Project Review: Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules

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J.-M. Gauthier | MEDAL

Award: DE-FE0026422

AIR LIQUIDE
Air Liquide: world leader in industrial and medical gases
68,000 employees
$18.1 billion sales (2015)

Air Liquide & MEDAL

Air Liquide Advanced Separations, MEDAL

**N₂ applications / markets**
- OBIGGS
- Maritime
- Food & Bev
- UB Oil Drilling
- CB Inerting

**H₂ applications / markets**
- HDT
- HCR/RDS
- CR
- CCR
- OPAL (C₂ cracker)
- GTL (CO/H₂ adj)
- MeOH
- Syngas (CO/H₂ adj)
- CO (coldbox)
- NH₃

**CO₂ applications / markets**
- NG Sweetening
- EOR
- NG Trimming
- Fuel Gas
- Biogas

**CO₂ Capture / CO₂ Sourcing**
Outline

➢ Project Overview

➢ Technology Background
  ➢ Process design
  ➢ PI-2 novel material

➢ Project Details / Progress
  ➢ Equipment set-up
  ➢ Formulation development
  ➢ Manufacturing development
  ➢ Acid gas tolerance
  ➢ Hybrid process analysis

➢ Conclusions & Future Work
Motivation: Increase Membrane Productivity

**PI-1 commercial product**
- 1,000’s of modules per year, dozens of applications
- Performance improves at low temp

**PI-2 novel material**
- Thin film properties near Robeson* upper bound
- Spinnable
- Performance at lab-scale over 500+ hours

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*Robeson, J. Membr. Sci. 2008(320), 390-
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Feed: 1800+ Nm³/h (0.6 MWe eq.)
18% CO₂, 200 psig, -45°C

12” OD x 34” L
(1 module, projected performance)

Permeate: >58% CO₂
(~1 psig)

Residue: <1.8% CO₂
(~190 psig)

*Robeson, *J. Membr. Sci.* 2008(320), 390-
Project Objectives

Objectives (Success Criteria):

- Design/manufacture 4” bundle(s)
  - >90 Nm³/h feed @ 90% CO₂ recovery, >58% CO₂ purity
- Identify other hybrid processes with possibility of economic feasibility

- Design/manufacture 6” bundle(s)
  - >400 Nm³/h feed @ 90% CO₂ recovery, >58% CO₂ purity
  - Manufacture at least one 12” bundle
- Field-test 6” bundles at 0.3 MWe scale with real flue gas at NCCC
- Techno-economic analysis achieving >90% CO₂ capture at a cost of electricity 30% less than DOE baseline

Total Budget - $3.98 MM (25% cost share), 9.4 man-years total

Partners – DRTC, MEDAL, and Parsons
Technology Background: Process Concept

- 2010 – 2012 DOE: DE-FE0004278
- Cold membrane hybrid process
- PI-1: synthetic flue gas (TRL 4)
- Techno-economic analysis

- Energy recovery by turbo-expansion and cold production
- Energy integration
- BFW generation
- Pumping liquid CO₂

![Diagram of the process concept]

- Power plant
- Flue gas pre-treatment and compression
- Cryogenic Heat Exchanger
- Low temperature Membrane System (bulk CO₂ removal)
- CO₂ Liquefier (Increase product purity)
- CO₂ depleted retentate
- Off-gas recycle
- Enriched permeate: 58%+ CO₂
- Liquid CO₂
2013 – 2016 DOE: DE-FE0013163
- 2x12” PI-1 bundles, real flue gas
- TRL 5 (PI-1)
- Techno-economic analysis

Projected CO₂ capture cost 42 - 48$/tonne (DOE Target – 40$/tonne of CO₂)

Areas of improvement:
- Reduce membrane cost – improve membrane performance
- Reduce pre-treatment / compression costs, lower operating pressure
Technology Background: PI-2 Fiber Development

- 2013 – 2016 DOE: DE-FE0013163
- 1” PI-2 modules (500+ fibers)
- TRL 4 (PI-2)

- PI-2 lab-scale spinning methodology
- 1” OD modules (500 fibers) achieved good performance in real flue gas

Graph:
- PI-2 Permeance Normalized with PI-1
- CO2 Purity

- 70% CO2 Recovery
- Feed Composition 19% CO2 in N2
- Feed Temperature -45°C
- Feed Pressure 100 - 200 psig
Outline

- Project Overview
- Technology Background
  - Process design
  - PI-2 novel material
- Project Details / Progress
  - Formulation development
  - Manufacturing development
  - Equipment set-up
    - Acid gas tolerance
    - Hybrid process analysis
- Conclusions & Future Work
### Project Milestones & Dates

<table>
<thead>
<tr>
<th>BP #</th>
<th>Expected</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1</td>
<td>03-31-2016</td>
<td>Complete prototype manufacturing setup and initiate 4” bundle fabrication</td>
</tr>
<tr>
<td></td>
<td>12-31-2016</td>
<td>Complete prototype bundle testing: &gt;90 Nm³/hr productivity @ 18% CO₂, 16 bar, 90% CO₂ recovery, and &gt;58% CO₂ permeate composition</td>
</tr>
<tr>
<td></td>
<td>03-31-2017</td>
<td>Complete verification of PI-2 flue gas contaminant testing</td>
</tr>
<tr>
<td></td>
<td>03-31-2017</td>
<td>Complete hybrid process analysis comparing different applicable process schemes</td>
</tr>
</tbody>
</table>

**GO/NO-GO Decision**

<table>
<thead>
<tr>
<th>BP2</th>
<th>Expected</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>03-31-2018</td>
<td>Complete PI-2 commercial bundle fabrication and testing: &gt;400 Nm³/h productivity @18% CO₂, 16 bar, 90% CO₂ recovery, and &gt;58% CO₂ permeate composition</td>
</tr>
<tr>
<td></td>
<td>01-31-2018*</td>
<td>Complete installation and commissioning of the 0.3 MWe field-test unit at NCCC</td>
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<td></td>
<td>09-30-2018*</td>
<td>Complete 0.3 MWe field-testing including parametric testing and at least 500 hours for one membrane</td>
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<tr>
<td></td>
<td>09-30-2018*</td>
<td>Techno-economic analysis of CO₂ capture at 550 MWe net AFPC plant using cold membrane technology</td>
</tr>
<tr>
<td></td>
<td>09-30-2018*</td>
<td>Environmental, Health, and Safety analysis of cold membrane technology at full scale</td>
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</table>
Polymer Formulation Development

Baseline

<table>
<thead>
<tr>
<th>Normalized Permeance</th>
<th>5</th>
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<tbody>
<tr>
<td>$\alpha$-$CO_2/N_2$</td>
<td>&gt;70</td>
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</table>

Alternate Formulations

<table>
<thead>
<tr>
<th>Normalized Permeance</th>
<th>5 - 15</th>
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<tbody>
<tr>
<td>$\alpha$-$CO_2/N_2$</td>
<td>40 - 85</td>
</tr>
</tbody>
</table>

Performance Improvement

Cost Reduction

Alternate Formulations

| Normalized Permeance | 0.5 – 1.5 |

<table>
<thead>
<tr>
<th>Dope 1</th>
<th>Blend A</th>
<th>Blend B</th>
<th>Blend C</th>
<th>Blend D</th>
<th>Blend E</th>
<th>Blend F</th>
<th>Blend G</th>
</tr>
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<tbody>
<tr>
<td>Neg</td>
<td>Neg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dope 2</td>
<td></td>
<td>Neg</td>
<td>Pos</td>
<td></td>
<td></td>
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<tr>
<td>Dope 3</td>
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<td>Pos</td>
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<tr>
<td>Dope 4</td>
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<tr>
<td>Dope 5</td>
<td></td>
<td></td>
<td></td>
<td>Neg</td>
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<td></td>
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<tr>
<td>Dope 6</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Neg</td>
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</tr>
<tr>
<td>Dope 7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pos</td>
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</tr>
</tbody>
</table>
## Manufacturing Development

<table>
<thead>
<tr>
<th>Device</th>
<th>OD (in)</th>
<th>Length (ft)</th>
<th>Fiber Count</th>
<th>Spinning Device</th>
<th>Fabrication Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mini permeator</td>
<td>0.25 - 0.5”</td>
<td>1.6’</td>
<td>&lt;1000</td>
<td>1-hole lab unit</td>
<td>Hand</td>
</tr>
<tr>
<td>Permeator</td>
<td>1”</td>
<td></td>
<td>1 – 5x</td>
<td></td>
<td>Skein</td>
</tr>
<tr>
<td>Skein module</td>
<td>2.5”</td>
<td></td>
<td>15 – 20x</td>
<td>12-hole “DSU”</td>
<td>Forming</td>
</tr>
<tr>
<td>R&amp;D prototype bundle</td>
<td>2.5 - 4”</td>
<td>2.8’</td>
<td>15 – 20x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6” bundle (commercial)</td>
<td>6”</td>
<td></td>
<td>50 – 90x</td>
<td>24/36-hole production unit</td>
<td></td>
</tr>
<tr>
<td>12” bundle (commercial)</td>
<td>12”</td>
<td></td>
<td>&gt;200x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Spinning Equipment (DSU)
- Spinning
- Post-spin handling

### Fiber Processing / Handling
- Washing
- Drying
- Bobbin winding

### Forming Equipment
- Tube-sheet forming
- Machining
Demonstration Scale Fiber Synthesis Equipment

Dry jet wet quench fiber spinning

12-filament Development Spin Unit

Liquid Bore Fluid
Spin Dope
Spinneret
Quench Bath

2-gallon mixer
15-gallon mixer

Batches of fiber
MEDAL manufacturing equipment for processing
Fiber Synthesis & Handling Damage

- Minor selectivity loss due to bobbin winding: minor handling damage
- No selectivity loss due to forming: little or no further handling damage

Samples taken and quality tested at ambient temperature

Normalized CO₂ Permeance ($P_{CO₂}/P_{CO₂,PI-1}$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ Permeance</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-1 Bobbin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI-1 Formed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI-2 As Spun</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI-2 Bobbin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI-2 Formed</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fiber Synthesis & Bundle Forming

1.9 lbs of PI-2 fiber synthesized on the DSU over 3 hours

Periodic samples for quality control:

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Normalized CO₂ Perm</th>
<th>CO₂/N₂ Selectivity</th>
<th>Fiber ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.1</td>
<td>27.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.7</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>14.3</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>11.0</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>13.2</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.4</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>12.1</td>
<td>29.1</td>
<td></td>
</tr>
<tr>
<td>Std Dev</td>
<td>11.6%</td>
<td>14.7%</td>
<td>3.6%</td>
</tr>
</tbody>
</table>

• Fiber performance was consistent and agreed with previous lab-scale results

• Fiber “formed” into two prototype bundles (to be tested at 0.1 MWe skid at DRTC)
Acid Gas Contaminant Testing

Fiber samples in three mini-permeators simultaneously exposed to 100 ppmv NO and SO\textsubscript{2} over two weeks

- Stable / slightly increasing permeance for all samples
- Stable selectivity for all samples
- No apparent effect of NO or SO\textsubscript{2} on the PI-2 fiber
- Still to do: 100 ppmv NO\textsubscript{2} (not stable in combination with NO & SO\textsubscript{2})
Air Liquide’s Unique Position on CO₂

Technology for the whole range of CO₂ feed and product purities from any CO₂ source
Hybrid Process Schemes

Membrane operated at 60 – 80% recovery

Second capture process to reach 90%+

<table>
<thead>
<tr>
<th>Specific Energy* [kW-h/tonne]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
</tr>
<tr>
<td>284</td>
</tr>
</tbody>
</table>

*CO₂ capture only
Hybrid Process Schemes (Cold Membrane + Amines)

Reboiler duty ~ CO₂ mass flow

Membrane @ 75% recovery

60% lower bundle count!

Amine system for 90%+ recovery

<table>
<thead>
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<th>Specific Energy* [kW-h/tonne]</th>
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</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>284</td>
</tr>
<tr>
<td>With Amines</td>
<td>402</td>
</tr>
</tbody>
</table>

*CO₂ capture only
Hybrid Process Schemes (Cold Water)

Direct contact towers for flue gas cooling

Very dry residue gas

<table>
<thead>
<tr>
<th></th>
<th>Specific Energy* [kW-h/tonne]</th>
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<td>Baseline</td>
<td>284</td>
</tr>
<tr>
<td>Cold Water</td>
<td>267</td>
</tr>
</tbody>
</table>

*CO₂ capture only
Conclusions & Future Work

Conclusions
- Prototype bundles fabricated (awaiting testing)
- Fiber tolerance towards NO and SO$_2$ demonstrated
- Hybrid processes modeled

Future Work (present to Mar ‘17)
- Prototype bundle fab / test
- Hybrid process development

Budget Period 2 (Apr ‘17 to Sept ‘18)
- Manufacturing scale-up (6” and 12” bundles)
- Field-test at NCCC (0.3 MWe unit)
- Techno-economic analysis
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- US DOE: José Figueroa, Sheldon Funk
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- Parsons: Brad Knutson
- Air Liquide: Rob Gagliano, Shilu Fu, Sudhir Kulkarni, Dave Hasse, Dean Kratzer, Dave Edwards, Jean-Marie Gautier

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