



# Advanced Hydrogen Liquefaction Process

Contract Number: DE-FG36-08GO18063

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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
<b>TOTAL</b>	<b>1,000,000</b>	<b>693,929</b>

**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<sub>2</sub>**



**Tube Trailer**  
**300 kg H<sub>2</sub>**

- **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
<i>Small-Scale Liquefaction (30,000 kg H<sub>2</sub>/day)</i>			
Installed Capital Cost (\$)	\$50M	\$40M	\$30M
Energy Efficiency (%)	70%	75%	85%
<i>Large-Scale Liquefaction (300,000 kg H<sub>2</sub>/day)</i>			
Installed Capital Cost (\$)	\$170M	\$130M	\$100M
Energy Efficiency (%)	80%	>80%	87%

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

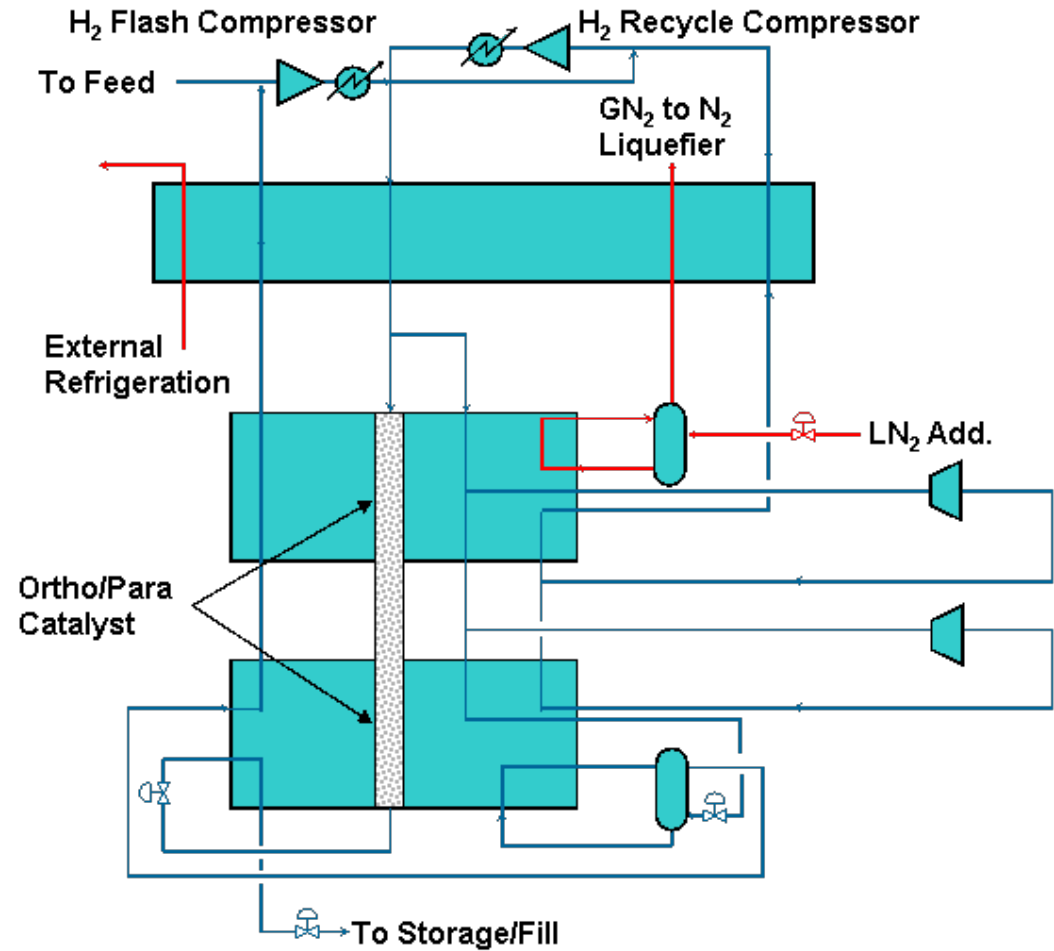
# ***Objectives - Relevance***



- **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
  - 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

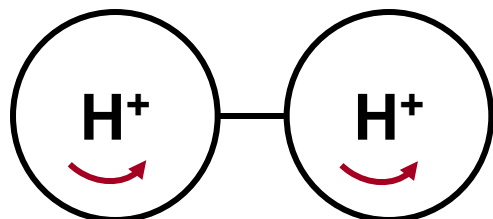
- Existing process is highly integrated with air separation
- Cannot clearly distinguish between power used for air separation and for H<sub>2</sub> liquefaction because LN<sub>2</sub> used for cooling



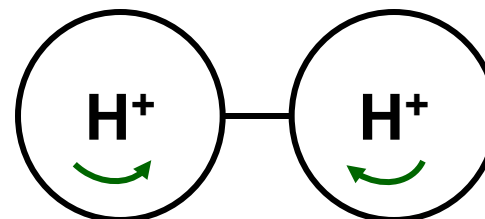


# Forms of Molecular Hydrogen

Ortho



Para

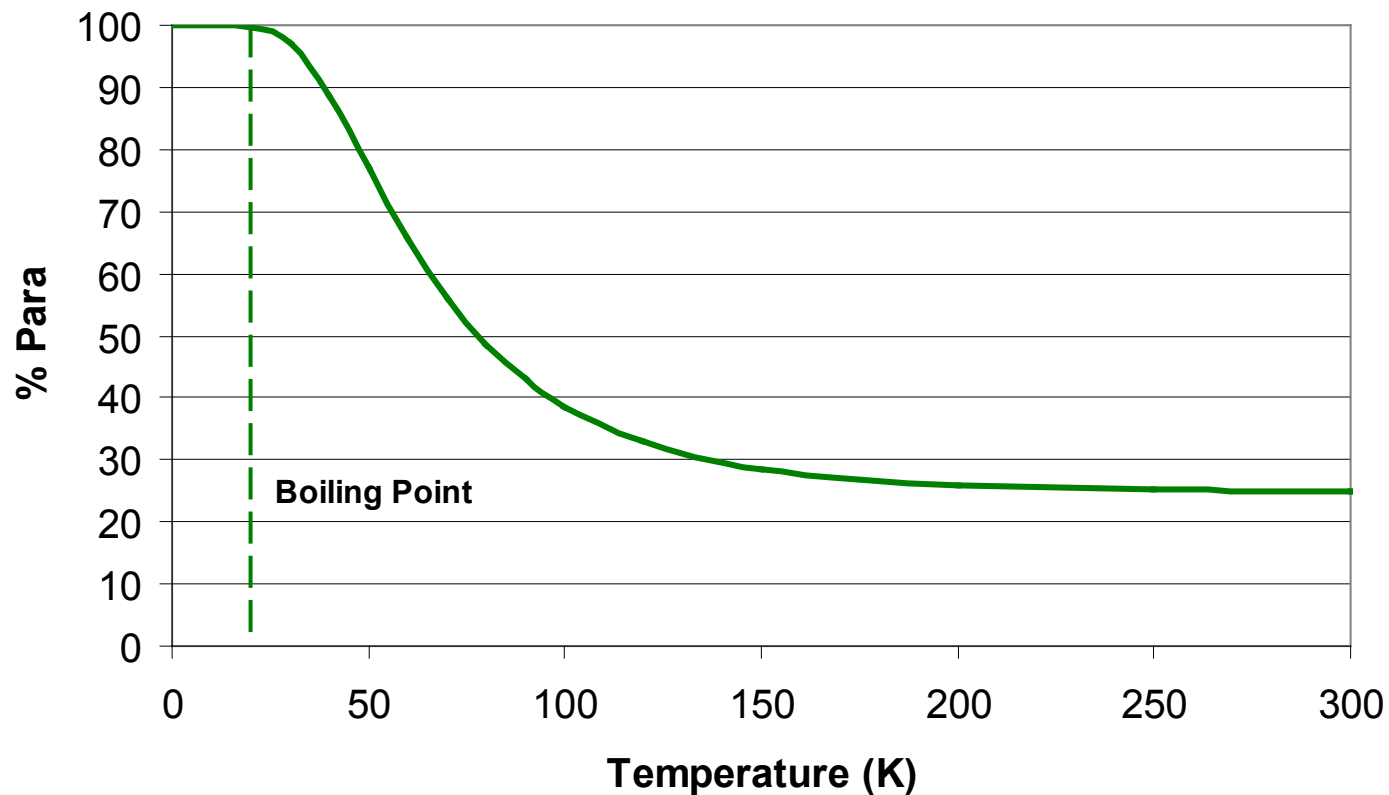


- **Difference is due to proton spin**
  - Normal Hydrogen is 75% Ortho, 25% Para
  - Equilibrium Liquid Hydrogen is 0.2% Ortho, 99.8% Para
- **Ortho-Para conversion requires 18 - 45% of the minimum work requirement for liquefaction\***
  - Depends on the conversion process used
  - No sensible heat 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.

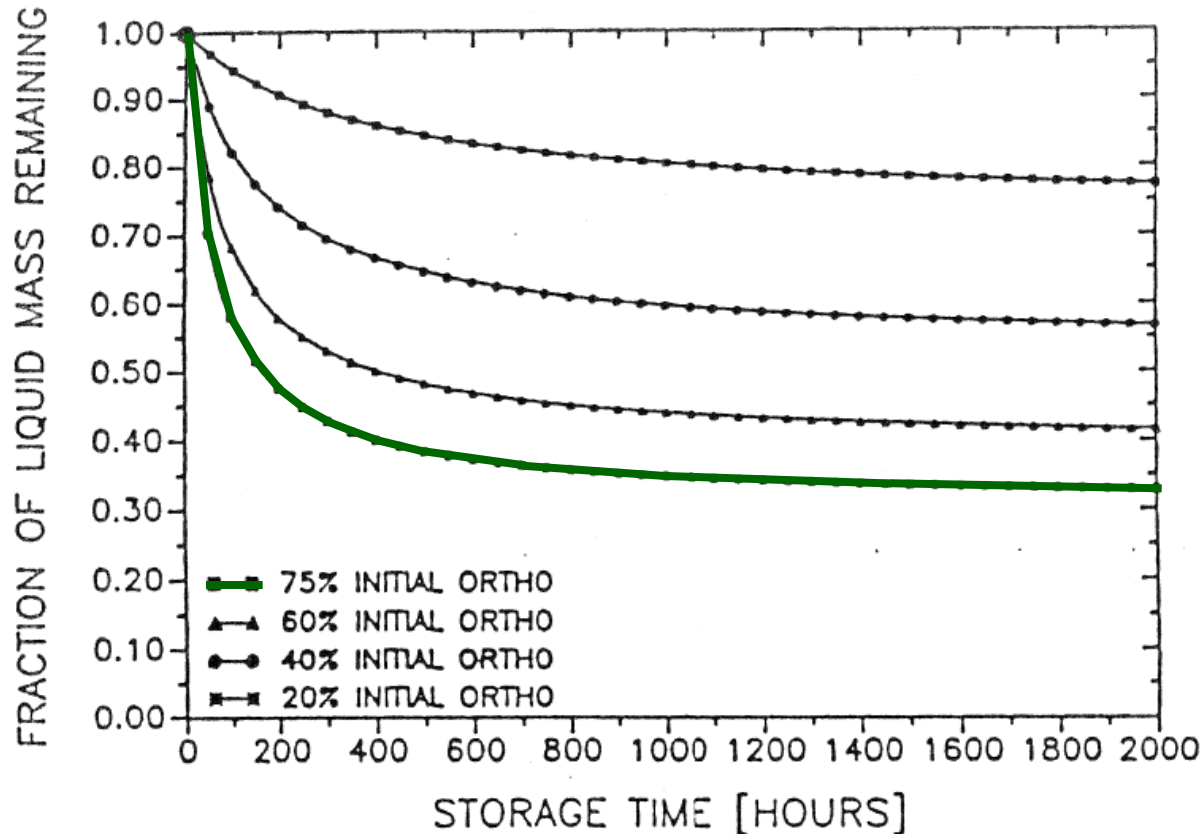


# Equilibrium Composition



- **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

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# ***Milestones - Approach***

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- **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

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# ***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***

- **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

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# ***Process Modeling - Progress***

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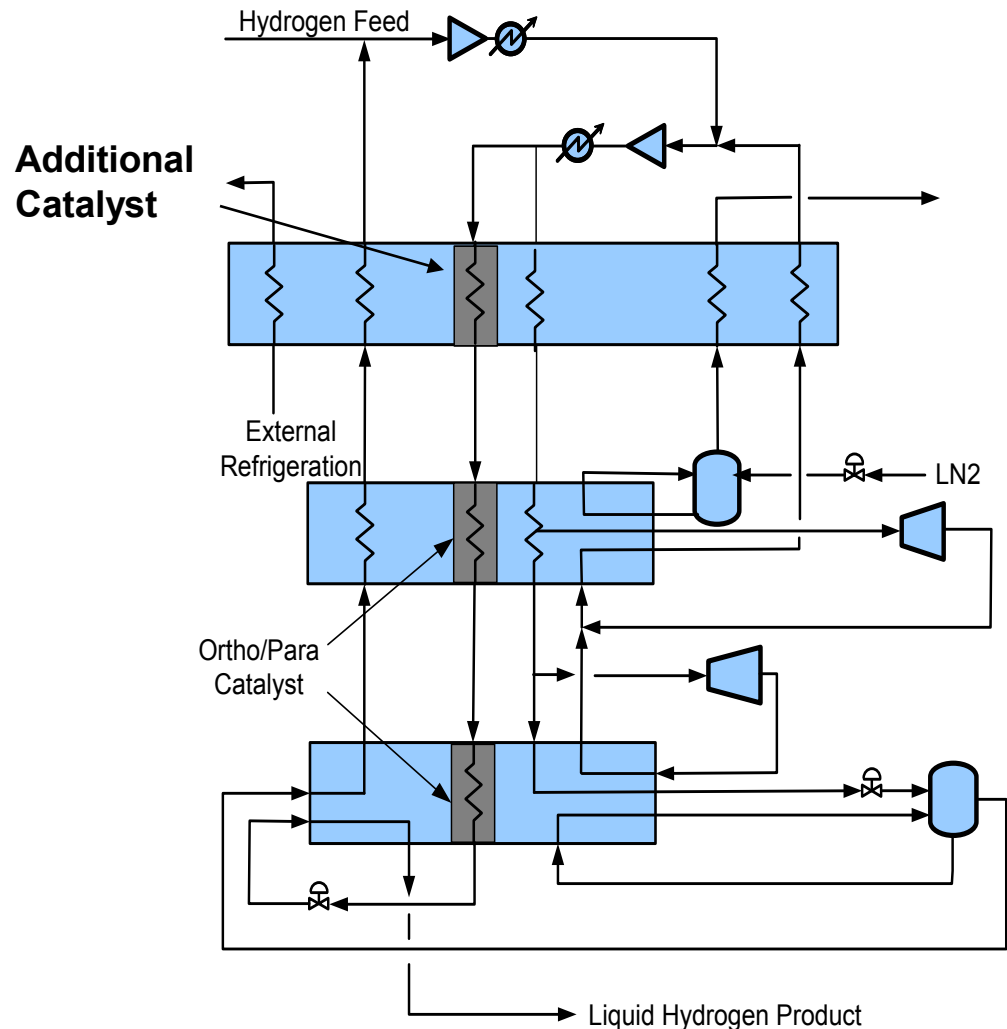


- **Both traditional and advanced liquefaction processes are being modeled**
  - Both models will be thoroughly examined to pinpoint areas where energy and cost savings can be achieved
  - Experimental results are used to evaluate ortho-para conversion performance
  - Different process configurations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



# Process Modeling - Progress

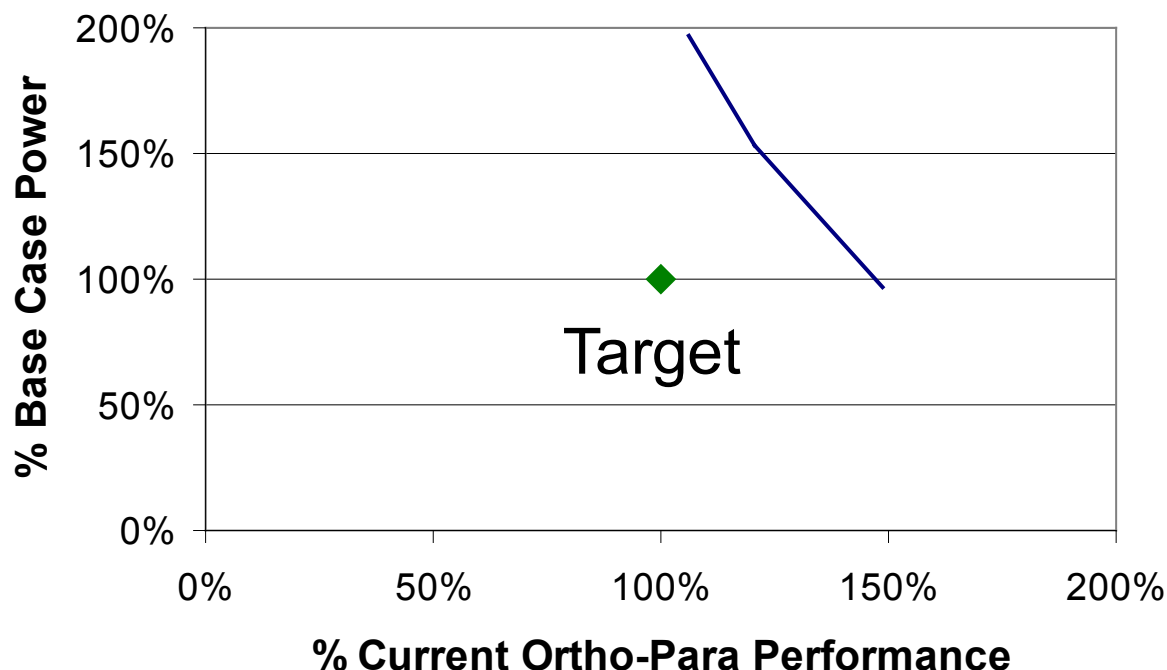
- Cooling load is moved from 2<sup>nd</sup> heat exchanger to 1<sup>st</sup> heat exchanger
- External refrigeration increases by 17%
- LN2 requirement decreases by 11%
- Overall power consumption decreases by 2.4%
- Recycle flow is reduced



# Process Modeling - Progress



## Improved Ortho-Para Conversion Process – Concept Alpha

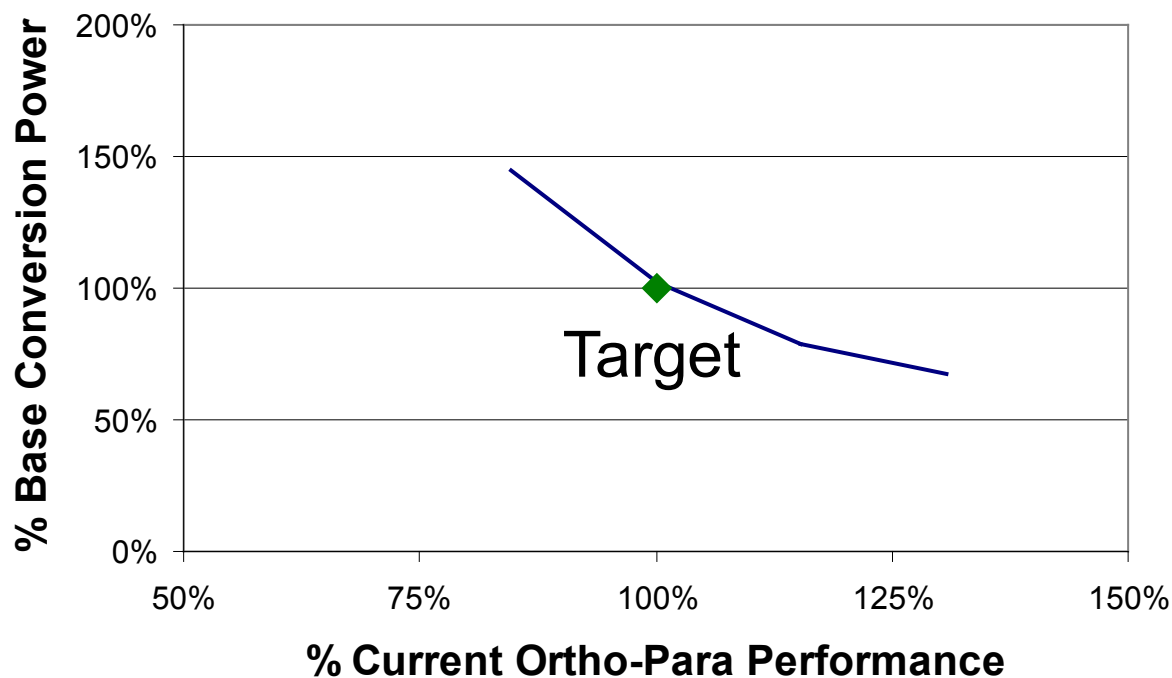


- **Demonstrated performance is not sufficient to provide benefit**
- **50% performance improvement required to reach target**
- **Target will be difficult to reach**

# 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



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# ***Future Work***

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- **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

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# ***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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# ***Acknowledgments***

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