Enabling 10 mol/kg swing capacity via heat integrated sub-ambient pressure swing adsorption

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DOE-NETL CO₂ Capture Technology Project review Meeting
Thursday, August 11th, 2016
Key Idea:

Combine:
(i) Sub-ambient gas processing and energy recovery with
(ii) ultra-porous metal-organic frameworks and
(iii) space- and energy-efficient fiber sorbent contactors
to yield a game-changing process strategy
Background: Metal-organic frameworks—State-of-the-art

CO₂ Capture Performance

Mmen-Co₂(dobpdc)

Decreasing temperature

25°C

75°C


Background: Hollow fiber sorbents, a mass producible structured sorbent inspired by hollow fiber membrane spinning

Sorbent sites, supported by porous fiber wall

Porous polymer matrix

Impermeable lumen layer

1000 µm

Ideal temperature swing adsorption

Cooling water

Desorbate

Hot water

Bundle of 40 fibers in a 1.5’ module at GT

Background: Fiber sorbents for PSA applications

H₂/CO₂ separations

Project scope—details on key ideas

- Rapid pressure swing adsorption is more straightforward than rapid temperature swing adsorption (has been commercialized)

- Sub-ambient conditions increase adsorption selectivity and working capacity

- Immense pore volume and surface area of MOFs are advantageous at sub-ambient conditions and moderate CO₂ partial pressures (~1-2 bar)

- Weaknesses of MOFs addressed through contactor (hollow fiber sorbents) and through process strategy
Process flow diagram: 1\textsuperscript{st} generation

Flue Gas

323K

Dehumidifier bed

Silica Gel

343K 18bar

1.5 bar

N\textsubscript{2} effluent with H\textsubscript{2}O

Sub-ambient HEX

363K 20bar

T\textsubscript{1} - DT

T\textsubscript{1}

T\textsubscript{2}

T\textsubscript{Liq}

PSA Unit

RCPSA Cycle

Q\textsubscript{c1}

T\textsubscript{Liq}

Q\textsubscript{c2}

CO\textsubscript{2} liquefaction & pumping

N\textsubscript{2}

Gas conditioning

295K Liquid CO\textsubscript{2}
Process Scope—Key Research Topics

Five major activity areas are proposed in this work:

(1) UiO-66 / MOF synthesis, sub-ambient adsorption characterization, and stability,

(2) Composite hollow fiber spinning (cellulose acetate/polysulfone fibers containing UiO-66 / MOF sorbents),

(3) RCPSA system construction and testing of fiber sorbent modules and hollow fiber sorbent modules with bore-side phase change material,

(4) Modeling and optimization of fiber and hollow fiber module operation as well as flue gas conditioning optimization, and

(5) Overall system techno-economic analysis.
Process Scope—Key Topics, BP1

Five major activity areas are proposed in this work for BP1:

Task 2.0: Generate >250 g/quarter of UiO-66, sub-ambient sorption isotherms, and simple fiber sorbents
Task 3.0: Spin fiber sorbents
Task 4.0: Stability of module seals at sub-ambient conditions
Task 5.0: Develop model for hollow fiber sorbent module
Task 6.0: RCPSA Testing and construction
UiO-66 can achieve impressive swing capacities at sub-ambient conditions—but higher pore volumes needed for 10+ mol/kg
Task 2—sorption isotherms from GCMC

**UMCM-152**
- Temperature (K) range: 210 to 280
- Pads = 2.0 bar
- Pdes = 0.1 bar
- Pdes = 0.2 bar
- Pdes = 0.3 bar

**IRMOF-1**
- Temperature (K) range: 210 to 280
- Pads = 2.0 bar
- Pdes = 0.1 bar
- Pdes = 0.2 bar
- Pdes = 0.3 bar

**Cu-BTC**
- Temperature (K) range: 210 to 280
- Pads = 2.0 bar
- Pdes = 0.1 bar
- Pdes = 0.2 bar
- Pdes = 0.3 bar

**Cu₄(TCPPDA)**
- Temperature (K) range: 210 to 280
- Pads = 2.0 bar
- Pdes = 0.1 bar
- Pdes = 0.2 bar
- Pdes = 0.3 bar
Many MOFs can achieve the 10+ mol/kg target! Integrating into fiber sorbents is a challenge.
Task 2, 3: UiO-66 scale-up and hollow fiber sorbents

325 g of UiO-66 from Inmondo Tech

UiO-66/Cellulose Acetate fiber sorbents: ~55 wt%

Water stable MOFs retain crystallinity and porosity after fiber sorbent spinning
Task 2,3: What about water-sensitive MOFs?

**Cu-BTC/Matrimid fiber sorbents: ~55 wt%**

**Metal Salt in Water**
- ZnO Fibers

**Organic linker + Metal Salt in solvent**
- (Zn,Cu) or (Zn,Zn) HDS Fibers
- Crystalline MOF Fibers

**ZnO particles**

**Hydroxy double salts**

**MOF particles**

Graph showing X-ray diffraction peaks.
Task 2,3: What about water-sensitive MOFs?

Cu-BTC/Matrimid fiber sorbents: ~55 wt%
Task 2,3: What about water-sensitive MOFs?

MOFs with water stability issues can now be integrated into fiber sorbents! Operational stability is less of an issue as flue gas is dehydrated + substantial industry experience with water sensitive sorbents (e.g., LiX)
Sub-ambient breakthrough experiments on UiO-66 and UiO-66 fiber sorbents currently underway
Task 4: Dynamic model development

- Combined heat, mass, and momentum balance on the fiber, including transient heat conduction with a heat source

Density values help to track the melting front.

Dynamic model guides experiments and RCPSA cycle development.
Task 4: Dynamic model development

- Combined heat, mass, and momentum balance on the fiber, including transient heat conduction w/ heat source

- Density values help to track the melting front

Dynamic model guides experiments and RCPSA cycle development
Process Scope—Key Topics, BP1

Five major activity areas are proposed in this work for BP1:

Task 2.0: Generate >250 g/quarter of UiO-66, sub-ambient sorption isotherms, and simple fiber sorbents—Complete

Task 3.0: Spin fiber sorbents—Complete

Task 4.0: Stability of module seals at sub-ambient conditions—Ongoing, 60% (sub-ambient exposure completed, leak rate of module seals ongoing)

Task 5.0: Develop model for hollow fiber sorbent module—Complete

Task 6.0: RCPSA Testing and construction—Ongoing, 80% complete (remaining items: breakthrough curves for UiO-66 powders and fibers).
Summary

- Novel polymer/MOF sorbent composite hollow fibers will be used in new sub-ambient RPSA process for post-combustion CO₂ capture
  - 50% experimental demonstration
  - 50% prediction, modeling, optimization, and economic feasibility analysis

- Viability of concept is being demonstrated
  - Potential for game-changing swing capacities by utilizing MOFs in sub-ambient conditions

- Georgia Tech and Inmondo Tech are partners on this project

- Annual reports, annual review meetings and conferences presentations and quarterly reports will be used to update DOE on team activities

- DOE contribution: ~$2.0M  Georgia Tech contribution: ~$0.5M
Budget

DOE Contribution
1st year: $705,441
2nd year: $681,845
3rd year: $599,698
Total: $1,986,984 (79%)

Cost Share Provided by Georgia Tech: $513,792 (21%)

Total Budget: $2,500,776

5 primary researchers supported (2 post-doctoral researchers, 3 graduate student researchers)

5 PIs supported (Lively, Kawajiri, Realff, Sholl, Walton)

Major equipment purchases/construction: Sub-ambient rapid pressure swing adsorption units
Personnel

**Principal Investigators:**

**Georgia Tech**
Ryan Lively, *Project Director*, Inmondo liaison, hollow fibers and RCPSA system
Yoshiaki Kawajiri, Process optimization, cyclic adsorption processes
Matthew Realff, Process systems engineering, technoeconomic analysis
David Sholl, Adsorption and diffusion in nanoporous materials
Krista Walton, Adsorption in MOFs and MOF synthesis

**Inmondo Tech**
Dr. Karen Tuleg, Inmondo PI, Sorption and gas storage
<table>
<thead>
<tr>
<th>Description of Risk</th>
<th>Probability (Low, Moderate, High)</th>
<th>Impact (Low, Moderate, High)</th>
<th>Risk Management Mitigation and Response Strategies</th>
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</thead>
</table>
| **Technical Risks:**                                                                                                                                                                                              |                                   |                             | (a) Technoeconomic analysis and modeling effort will determine impact of > 10 mol/kg swing vs. 5-10 mol/kg swing.  
(b) Other scalable MOFs can be considered if >10 mol/kg is critical                                                                                                                                 |
<p>| MOFs do not exhibit ~10 mol/kg swing capacity between 1 and 2 bar CO₂ partial pressure                                                                                                                             | Moderate                          | Moderate                    |                                                                                                                                                                                                     |
| MOF particles do not survive spinning process                                                                                                                                                                       | Low                               | High                        | If required, MOFs can be grown within porous polymer supports post-spinning. Preliminary data from Lively indicates that MOFs retain their porosity and crystallinity post-spinning.                             |
| Failure of sealing for fiber modules                                                                                                                                                                             | Low                               | Moderate                    | If required, specialty epoxies resistant to temperature changes will be used to seal modules.                                                                                                                                                                           |
| Instability of MOF to flue gas contaminants                                                                                                                                                                        | Low                               | High                        | Functionalized MOFs will be tested, providing various materials for use. Additional flue gas processing can be used if necessary.                                                                                                                                     |
| <strong>Resource Risks:</strong>                                                                                                                                                                                               |                                   |                             |                                                                                                                                                                                                     |
| Delays in production of MOFs by Inmondo Tech                                                                                                                                                                       | Low                               | High                        | MOFs will be produce in excess of minimum requirement in year 1 to ensure availability. Capability to deliver materials in this manner has already been demonstrated.                                            |
| <strong>Management Risks:</strong>                                                                                                                                                                                             |                                   |                             |                                                                                                                                                                                                     |
| Difficulty in recruiting postdocs/grad students at GT                                                                                                                                                               | Low                               | Moderate                    | Shift personnel between tasks to manage temporary vacancies                                                                                                                                                                                                     |
| Lack of coordination among project partners                                                                                                                                                                        | Low                               | Moderate                    | Project partners already have a proven record of collaboration; regular project meetings are scheduled with all partners.                                                                                                                                         |</p>
<table>
<thead>
<tr>
<th>Budget Period</th>
<th>Task/Subtask No.</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
<th>Actual Completion</th>
<th>Verification Method</th>
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<td>UiO-66 @ &gt;900 m²/g</td>
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## BP2 Task List & Milestones

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<tr>
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<th>Milestone</th>
<th>Description</th>
<th>Due Date</th>
<th>Report to DOE</th>
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<tr>
<td>2</td>
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<td>Test PSA using syringe fiber samples</td>
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<td>Report to DOE</td>
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<td>7</td>
<td>Produce 250+ g of UiO-66 @ &gt;900 m²/g surface area and &gt;2.5 mol CO₂/kg @ 273K &amp; 1 bar</td>
<td>01/31/17</td>
<td>Report to DOE</td>
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<td>MOF moisture and acid gas test (SO₂ and steam exposure)</td>
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<td>Lumen layer synthesis and barrier properties</td>
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<td>Demonstrate hollow fiber lumen layer synthesis</td>
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<td>PCM integration into modules</td>
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<td>Model development of fibers with PCM</td>
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<td>Modeling phase change and adsorption using experimental data</td>
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<td>Process flowsheet optimization</td>
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<td>Process flowsheet refinement</td>
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<td>Produce 250+ g of UiO-66 @ &gt;900 m²/g surface area and &gt;2.5 mol CO₂/kg @ 273K &amp; 1 bar</td>
<td>01/31/18</td>
<td>Report to DOE</td>
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<td>3</td>
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<td>Construct/test RCPSA for dirty gas testing</td>
<td>04/30/18</td>
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<td>Model validation for hollow fiber module—model validation for composite fibers</td>
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<td>Report to DOE</td>
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<td>Monolithic fiber sorbent stability in dirty gas RCPSA</td>
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<td>Report to DOE</td>
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<td>Test hollow fibers containing phase change material in PSA</td>
<td>09/30/2018</td>
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<td>Complete Technoeconomic assessment</td>
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<td>Test a demonstration module</td>
<td>09/30/2018</td>
<td>Report to DOE</td>
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</table>
Initial high level process analysis using 10 mol/kg swing

- Plant parasitic load: 16.7%
- Installed capital costs: $188.2 \times 10^6$
- Total annual cost (operating expenses + amortized capital): $72.8 \times 10^6$/yr
- CO$_2$ captured per year: $4.50 \times 10^6$ tons CO$_2$/yr
- CO$_2$ capture cost: $19.0$/ton, $21$/tonne
- Number of 8” module elements needed: 36,000
- Estimated footprint (assuming modules stacked 10 high): ~200 m$^2$ for a 500 MW$^e$ coal-fired power plant