td>
<td>Reciprocating Screw</td>
<td>Reciprocating Centrifugal</td>
<td>Centrifugal Hydride Shockwave</td>
</tr>
<tr>
<td>Pre-Cooling</td>
<td>Liquid N$_2$</td>
<td>Mixed gas</td>
<td>Magnetic</td>
</tr>
<tr>
<td>Low-Temp Refrigeration</td>
<td>Reverse Brayton</td>
<td>Reverse Brayton with advanced turbines</td>
<td>Magnetic Acoustic</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>Brazed aluminum</td>
<td>Brazed aluminum Micro-channel</td>
<td>Micro-channel</td>
</tr>
<tr>
<td>Ortho-Para Conversion</td>
<td>Catalytic conversion</td>
<td>Improved ortho-para process</td>
<td>Advanced ortho-para process</td>
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</tbody>
</table>
Multi-faceted approach to improving hydrogen liquefaction by improving process efficiency and reducing capital cost

Goal is to define a new liquefaction process that integrates state-of-the-art equipment and takes full advantage of its increased capability

Incorporate improved ortho-para conversion process already under development