Praxair’s Oxygen Transport Membranes for Oxycombustion and Syngas Applications

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Praxair At A Glance

27,000 employees in more than 50 countries

FORTUNE 100 COMPANY

market capitalization

MORE THAN 63,000 hours contributed to community engagement efforts benefiting 300,000 people

Applications enabled twice as many GHG emissions to be avoided as were emitted

$12B in sales

TOTAL SHAREHOLDER RETURN

SIXTH YEAR selected for the CDP’s Carbon Disclosure Leadership Index

143%

Over the past five years

Selected for DOW JONES Sustainability World Index for Eleventh Consecutive Year

Praxair White Martins received the Best Innovator Award from A.T. Kearney for the 4th consecutive year
Presentation Outline

- OTM Technology and Process Integration
- Project Scope Overview
- Phase III Development Progress
- Power Cycle Update
Praxair Oxygen Transport Membranes (OTM)

Solid-state, perfect air separation and compression
OTM Process Thermal Integration

**OTM Boiler**
- Steam generation
- Enables power cycle w/CCS

**OTM Process Heater**
- Process gas heating
- Enables oxycombustion power cycle w/CCS

**OTM Syngas**
- Autothermal reforming of NG
- Enables downstream synthesis
- Enables NG oxycombustion power cycle w/CCS

High temperature processes with integrated air separation

US Patent Nos. 7,856,829 & 8,196,387

US Patent Nos. 8,349,214
Praxair’s Advanced Power Cycle

70% O₂ from OTM

<table>
<thead>
<tr>
<th>Case</th>
<th>Praxair/DOE No CCS SC</th>
<th>1 Main</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Net Efficiency</strong></td>
<td>39.7</td>
<td>38.2</td>
</tr>
<tr>
<td><strong>Cost Basis (year)</strong></td>
<td>3/2008</td>
<td>3/2008</td>
</tr>
<tr>
<td><strong>Plant Cost ($/kW)</strong></td>
<td>$1,908</td>
<td>$3,712</td>
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<table>
<thead>
<tr>
<th>Increase in COE over Reference</th>
<th>$/ton CO₂ captured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Price ($/MMbtu)</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>$37.66</td>
</tr>
<tr>
<td>3</td>
<td>$38.23</td>
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<td>4</td>
<td>$38.68</td>
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</table>

- Achievable goal of < 35% increase COE w/CCS
- < $40/ton CO₂ removed

OTM technology enables economic utility scale power with CCS
Project Scope Overview

- Oxygen Transport Membrane Based OxyCombustion for CO₂ Capture from Coal Power Plants:
  - **Phase I (2007-2009)**
    - OTM development (materials, proof of concept)
    - TEA: OTM-enabled coal power cycle w/CCS
  - **Phase II (2010-2012)**
    - Single tube testing on gasified coal syngas (U-Utah, UConn)
    - Basic engineering design and cost OTM boiler/process heater
    - $10.3MM, 65% DOE Share

- OTM for Industrial Applications (ARRA):
  - 5yr. $55MM, 63% DOE share
  - **Phase III (2010-2015)**
    - Develop robust, cost effective membranes
    - Develop multi-tube modules for NG→syngas
    - Engage world-class ceramics mfg. supplier
    - Updated basic design for OTM boiler
    - TEA: NG-fired oxycombustion power cycle with CCS
Saint-Gobain Ceramics Manufacturing

- 43.2B € Revenue (2012)
  - Experienced world class ceramic manufacturer
- Competencies in critical areas:
  - Ceramic powder manufacturing
  - Industrial ceramic component manufacturing
  - SOFC development experience
- Phase III Development Subcontract
  - Currently supplying membranes, seals, and ceramic subassemblies

Focus on high-volume ceramics meeting cost targets
Phase III Progress - Membrane

- **Gen.1 Membrane**
  - 2X increase in O$_2$ flux
  - 4X increase in creep life
  - 10X reduction in degradation
  - Homogenous substrate
  - Simplified, stable chemistry
  - Thermal/chemical compatibility
  - Improved manufacturing process

- **Membranes achieve early commercialization targets**

- **Gen.2 Membrane**
Phase III Progress: Syngas Module

Panel Array module enables commercial-scale up

Radial

- 2X membrane area / unit volume
- 60% less reformer metal
- Increased natural gas conversion

Panel Array

- Improved tube arrangement
- Small diameter reformer tubes
- Simplified manifolding
- Improved seals
Phase III Progress: Seal and Membrane

Pressure integrity: > 4X safety factor

Accelerated life and reliability testing of tubes & seals in progress

~4X increase in OTM creep life

Proven durability under required operating conditions
Test Systems Developed in Current Phase

Membranes can deliver requirements of the process

- Flux and fuel conversion demonstrated
- >20,000 hrs over 25 tubes
- Focus on Gen 2 membrane characterization at high pressure

Module Testing

- Modules have shown excellent operational flexibility
  - 13 Modules tested (>200 OTM tubes)
  - More than 4,700 hrs of flux testing
  - >25 module thermal cycles
  - Ceramics robust to thermal and chemical cycling

System Testing

- Successful multi-module syngas production (radial modules)
  - Operating with 5 radial modules (60 OTM tubes)
  - Representative commercial process elements
  - Multiple successful heating / cooling cycles
  - Capacity up to 190 Nm³/hr syngas

Successful integration of membranes into systems
Panel Array Operation

Syngas module robust to thermal cycles, trips, and transients

Elapsed time = 10 seconds
Panel Array Operation

<table>
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<tr>
<th>Gas</th>
<th>66% NG + 34% CO₂ Feed</th>
<th>100% NG Feed</th>
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<tbody>
<tr>
<td>H₂</td>
<td>55.7%</td>
<td>70.5%</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.04%</td>
<td>0.13%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.00%</td>
<td>1.60%</td>
</tr>
<tr>
<td>CO</td>
<td>26.3%</td>
<td>21.6%</td>
</tr>
<tr>
<td>CO₂</td>
<td>17.9%</td>
<td>6.20%</td>
</tr>
<tr>
<td>H₂/CO Ratio =</td>
<td>~ 2.12</td>
<td>~ 3.26</td>
</tr>
<tr>
<td>O₂/C Ratio =</td>
<td>~ 0.4</td>
<td>~ 0.38</td>
</tr>
<tr>
<td>S/C Feed Ratio =</td>
<td>~ 1.5</td>
<td></td>
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Syngas module robust to thermal cycles, trips, and transients
Panel Array Scale-Up

Expanded Quad Array (Large-scale syngas, OTM Boiler)

Quad Array
600 OTM tubes
(Medium-scale syngas)

Double Array
(Small-scale syngas)

Single Array
(Development)

Capacity:
4X -> 2X
Phase III Progress: Boiler Design Advancements

Tubesheet Boiler
- 10X unit capacity
- 45% increased duty/unit volume
- 40% increased O₂/unit volume
- Reduced capital cost

Panel Array Boiler
- Adopt panel array design
- Increase syngas pressure
- Increased module capacity

7.5 MW\textsubscript{th}  

Improved approach to large-scale power boiler

20-50 MW\textsubscript{th}
OTM Advanced Power Cycle (APC) Update

Phase II: Coal APC

- Single or dual feedstock
- Plant co-products as base or off-peak production

Phase III: NG/Coal APC

- NG APC Advantages (Preliminary):
  - Up to 90% O₂ from OTM (non-Cryo)
  - Up to 50% less CO₂ produced and 97+% CO₂ capture
  - 5 point efficiency increase over NGCC
In Summary:

- **Key Results**
  - Step change in membrane materials and mfg. process
  - Demonstrated stability in coal-derived syngas
  - Demonstrated high strength membrane and seals robust to pressure and thermal cycles
  - Demonstrated process to make syngas with ceramic membranes
  - Module design to achieve thermal integration and facilitate scale-up
  - Compelling economics for both chemicals synthesis and power w/CCS applications

- **Next Steps**
  - Transition Gen 2 membranes into Panel Array modules
  - Transition from Radial to Panel Array modules in syngas development system and walk capacity to 160,000 scfd syngas (1 TPD O₂)
  - Update capital cost estimates for improved OTM boiler design
  - Complete TEA for OTM-based NG-IGCC OTM
Acknowledgements

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Thank you!