Advanced Hydrogen Liquefaction Process

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Jerry Jankowiak
Joe Schwartz
Praxair - Tonawanda, NY

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Overview

PRAXAIR

Program Timeline

7/08 – 12/09	1/10 – 12/10	1/11-12/11
Phase I	Phase II	Phase III

- **Phase I – Feasibility**
  1. Develop Alternative Hydrogen Liquefaction Processes
  2. Validate Ortho-Para Conversion Process Performance
- **Phase II – Hydrogen Liquefaction Process Development**
  3. Establish Efficiency, Equipment, and Material Performance Targets
  4. Estimate Capital Cost
- **Phase III – Process Performance Evaluation**
  5. Demonstrate Improved Ortho-Para Conversion Process
  6. Evaluate Potential Cost Reduction and Efficiency Improvement

Phase I Budget

	Total	Spent (as of March 15)
DOE	500,000	63,222
Praxair	125,000	15,805
TOTAL	625,000	79,027

13% Complete

Barriers Addressed

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

Hydrogen Delivery - Relevance

- Pipeline (~ 1 billion scfd)
  - Refineries and other large hydrogen consumers
- Liquid (~ 10 million scfd)
  - 1.8 million scf/truck
  - Liquefaction is energy intensive and expensive
  - Liquid serves an important market segment
- Tube Trailers
  - 125,000 scf/truck
- Cylinders
  - 250 scf/cylinder

DOE Targets – Relevance

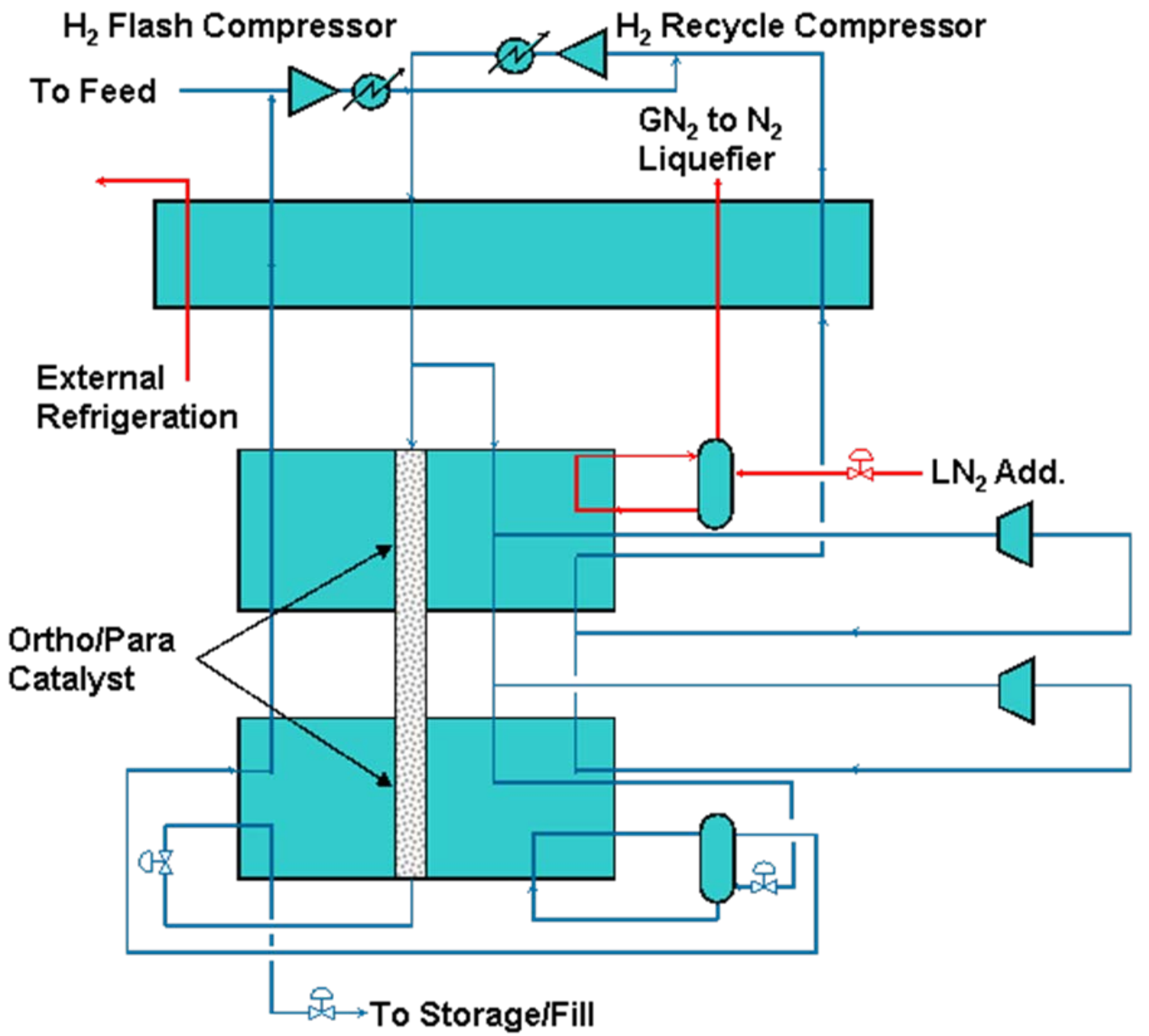
Category	2005 Status	2012	2017
Small-Scale Liquefaction (30,000 kg H_2/day)			
Installed Capital Cost ($)	$50M	$40M	$30M
Energy Efficiency (%)	70%	75%	85%
Large-Scale Liquefaction (300,000 kg H_2/day)			
Installed Capital Cost ($)	$170M	$130M	$100M
Energy Efficiency (%)	80%	>80%	87%

$$\text{Efficiency} = \frac{\text{Liquefied Hydrogen LHV}}{\text{Liquefied Hydrogen LHV + Liquefaction Energy}}$$

Objectives - Relevance

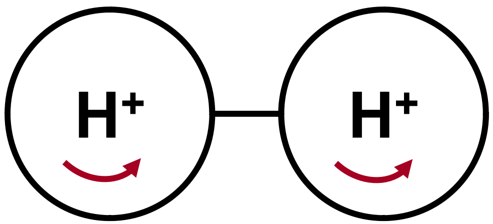
- **Program - Develop a low-cost hydrogen liquefaction system for 30 and 300 tons/day that meets or exceeds DOE targets for 2012**
  - Improve liquefaction energy efficiency
  - Reduce liquefier capital cost
  - Integrate improved process equipment invented since last liquefier was designed
  - Continue 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
Existing Process Flow Diagram

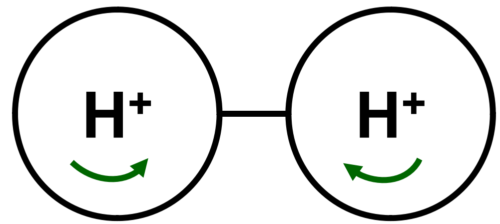


Forms of Molecular Hydrogen

Ortho



Para

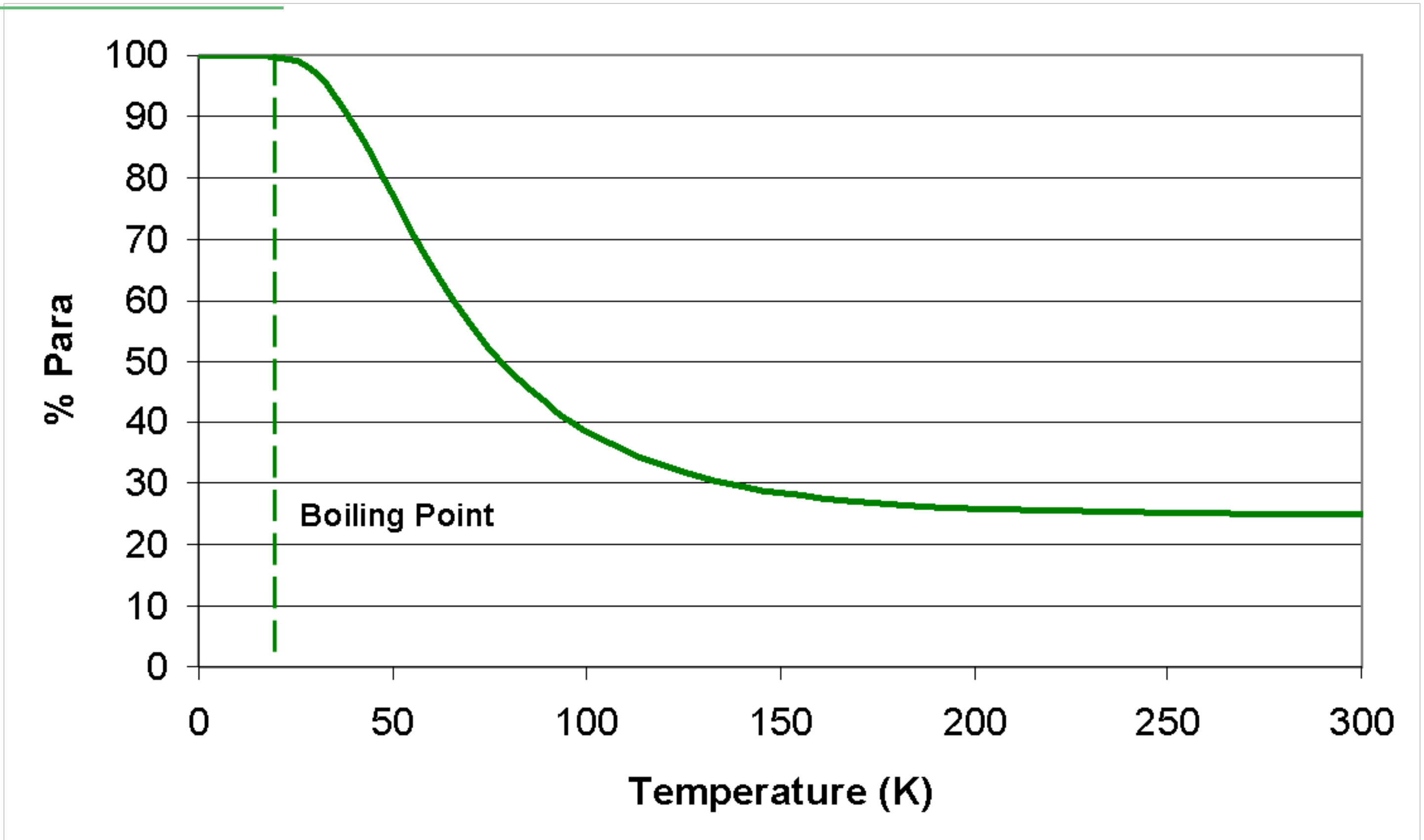


- **Difference is due to proton spin**
  - Normal Hydrogen is 75% Ortho, 25% Para
  - Equilibrium Liquid Hydrogen is 0.2% Ortho, 99.8% Para

- **Ortho-Para conversion requires 18 - 45% of the minimum work requirement for liquefaction***
  - Depends on the conversion process used
  - No sensible heat removed

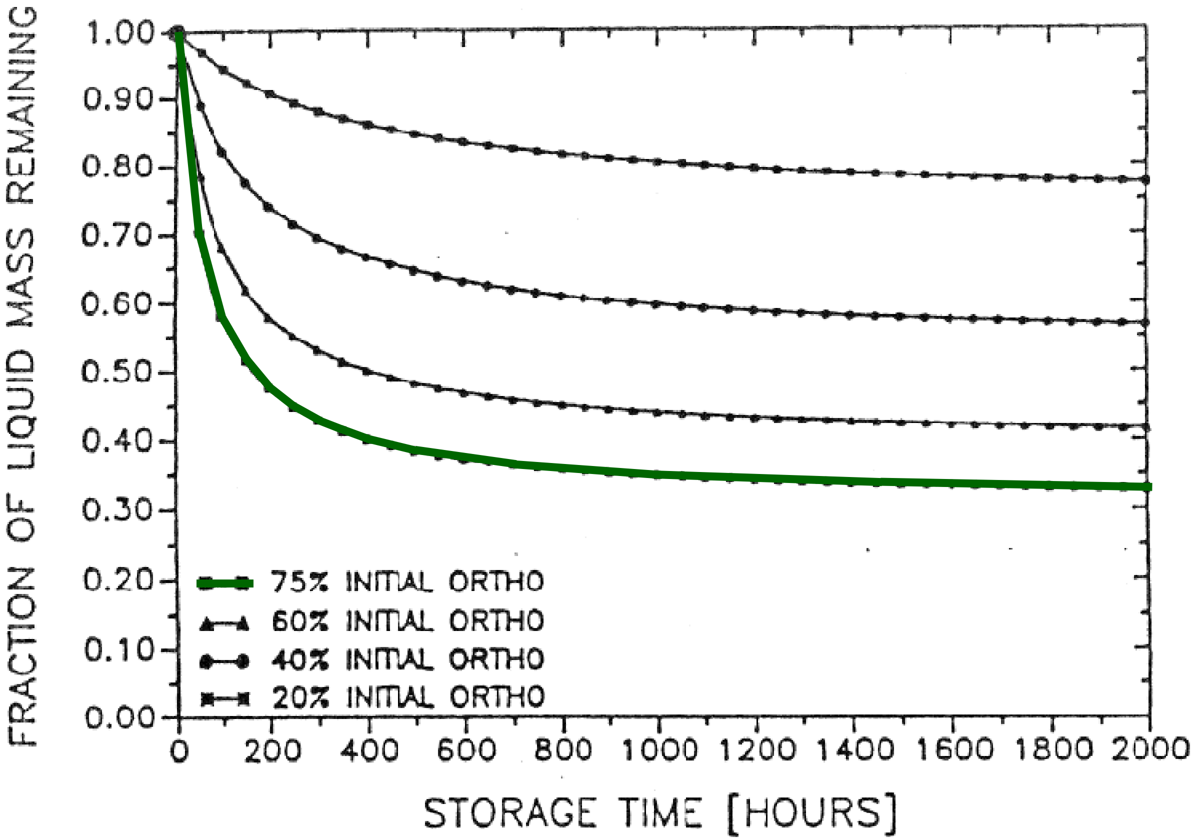
* From Baker, C. R. and Shaner, R. L. *A Study of the Efficiency of Hydrogen Liquefaction,* Int. J. Hydrogen Energy, v. 3, p. 321, 1978.

Equilibrium Composition



- **Para fraction increases as temperature approaches liquid range**
  - Catalyst is used to reach equilibrium composition during cooling

Why It Matters - 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:

Gursu, S. et al. *An Optimization Study of Liquid Hydrogen Boil-Off Losses,* Int. J. Hydrogen Energy., v. 17, p. 227, 1992.

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
- **Expand program to incorporate other process improvements beyond improved ortho-para conversion to increase efficiency and reduce cost**
  - Design a process with higher efficiency
  - Implement improved process equipment
  - Optimize improved ortho-para conversion process

Milestones - Approach

- **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

Phase I Plan - Approach

- **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

Thermodynamic Model - Progress

- **Typical models are not accurate near the critical point**
  - Need to handle temps from 20K to 300K. Critical point is at 33K which is near where the liquefaction occurs.
- **Typical models do not distinguish between ortho and para**
  - Cannot predict heat of conversion from ortho to para
  - Need to predict this accurately in order to maximize energy savings around this step of the process.
- **New model developed by Leachman *et al*. handles these issues**
  - Accurate equations of state for both ortho and para hydrogen.

Leachman, J. W. et al., *Fundamental Equations of State for Parahydrogen, Normal Hydrogen and Orthohydrogen,* Journal of Physical and Chemical Reference Data, (In Review).

Thermodynamic Model - Progress

- **Written in terms of the Helmholtz free energy along with an expression for the ideal gas heat capacity**
  - All other thermodynamic properties can be determined from this equation
- **Our new process modeling software does not include these equations of state**
- **Next step is to program a thermo “socket” that works with our new process modeling software to implement these equations**
- **NIST provides a software package that generates thermodynamic data from equations of state and implements the Leachman equations**
  - This will be used to check our thermo socket and to validate any data that comes from the process model.

Process Models - Progress

- **Both traditional and advanced liquefaction processes are being modeled**
  - Both models will be thoroughly examined to pinpoint areas where energy and cost savings can be achieved
  - Experimental results will be used to model ortho-para covnersion performance
  - The model will also be used to propose new experiments when better operating conditions are discovered

Ortho-Para Conversion - Progress

- Large and small test systems have been constructed
- Safety reviews completed
- Liquid nitrogen used for cooling
- Testing scheduled to begin in 2Q09

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
  - 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

Summary

- 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 improved ortho-para conversion with state-of-the-art equipment and takes full advantage of its increased capability
- Program is in the initial part of Phase I