III.9 Advanced Hydrogen Liquefaction Process

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Objectives

Develop a low-cost hydrogen liquefaction system for 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 Production section (3.2.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) High Cost and Low Energy Efficiency of Hydrogen Liquefaction

Technical Targets

TABLE 1. Technical Targets for Liquid Hydrogen Delivery

Characteristic	Units	2012 Target	2017 Target
Small Scale Liquefaction (30,000 kg/day)			
Installed Capital Cost	$	40M	30M
Energy Efficiency	%	75	85
Large Scale Liquefaction (300,000 kg/day)			
Installed Capital Cost	$	130M	100M
Energy Efficiency	%	>80	87

We are addressing the capital cost and energy efficiency targets. We are not at the point in the project where we know enough about possible energy savings or capital cost reduction to show quantitative progress toward the goals yet.

- 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 develop a plan for solving 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.

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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 will attempt 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.
- 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 does not allow for testing over a temperature range. It 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 has now been built (Figure 2). All components of the system have been tested to ensure proper operation. Testing is scheduled to begin in the third quarter of 2009.

This 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

FIGURE 1. Material Screening Test System

FIGURE 2. Pilot-Scale Test System

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.

Modeling

Two models of existing hydrogen liquefiers have been constructed using process modeling software. The models are based on Praxair's 20 ton/day liquefiers in McIntosh, AL and Ontario, CA. The current models will utilize the Peng-Robinson Stryjek-Vera equation of state until the more accurate Modified Benedict Webb Rubin (MBWR) equation of state can be implemented into the process modeling software. The purpose of modeling the existing liquefiers is to enable the identification of possible energy savings. Thermodynamic analysis of the current process can be performed to pinpoint areas of inefficiency and lead to process design improvements.

The standard hydrogen liquefier is usually integrated with a nitrogen liquefier so that liquid nitrogen can be used in the initial cooling stage to cool the hydrogen stream down to about 75-90 K. The hydrogen stream is then split into a small and large stream. The small stream ultimately becomes the liquefied product while the large stream is sent through a series of turbine expanders and used as the refrigerant in the liquefier. The refrigerant stream is then recompressed and recycled to the beginning of the process. Compression is the most energy intensive part of the liquefaction process. Both the compression and expansion steps are areas where efficiency improvements could have a large effect on the overall energy usage of the process. Other technologies such as magnetic cooling and using helium as the refrigerant will be looked at for potential efficiency improvements.

Perhaps the largest improvement will come from the implementation of the improved ortho-para conversion process. In the current system, the heat exchangers are responsible for removing all the additional heat released during the transformation from ortho to para hydrogen. This additional heat removal results in additional power needed for the cooling loop. The improved ortho-para conversion process could significantly reduce the overall energy consumed. In order to properly model the ortho-para transformation, it is necessary to implement an accurate thermodynamics package for both ortho and para hydrogen. We are currently working with the process simulator supplier to improve the ability to model the behavior of normal and para-hydrogen.

Once the MBWR fix is completed, we will model the ortho-para conversion process and integrate it into the process model. We will also include any additional efficiency improvements into the model. We will then compare power consumption and capital cost to the current base case systems. We will include multiple energy saving solutions along with the improved ortho-para conversion process to maximize cost reduction and energy efficiency to meet the DOE goals.

While working on implementing the MBWR equations, we have also constructed a simple Excel-based model to track the energy requirements for liquefying hydrogen as a function of temperature in the cold box heat exchanger. This model gets its thermodynamic information using data supplied by the National Institute for Standards and Technology for ortho-para hydrogen. This model shows that the energy needs to be removed at a higher rate during the last 50 K or so of liquefaction. This also shows that implementing the improved ortho-para conversion process could potentially reduce the energy required for hydrogen liquefaction.

Conclusions and Future Directions

- We are working with the process simulation software vendor to fix problems modeling ortho and para hydrogen and intend to have the problem solved later this year. We will use the corrected version of the software to model different liquefaction processes to identify possible energy savings.
- Testing will begin next quarter using the new test reactor that is capable of testing ortho-para conversion over a temperature range.

FY 2009 Publications/Presentations

1. DOE Annual Hydrogen Review Meeting

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