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Advanced Hydrogen Liquefaction Process

Contract Number: DE-FG36-08GO18063

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DOE Annual Merit Review Meeting
May 10, 2011

Project ID
PD018

This paper was written with support of the U.S. Department of Energy under Contract No. DE-FG36-08GO18063.

Overview

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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. Evaluate Potential Cost Reduction and Efficiency Improvement
- **Phase III – Process Performance Evaluation**
  5. Demonstrate Improved Ortho-Para Conversion Process
  6. Estimate Capital Cost

Current Budget

	Total	Spent (as of March 1)
DOE	800,000	667,684
Praxair	200,000	166,921
TOTAL	1,000,000	834,605

100% Complete

Barriers Addressed

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

Hydrogen Liquefaction
Existing Process Flow Diagram

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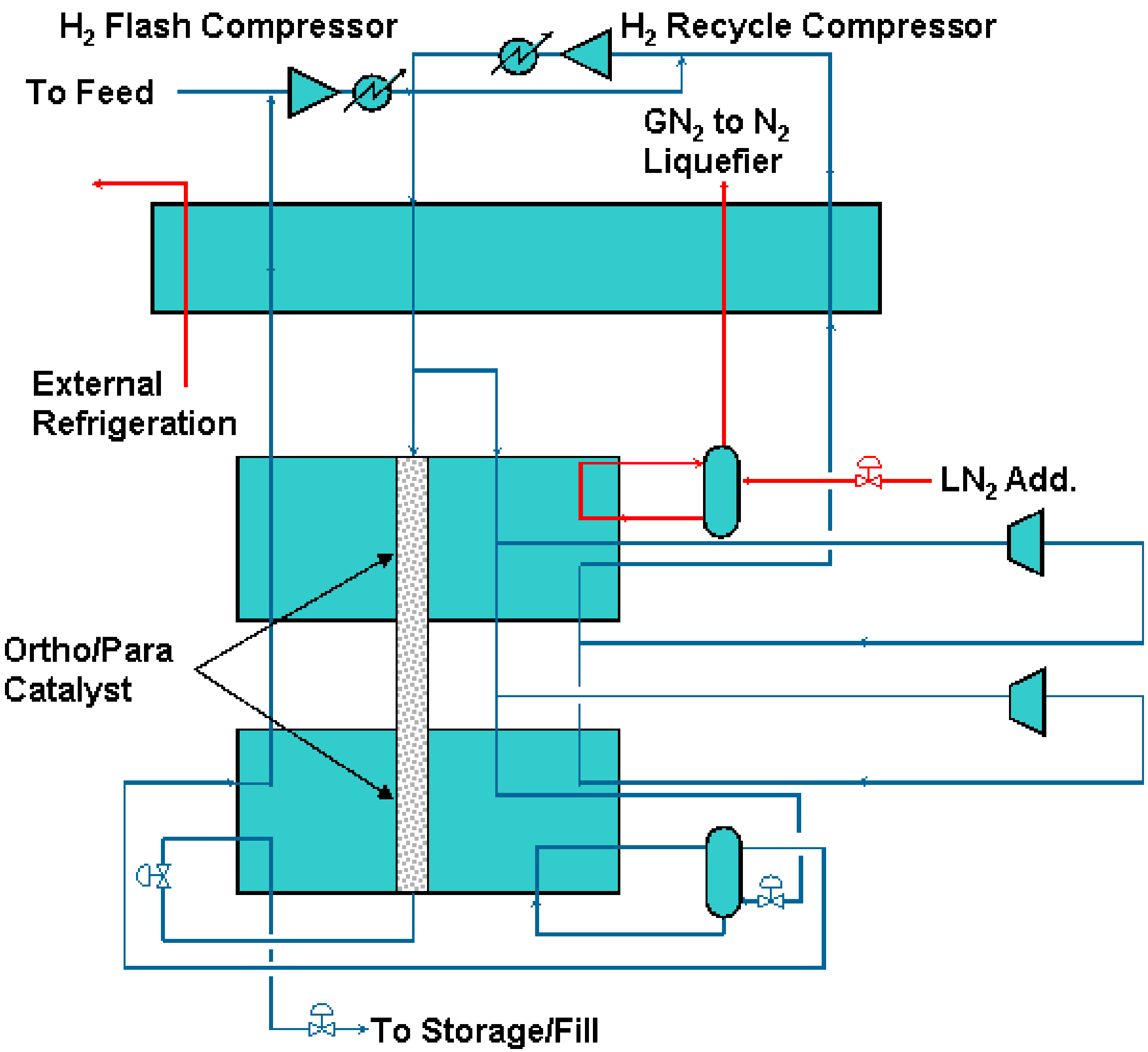
- Existing process is highly integrated with air separation
- Liquid nitrogen typically used as a coolant in the process



Joule-Thomson Inversion Curve

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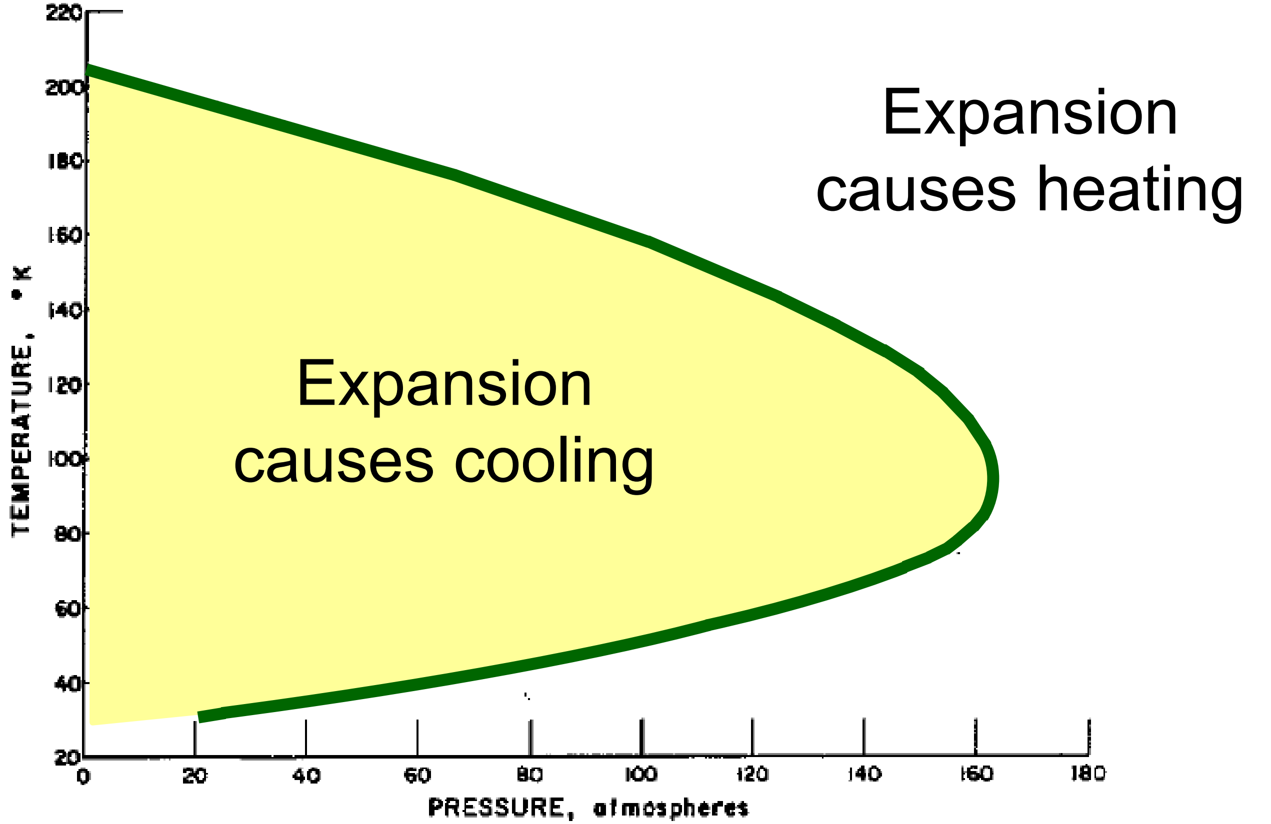

- Hydrogen will cool upon expansion only if it is already cold
- Hydrogen has an exceptionally low critical temperature (33 K)
- N_2 (126 K), O_2 (155), CH_4 (190), Ar (151), CO (133), Kr (209), Xe (290) all have inversion temperatures about 5 – 5.5 * T_{crit}

* From Scott, R.B. et al. Technology and Uses of Liquid Hydrogen, p.42, The MacMillan Company, New York, 1964.

Hydrogen Liquefier
Equipment Design Considerations

Component	State of the Art	Near Term	Long Term
Compressors	Reciprocating Screw	Reciprocating Centrifugal	Centrifugal Hydride Guided Rotor
Pre-Cooling	Liquid N_2	Mixed gas	Magnetic
Low-Temp Refrigeration	Reverse Brayton	Reverse Brayton with advanced turbines	Magnetic Acoustic
Heat Exchangers	Brazed aluminum	Brazed aluminum Micro-channel	Micro-channel
Ortho-Para Conversion	Catalytic conversion	Improved ortho-para process	Advanced ortho-para process

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 from 14 kWh/kg (2005 status) to 11 kWh/kg (2012 goal) - 22% improvement
  - Reduce liquefier capital cost
  - Integrate improved process equipment
  - 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 to meet the cumulative efficiency improvement required by the 2012 goal (22% improvement)

DOE Targets – Relevance

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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%

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

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

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Liquid Tanker

4500 kg H_2

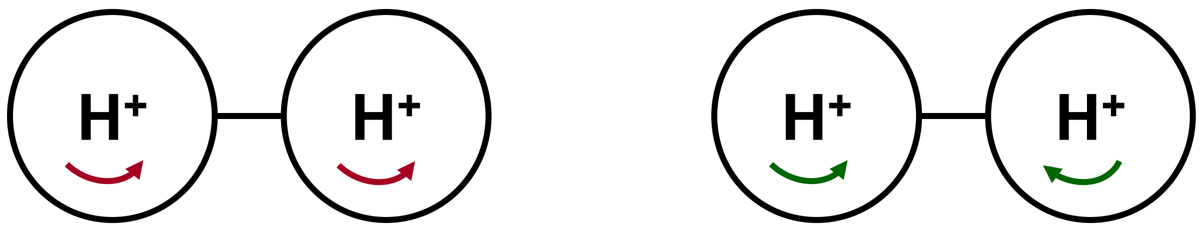
Tube Trailer

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**

Forms of Molecular Hydrogen

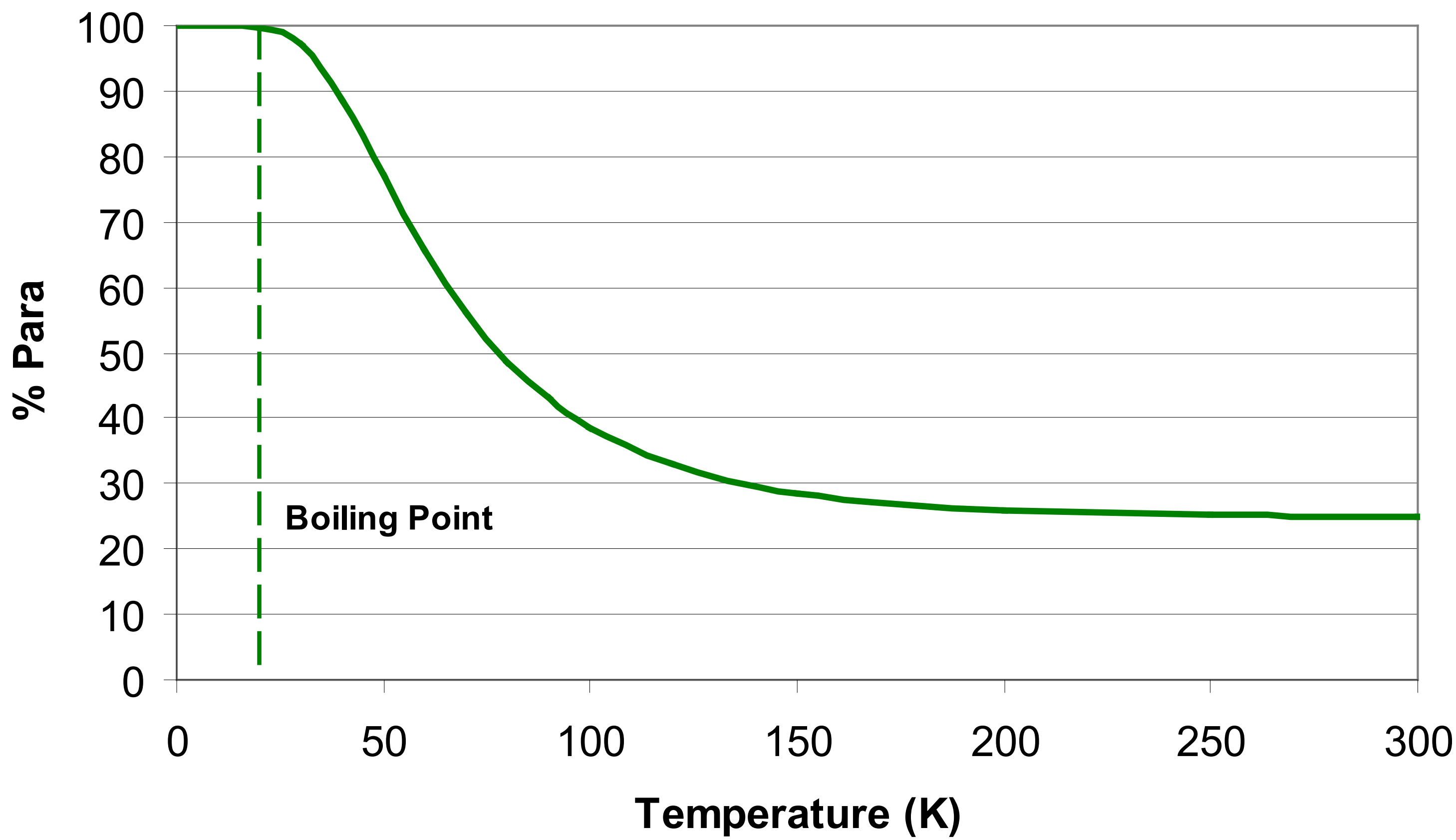
Ortho **Para**



- **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

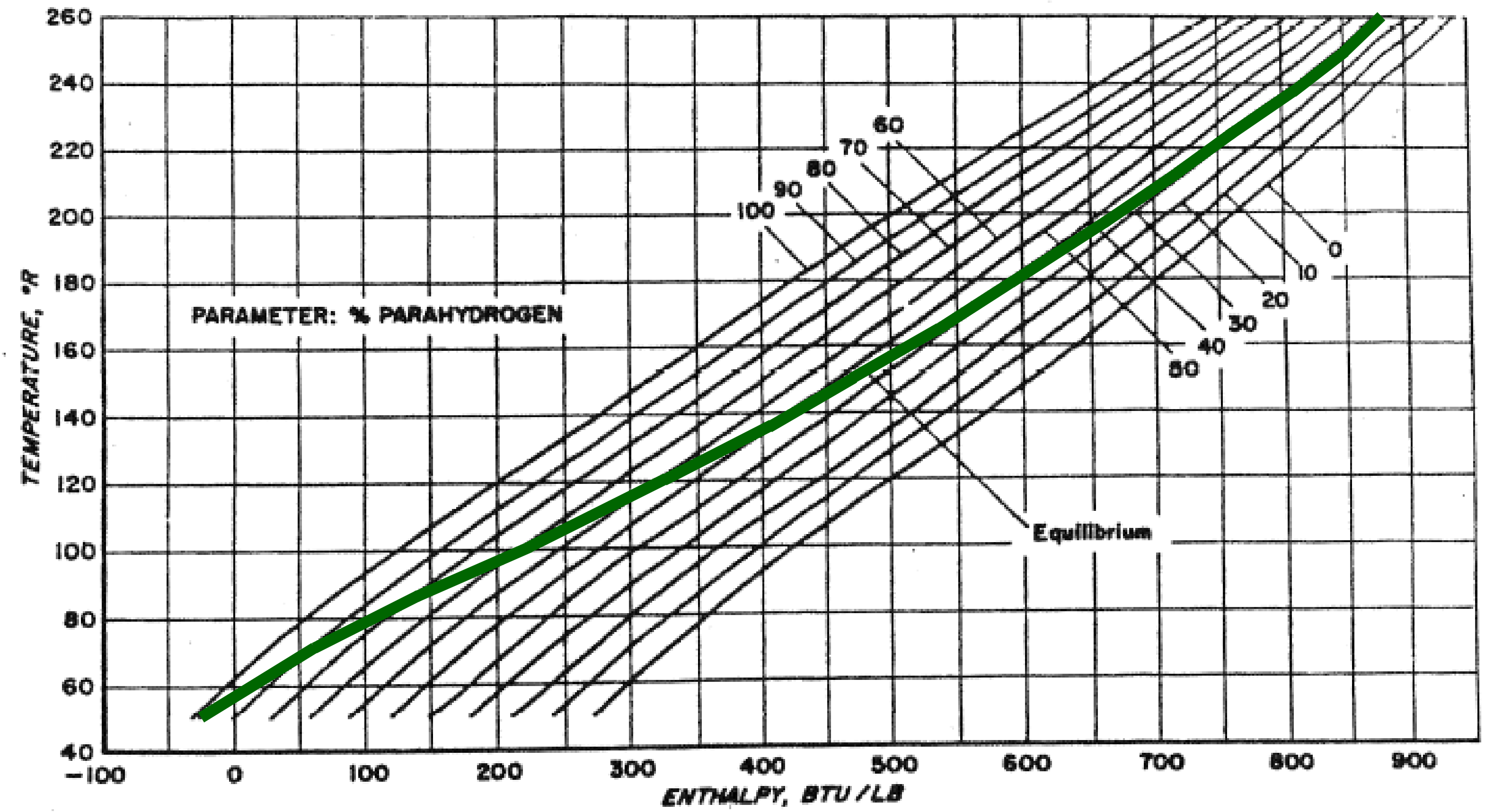
* From Baker, C. R. and Shaner, R. L. *A Study of the Efficiency of Hydrogen Liquefaction,* Int. J. Hydrogen Energy, v. 3, p. 321, 1978.

Equilibrium Composition



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

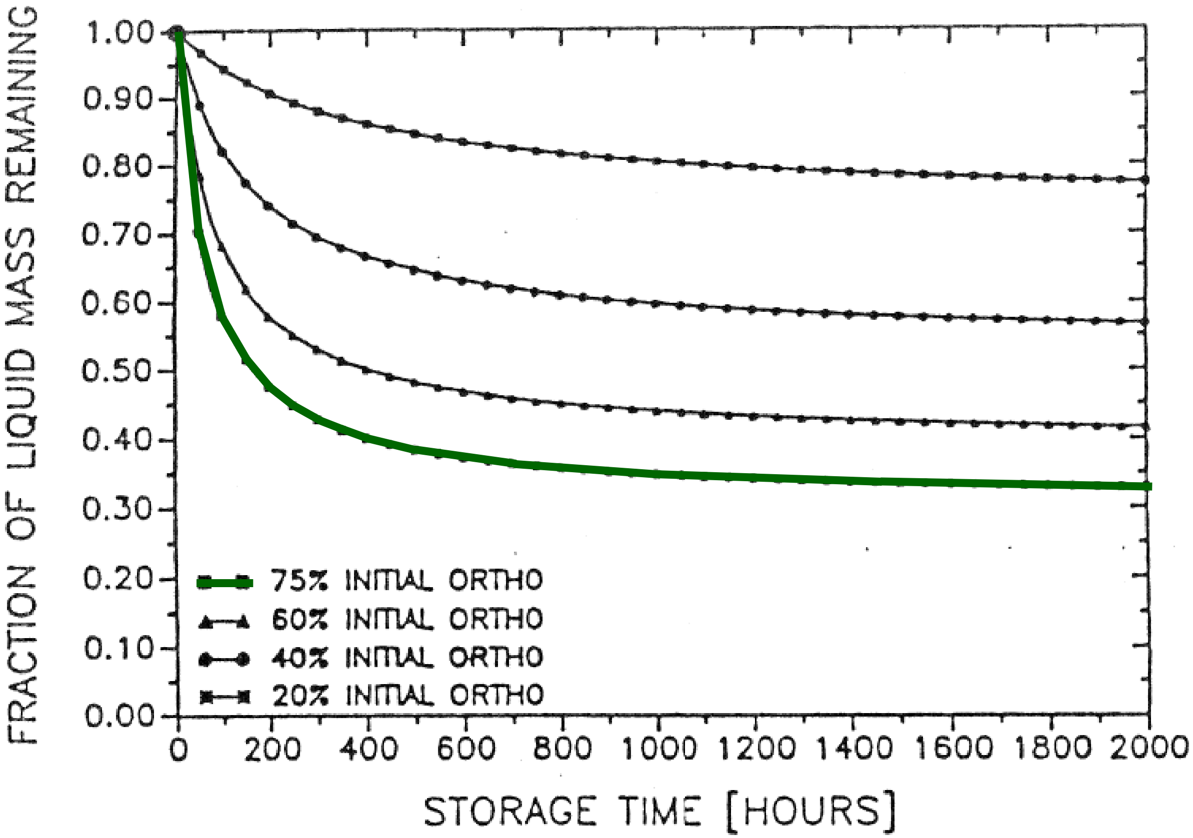
Ortho-Para Enthalpy



- **Heat of liquefaction/vaporization is 192 Btu/lb**
- **Heat of conversion from n-H_2 to e-H_2 in liquid is higher**

From Singleton, A. H. and Lapin, A. *Design of Para-Orthohydrogen Catalytic Reactors,* Adv. Cryo. Eng., v. 11, p. 617, 1965.

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
  - Evaluate Process Efficiency
- **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**
  - 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**
  - Evaluate commercially available critical equipment
  - Evaluate novel turbomachinery
- **Ortho-Para Conversion Optimization**
  - Construct larger-scale test facility
  - Validate process performance at larger scale

Thermodynamic Model - Progress

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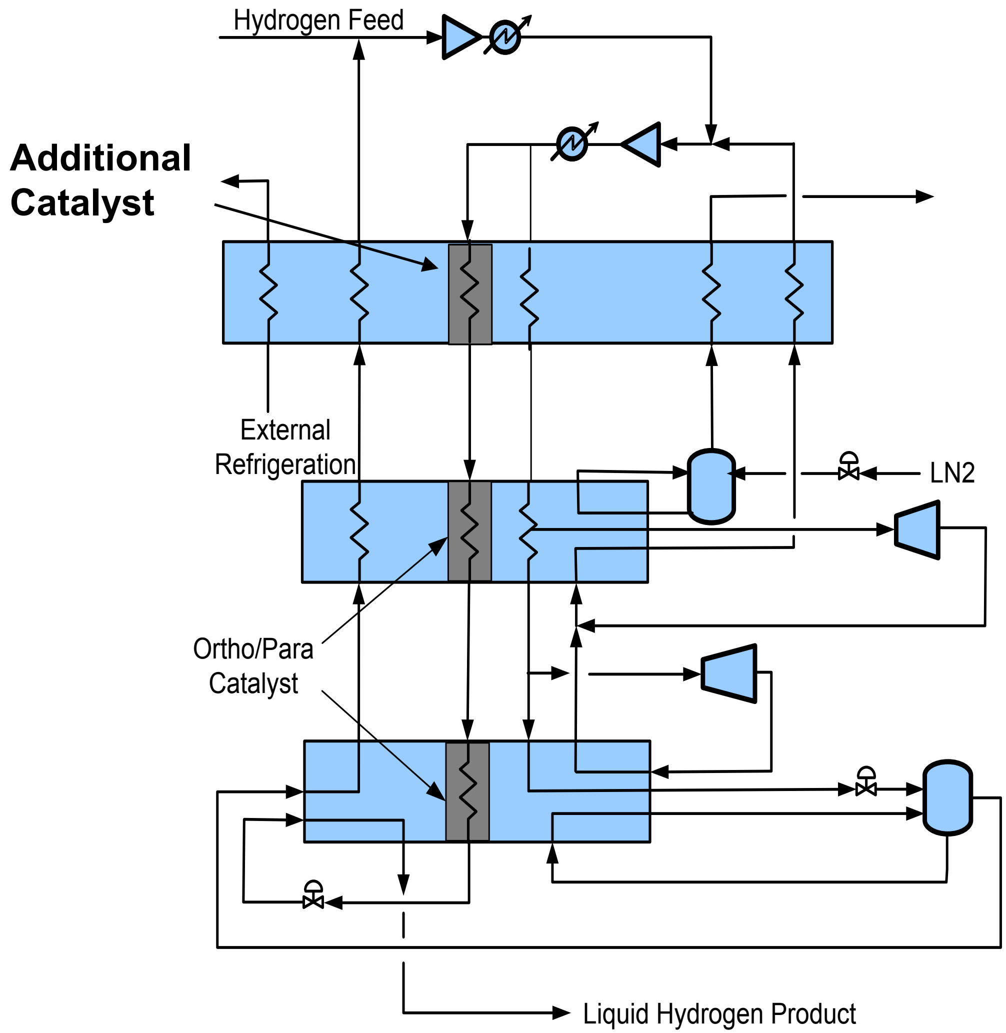
- **Typical models are not accurate near the critical point**
  - Need to handle temps from 20K to 300K
  - Critical point is 33K, which is near where liquefaction occurs
- **Typical models do not distinguish between ortho and para**
  - Cannot predict heat of conversion from ortho to para
  - Cannot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

Process Modeling - Progress

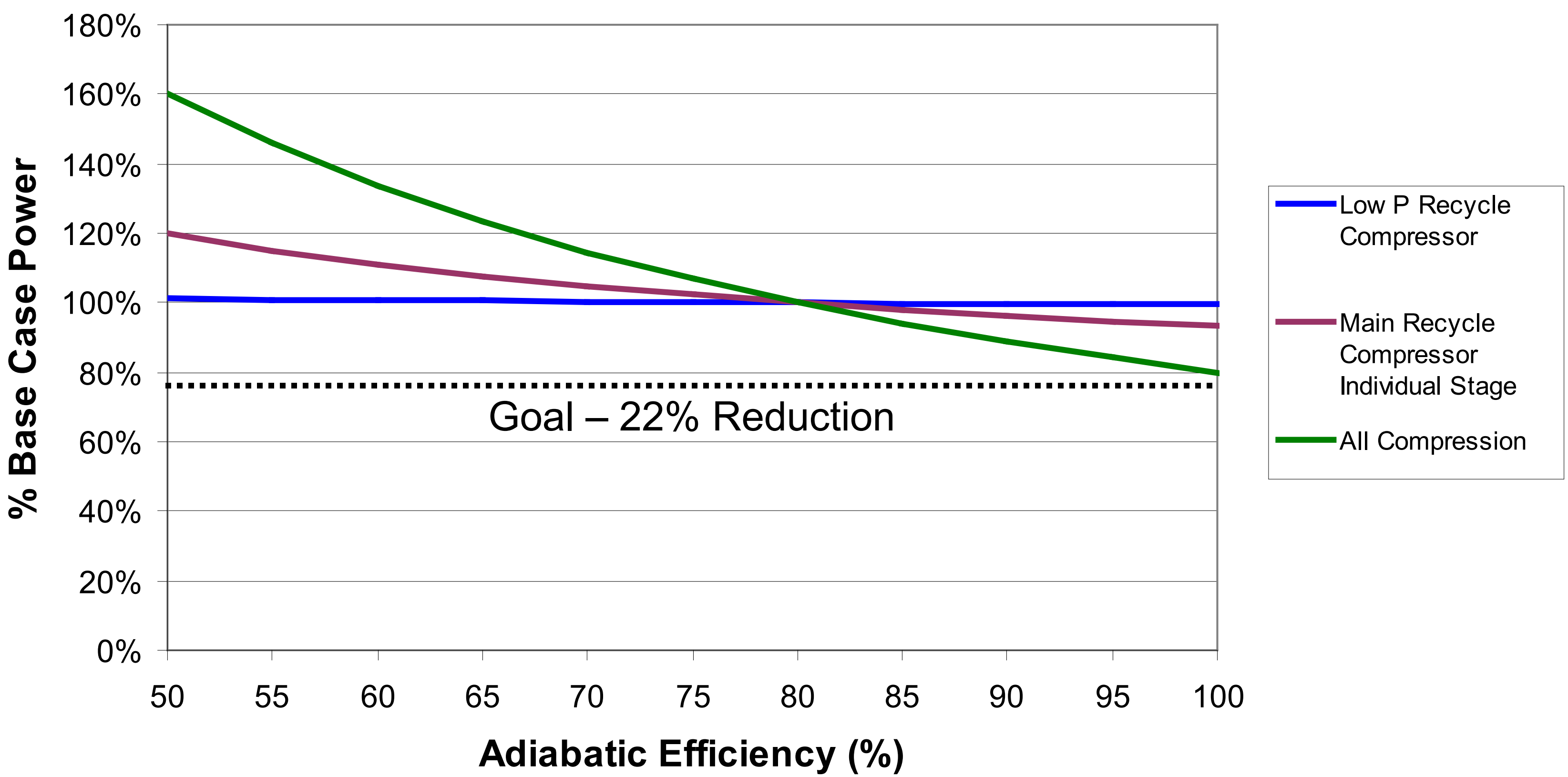
- **Both traditional and advanced liquefaction processes were modeled**
  - Both models thoroughly examined areas where energy and cost savings could be achieved
  - Experimental results were used to evaluate ortho-para conversion performance
  - Different process configurations were evaluated based on experimental results
  - Small efficiency improvements possible through improved ortho-para conversion and adding catalyst in the first heat exchanger

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



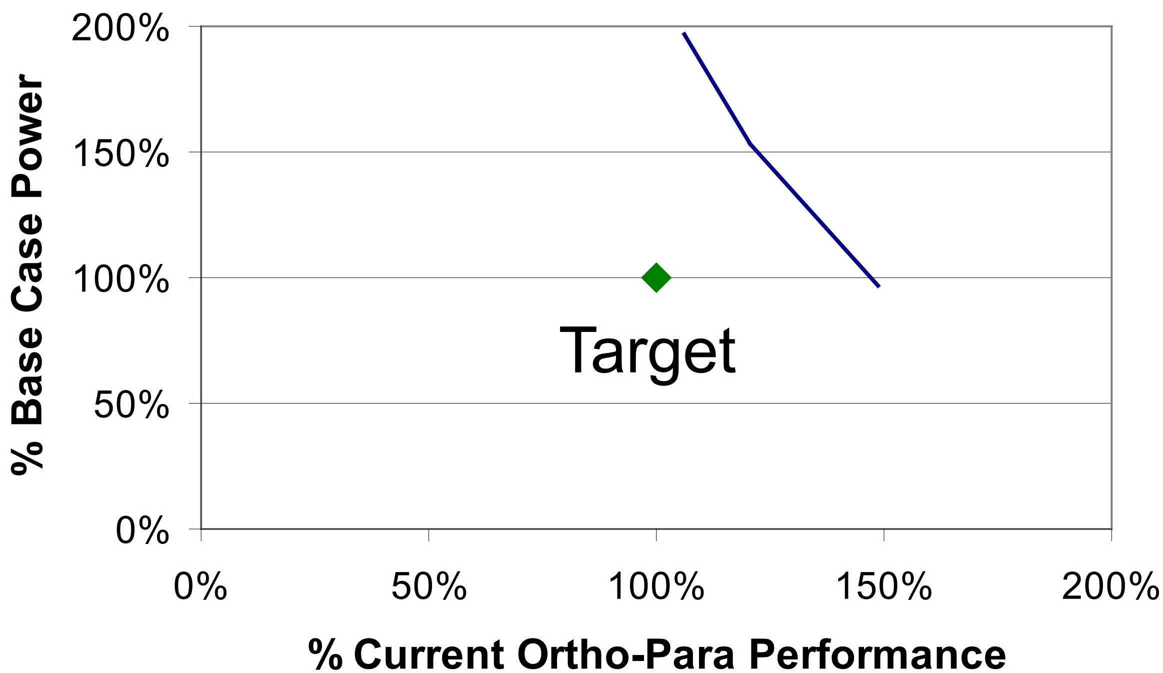
- **Most process power is consumed by compression**
- **Base case assumes 80% adiabatic efficiency for all stages**
- **100% turbine efficiency reduces power consumption < 10%**

Ortho-Para Conversion - Progress

- Large and small test systems were constructed
- Liquid nitrogen used for cooling
- Testing completed
- Performance exceeded requirements in one area, but fell short in another
- Overall performance was not sufficient to improve efficiency by 20%

Process Modeling - Progress

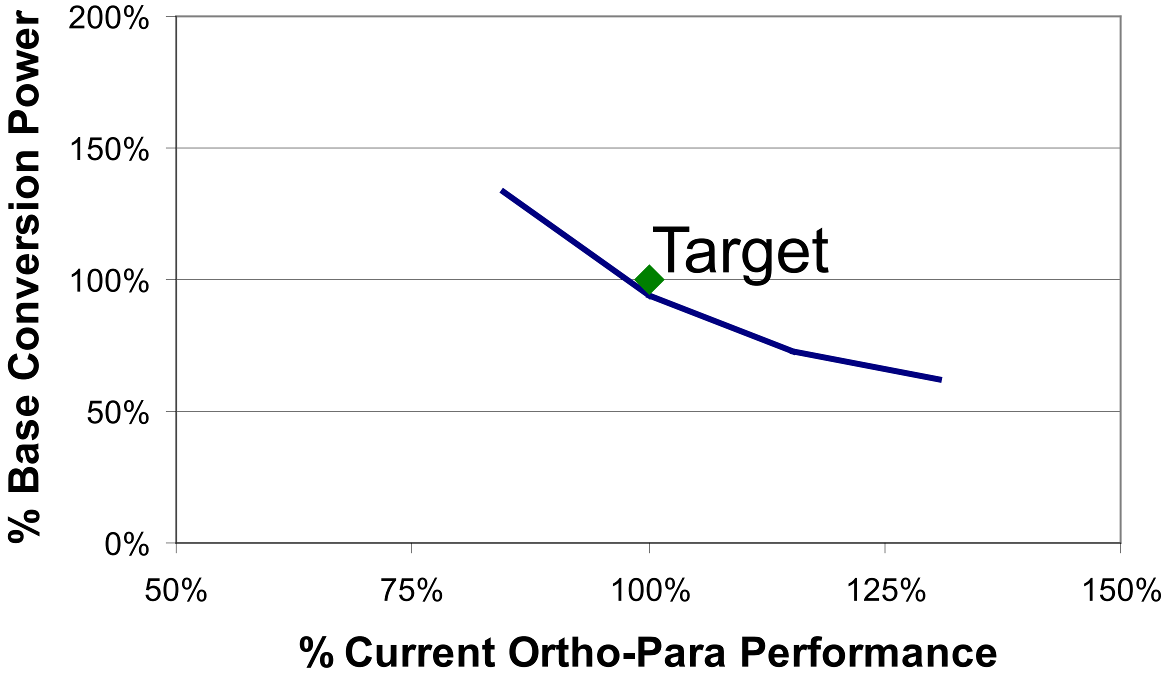
Improved Ortho-Para Conversion Process – Concept Alpha



- **Demonstrated performance was not enough to provide benefit**
- **50% performance improvement required to meet the target**
- **Target was not reached**

Process Modeling - Progress

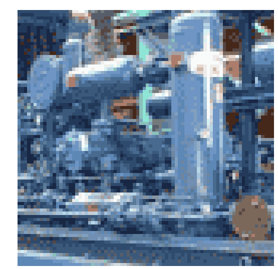
Improved Ortho-Para Conversion Process – Concept Beta



- **Demonstrated performance reached the target**
- **Overall process improvement of 8%**

Compressor Options

- Compressor Types
  - Positive Displacement
    - Linear
      - Reciprocating
      - Diaphragm
      - Ionic Liquid
    - Rotating
      - Rotary Vane
      - Guided Rotor
      - Screw
      - Scroll
  - Dynamic
    - Centrifugal
    - Axial
    - Super-Sonic Shock Wave
  - Adsorptive Metal Hydride



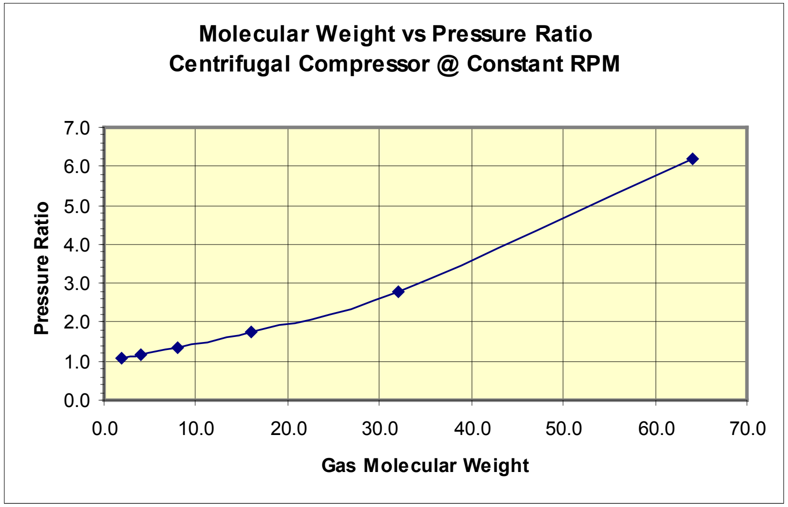
Compressor Options

- **Positive Displacement**
  - Reciprocating
    - Commercial, high efficiency, high first cost, large footprint, high maintenance
  - Screw
    - Commercial, low efficiency, medium first cost, compact, low maintenance
  - Metal Hydride
    - In development, too small for 30 TPD hydrogen liquefaction system
  - Guided Rotor
    - In development for hydrogen service, high efficiency, low maintenance
- **Dynamic**
  - Centrifugal
    - In development, high efficiency, high first cost, small footprint, low maintenance
  - Axial
    - Not suited for low molecular weight gas
  - Shock Wave
    - Not suited for low molecular weight gas

Compressor Options

Technology	Flow Range	First Cost	Relative Maintenance	Adiabatic Efficiency	Number of Units required	
	CFM				**30 tpd**	**300 tpd**
Screw	**20,000**	**Low**	**Medium**	**70 to 75%**	**2**	**20**
Reciprocating	**40,000**	**High**	**High**	**83 to 89%**	**1**	**10**
Centrifugal	**80,000**	**Medium**	**Low**	**80 to 89%**	**1**	**5**

- **Centrifugal**
  - Ratio per stage ~ 1.07 for typical wheel speeds
  - Need high speed wheel (~2000 feet/sec tip speed) for reasonable ratio ~1.3
  - Speed of sound in hydrogen is 4300 feet/s vs. 1100 for air



Summary

- **Multi-faceted approach to improving hydrogen liquefaction by improving process efficiency and reducing capital cost**
  - 22% power reduction required to meet DOE 2012 goal
- **Many small improvements required to meet target**
  - Improved equipment efficiency
  - Novel ortho-para conversion process
  - Other incremental improvements and process integrations
- **Several accomplishments in the program, but unable to reach the required 22% improvement**

Summary

- **Process simulation software improved to include para and normal hydrogen**
- **Efficiency improvements and improved process equipment were identified**
  - 100% compressor efficiency would save 20%, not enough to meet the 2012 DOE goal without other process improvements
- **Improved ortho-para conversion performance**
  - Adding catalyst to the high-temperature heat exchanger saves 2.4% of total power
- **Novel ortho-para conversion process met some, but not all performance requirements**
  - No power required for ortho-para conversion would save 18%

Acknowledgments

- Phil Barrett
- Joe Hrab
- Jerry Jankowiak
- Brian Kromer
- Ben Neu
- Steve Pontonio