Advanced Hydrogen Liquefaction Process

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Project ID
PD018

Overview

Program Timeline

7/08 – 12/09 | 1/10 – 12/10 | 1/11-12/11

Current Budget

	Total	Spent (as of April 1)
DOE	800,000	555,143
Praxair	200,000	138,786
TOTAL	1,000,000	693,929

69% Complete

- **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

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**

Hydrogen Distribution - Relevance

Liquid Tanker

4500 kg H_2

Tube Trailer

300 kg H_2

- **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**

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

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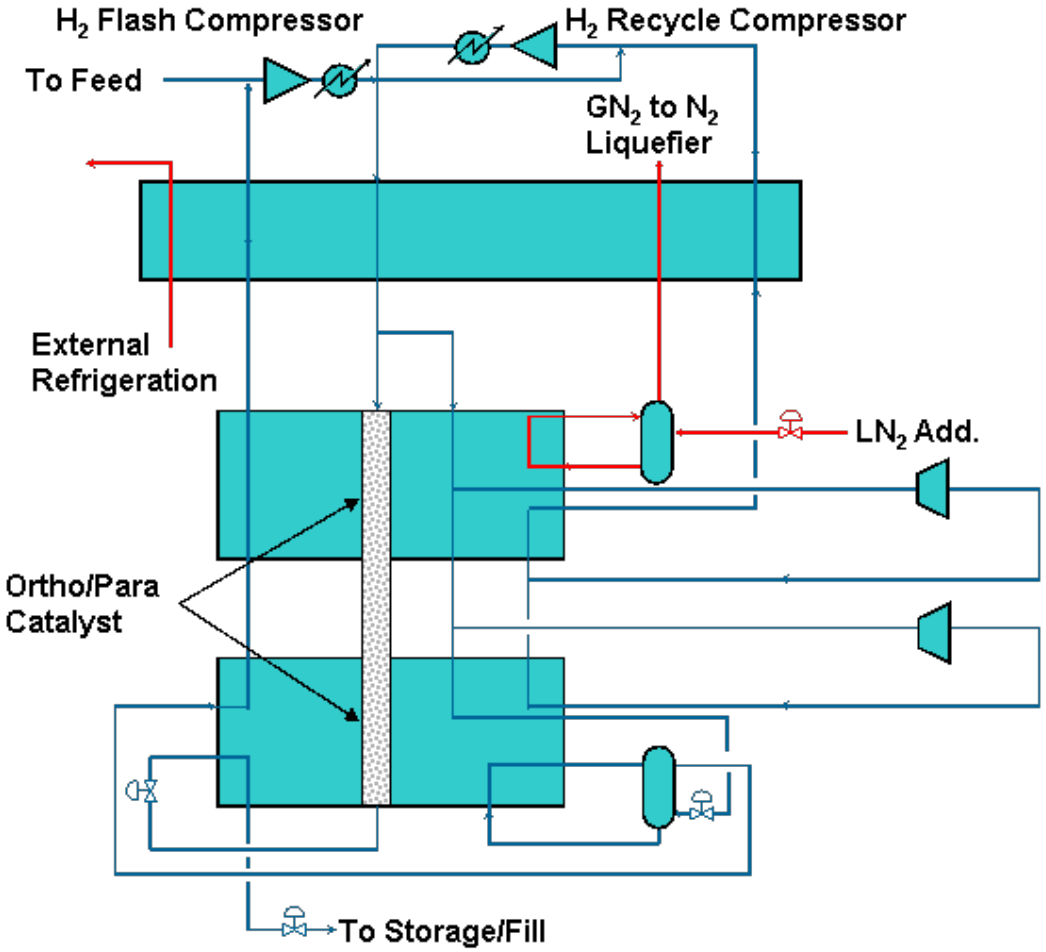
- **Program - Develop a low-cost hydrogen liquefaction system for 30 and 300 tons/day that meets or exceeds DOE targets for 2012**
  - Improve liquefaction energy efficiency
  - Reduce liquefier capital cost
  - Integrate improved process equipment
  - Continue ortho-para conversion process development
  - Integrate improved ortho-para conversion process
  - Develop optimized new liquefaction process based on new equipment and new ortho-para conversion process
- **Phase II – Process Development**
  - Establish performance targets for process equipment and ortho-para conversion
  - Develop preliminary capital cost estimate

Hydrogen Liquefaction
Existing Process Flow Diagram

- Existing process is highly integrated with air separation
- Cannot clearly distinguish between power used for air separation and for H_2 liquefaction because LN_2 used for cooling



Forms of Molecular Hydrogen

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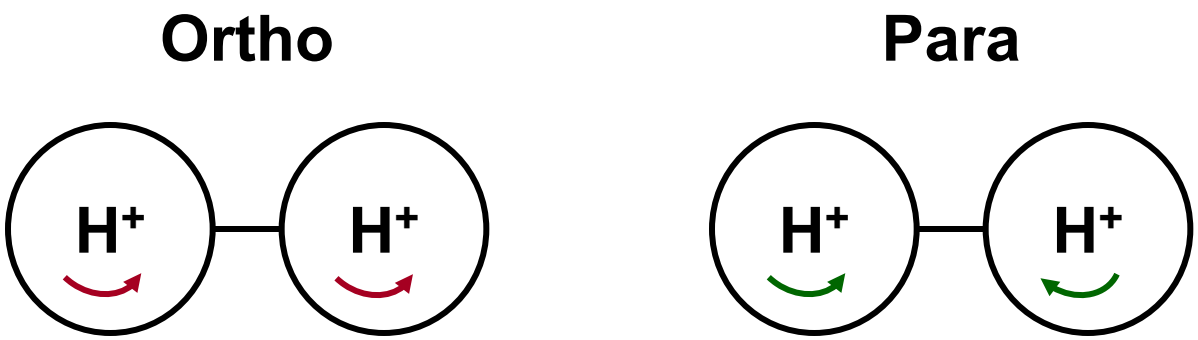
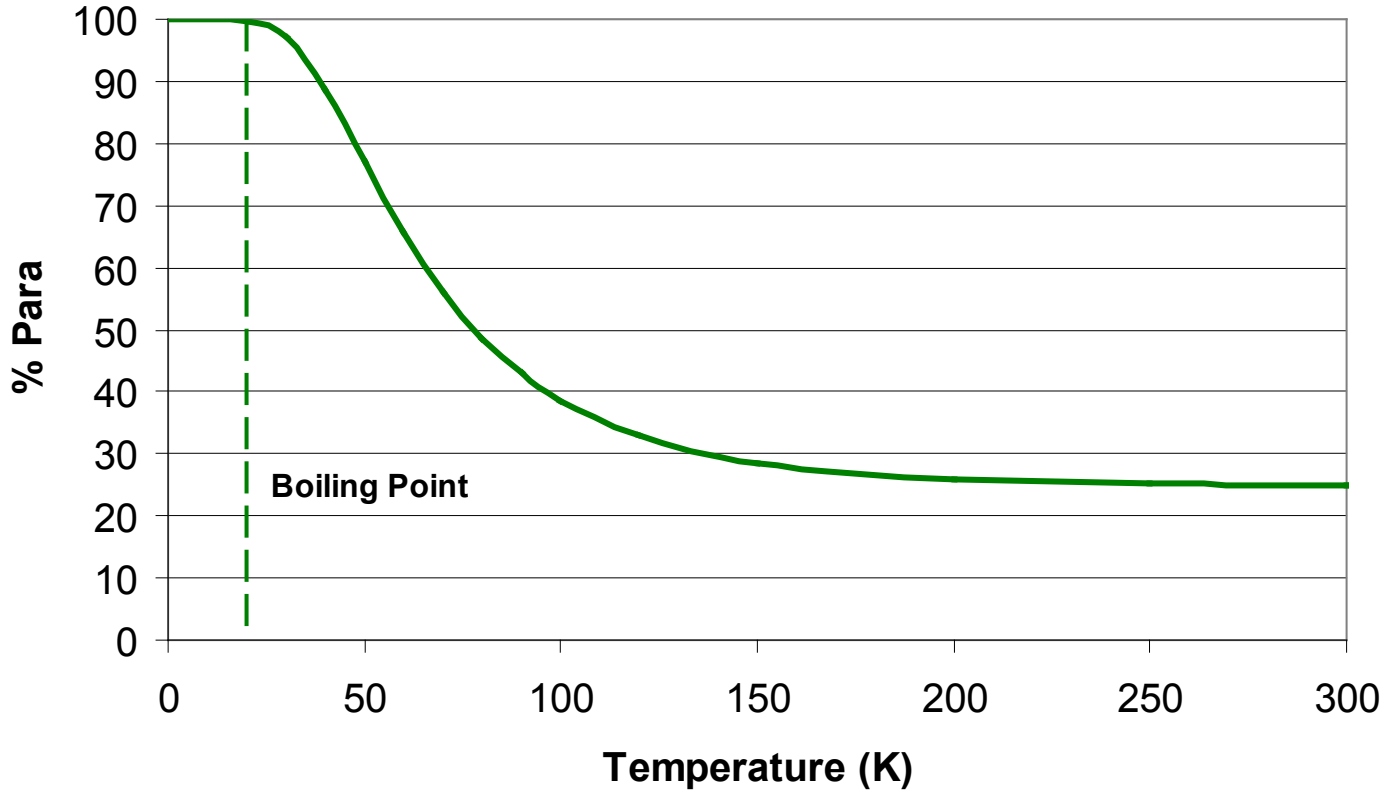


- **Difference is due to proton spin**
  - Normal Hydrogen is 75% Ortho, 25% Para
  - Equilibrium Liquid Hydrogen is 0.2% Ortho, 99.8% Para

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

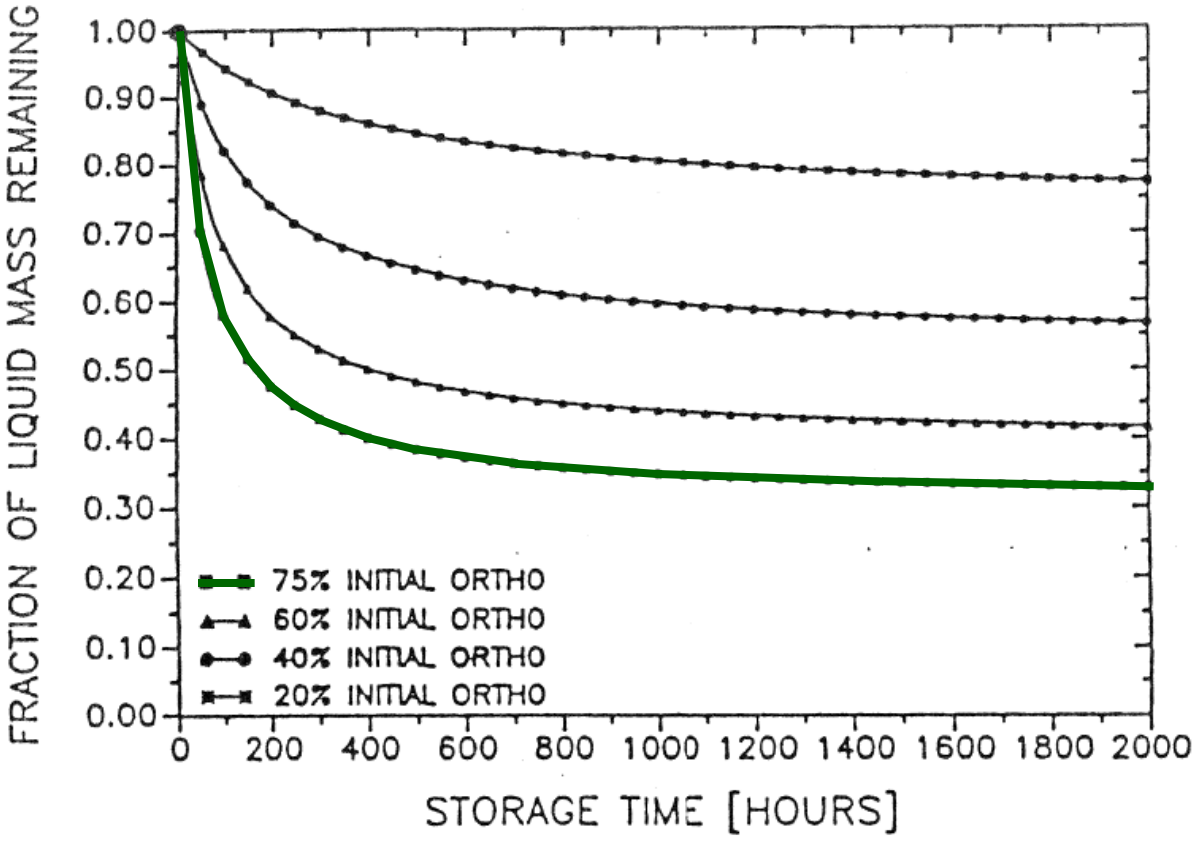
* From Baker, C. R. and Shaner, R. L. *A Study of the Efficiency of Hydrogen Liquefaction,* Int. J. Hydrogen Energy, v. 3, p. 321, 1978.

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 II Plan - Approach

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- **Process Optimization, Design, and Economics (30%)**
  - Develop alternative hydrogen liquefaction processes that can optimally integrate new equipment and improved ortho-para process
  - Establish targets for equipment and ortho-para conversion
- **Process Equipment Evaluation (25%)**
  - Evaluate commercially available critical equipment
  - Evaluate novel turbomachinery
- **Ortho-Para Conversion Optimization (45%)**
  - Construct larger-scale test facility
  - Validate process performance at larger scale

Thermodynamic Model - Progress

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- **Typical models are not accurate near the critical point**
  - Need to handle temps from 20K to 300K
  - Critical point is 33K, which is near where liquefaction occurs
- **Typical models do not distinguish between ortho and para**
  - Cannot predict heat of conversion from ortho to para
  - Cannot predict hydrogen stream composition
  - Need accurate prediction to evaluate energy savings from ortho-para conversion processes
- **Para and normal hydrogen have been implemented by the supplier of our process modeling software**
  - Now possible to model ortho-para conversion
  - Accurate thermodynamic properties for equilibrium mixtures

Process Modeling - Progress

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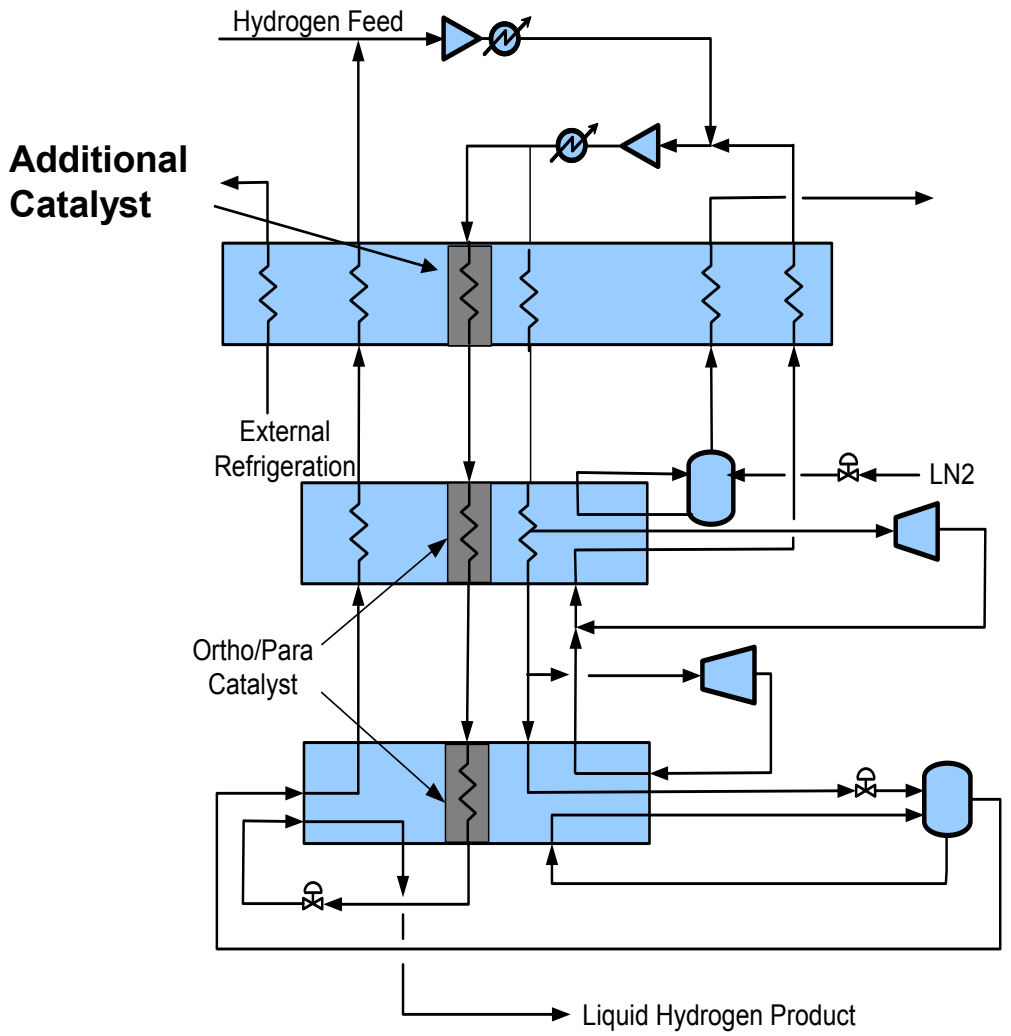
- **Both traditional and advanced liquefaction processes are being modeled**
  - Both models will be thoroughly examined to pinpoint areas where energy and cost savings can be achieved
  - Experimental results are used to evaluate ortho-para conversion performance
  - Different process configurations have been evaluated based on experimental results
  - Modeling and experimental results have guided process selection and focus of future testing

Process Modeling - Progress

- Cooling load is moved from 2nd heat exchanger to 1st heat exchanger
- External refrigeration increases by 17%
- LN2 requirement decreases by 11%
- Overall power consumption decreases by 2.4%
- Recycle flow is reduced



Process Modeling - Progress

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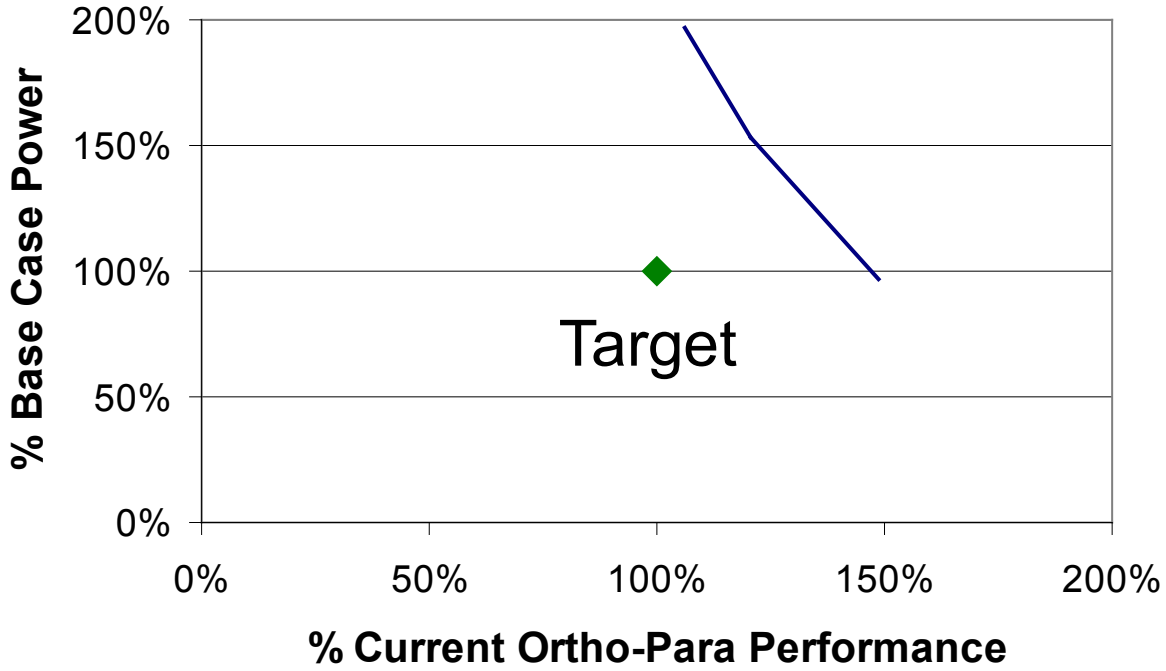
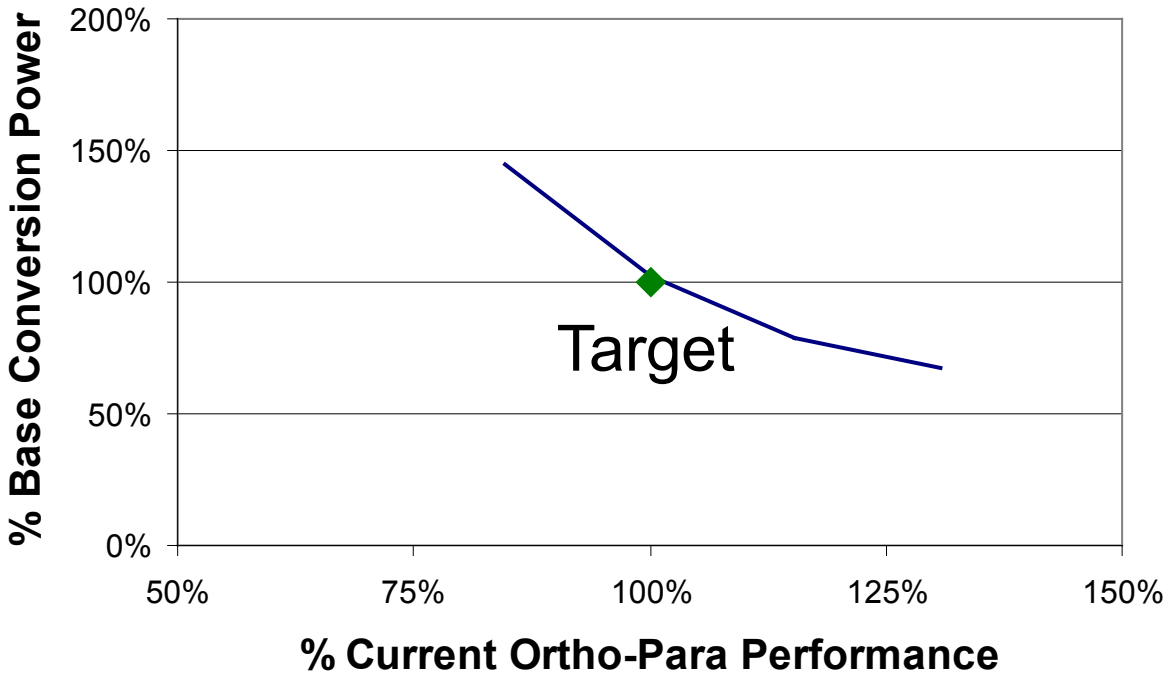
Improved Ortho-Para Conversion Process – Concept Alpha



- **Demonstrated performance is not sufficient to provide benefit**
- **50% performance improvement required to reach target**
- **Target will be difficult to reach**

Process Modeling - Progress

Improved Ortho-Para Conversion Process – Concept Beta



- **Demonstrated performance is close to target**
- **Future improvement in performance could improve overall process efficiency**

Ortho-Para Conversion - Progress

- Large and small test systems have been constructed
- Liquid nitrogen used for cooling
- Testing is underway
- Demonstrated performance and process analysis show potential advantage with slight improvement

Future Work

- **Process Optimization, Design, and Economics**
  - Estimate capital cost
- **Process Equipment Evaluation**
  - Evaluate commercially available critical equipment
  - Evaluate novel turbomachinery
- **Ortho-Para Conversion Process Optimization**
  - Select best candidate ortho-para process

Equipment development is beyond the scope of this program

Summary

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- **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**
- **Process simulation software now includes para and normal hydrogen**
  - Efficiency improvements have been identified
  - Improved ortho-para conversion performance is required

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