III.5 Advanced Hydrogen Liquefaction Process

Objectives

Develop low-cost hydrogen liquefaction systems to produce 30 and 300 tons/day:

- 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.

Technical Barriers

This project addresses the following technical barrier from the Delivery section (3.2.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- High Cost and Low Energy Efficiency of Hydrogen Liquefaction

Technical Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2012 Target</th>
<th>2017 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small Scale Liquefaction (30,000 kg/day)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installed Capital Cost</td>
<td>$</td>
<td>40M</td>
<td>30M</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>Large Scale Liquefaction (300,000 kg/day)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installed Capital Cost</td>
<td>$</td>
<td>130M</td>
<td>100M</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>&gt;80</td>
<td>87</td>
</tr>
</tbody>
</table>

We are addressing the capital cost and energy efficiency targets.

- Capital Cost:
  - Improved process design.
  - Improved process equipment.

- Energy Efficiency:
  - Increased equipment efficiency.
  - Improved process efficiency.
  - Improved ortho-para conversion efficiency with a goal of reducing energy required for ortho-para conversion by at least 33%.

Accomplishments

- Constructed improved test unit capable of operating over a temperature range from 77 K to about 150 K.
- Developed spreadsheet model to calculate energy requirements for hydrogen liquefaction.
- Identified problems with commercial process simulation software for modeling ortho and para hydrogen and worked with program supplier to solve the problems.
- Prepared and tested new materials for improved ortho-para conversion using recipes and equipment that produce materials similar to those that could be produced in commercial quantities.
- Developed process models for existing and proposed liquefier designs.
- Showed that overall power consumption can be reduced by about 2.5% if catalyst is used in the high-temperature heat exchanger.
- Identified a process where the performance of the improved ortho-para conversion process is sufficient to reduce total power consumption.
• Identified a process where the performance of the improved ortho-para conversion process, even when accounting for future improvement, is unlikely to be sufficient to reduce total power consumption.

Introduction

Hydrogen liquefiers are highly capital intensive and have a high operating cost because they consume a significant amount of electrical power for refrigeration. There are only a few hydrogen liquefiers in the world and only six currently operating in the U.S. These plants are not built frequently, so they have not been thoroughly optimized for today’s equipment. Furthermore, many of them were built when power was much less expensive than it is today, so those plants do not have optimized efficiency.

Approach

This project focuses on improving liquefier efficiency and reducing overall liquefaction cost, including reducing capital cost. The project is attempting to accomplish these goals using three different aspects of an integrated approach:

• Improved process design – Develop a more efficient refrigeration process including ortho-para conversion and refrigeration using available streams and equipment.

• Improved process equipment – Integrate improvements made in process equipment since the most recent liquefier design to take full advantage of the increased capabilities and improved efficiency. Project the impact of further improvements in process equipment, including novel devices currently being developed.

• Improved ortho-para conversion process – Ortho-para conversion consumes a significant amount of refrigeration energy because it requires cooling at low temperatures. Improvements in ortho-para conversion can lead to a significant reduction in power requirements.

This project builds on previous work done at Praxair, some of which was part of a project funded through Edison Materials Technology Center (EMTEC). The previous project demonstrated that the improvements in ortho-para conversion were possible, but developing the complete optimized process design was beyond the scope of the project.

Results

The material screening test system used during the EMTEC project has been recommissioned to perform additional material testing. We are developing new materials to test. This system can test materials at the boiling point of the cooling fluid, such as liquid nitrogen. The system can test ortho-para conversion at pressures up to 400 psig. This was a significant limitation in earlier testing because it did not allow for testing over a temperature range. The previous system has the advantage of being a simple system that is excellent for preliminary screening of materials. Figure 1 shows this system. New materials work has proceeded from the EMTEC project with new recipes and methods developed to provide samples with properties that more closely approximate those that would be obtained using commercial-scale materials manufacturing.

A pilot-scale system to conduct process testing on desired materials over a range of temperatures was built and testing has begun (Figure 2). This new test system is fully automated to allow for both remote control and eventual material life testing. The system consists primarily of a series of pressure vessels, each of which houses a material bed. The annular space between the inside of the pressure vessel and the outside of the material bed contains a liquid coolant that can be pressurized. The ortho-para conversion process is conducted at very low temperatures (<150 K) and therefore a liquid coolant such as liquid nitrogen or liquid argon is required to achieve temperatures in this range. Each pressure vessel contains a vent line equipped with a back pressure control valve to allow for control of the liquid boiling pressure. By controlling the liquid boiling pressure, temperature can be controlled indirectly over a range of 77 K to 126 K using liquid nitrogen as the coolant and temperatures up to about 150 K using liquid argon.

![Material Screening Test System](image-url)
This new test system has been used to determine performance characteristics of the ortho-para conversion system. These results have been used in the process model to determine the overall performance of a system using the improved ortho-para conversion process. These results are shown in Figures 3 and 4.

**Modeling**

Process simulations were developed for hydrogen liquefaction processes that used the improved ortho-para conversion process to compare those to processes that did not. Of the processes that did not use the improved ortho-para conversion process, it was found that adding ortho-para conversion catalyst to the high-temperature heat exchanger reduced overall energy consumption by about 2.5%.

Several different processes have been conceived that use the improved ortho-para conversion process. The modeling portion of the project will compare these processes to hydrogen liquefaction processes with standard ortho-para conversion. Concept α and Concept β have been evaluated to this point. Figures 3 and 4 show the results.

The point in the center is the target based on ortho-para performance meeting the base case power target. The y-axis represents the power required for hydrogen liquefaction as a percentage of the base case power target. The x-axis shows ortho-para performance as a percentage of demonstrated performance in the laboratory. The target is based on demonstrated performance (100% of current ortho-para performance) meeting the base case power target. In Figure 3, about 150% of the current demonstrated performance is required to meet the base case power target. Although there has been steady improvement in demonstrated performance throughout the project, marginal gains are lower than they were earlier in the project. It is unlikely that Concept α will meet the target required to be an economically viable process.

In Figure 4, 100% of the current demonstrated performance results in total power consumption below the base case power target. There has been steady improvement in demonstrated performance throughout the project and some future advancement is expected. Concept β has already met the target required to be an economically viable process on an energy basis. The difference in capital cost will be evaluated later this year and compared to the power cost savings possible through Concept β.

**Conclusions and Future Directions**

- Ortho-para conversion performance has been measured using laboratory and pilot reactors.
- The demonstrated performance is sufficient for at least one identified process concept to show reduced power cost when compared to hydrogen liquefaction processes using conventional ortho-para conversion.
• The impact of improved ortho-para conversion can be significant, but ortho-para conversion uses only about 20-25% of the total liquefaction power.
• Most of the energy used in liquefaction is for gas compression. The focus of the project will now be to evaluate different compressors and compression schemes to find possible efficiency improvements.

**FY 2010 Publications/Presentations**

1. DOE Annual Hydrogen Review Meeting