Rapid Temperature Swing Adsorption using Polymer/Supported Amine Composite Hollow Fibers

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Post-Combustion Sorbent-Based Capture
2012 NETL CO₂ Capture Technology Meeting
Sheraton Station Square, Pittsburgh, PA
Tuesday, July 10, 2012
Budget:

DOE contribution:

- Year 1: $691,955
- Year 2: $847,672
- Year 3: $847,006
- Total: $2,386,633 (79%)

Cost Share Partners:

- GE Energy: $420,000
- Algenol Biofuels: $183,900
- Southern Company: $33,147
- Total: $637,047 (21%)

Total Budget: $3,023,680

Project Performance Dates – October 2011 to September 2014
Key Idea:

Combine:

(i) state-of-the-art supported amine adsorbents, with
(ii) a new contactor tuned to address specific weaknesses of amine materials,

to yield a novel process strategy
Supported Amine Adsorbent

Pros:  
1) Can achieve high capacity in lab studies  
2) Appear to achieve acceptable kinetics  
3) Simple, scalable synthesis  
4) High heat of adsorption (heat integration!)

Cons:  
1) High heat of adsorption  
2) Deactivation with \( \text{O}_2, \text{steam, NOx, SOx} \)  
3) Low working capacity or degradation in practical contactors (fluidized bed)  
   (i) can deactivate with direct steam contact  
   (ii) can deactivate at high T in concentrated \( \text{CO}_2 \)

No effective contactor demonstrated that addresses multiple “cons.”
Hollow Fiber Contactor:

Fiber Bed: Achieves high surface area without excessive pressure drop

Hollow Fiber: Allows rapid heat transfer without contact of steam with amine

1) Spinning of high solid content (50-66 volume%), flexible hollow fibers, using low cost commercial polymers (e.g. cellulose acetate)

2) Building and demonstrating an RTSA system for CO₂ capture from simulated flue gas (13X as sorbent).


Lively et al, International Journal of Greenhouse Gas Control, Accepted (In Press July 13th)

3) Constructing a barrier lumen layer in the fiber bore, allowing the fibers to act as a shell-in-tube heat exchanger.

Parallel Flow Hollow Fiber Contactors:

- Pressure drop through fiber modules is very low compared to fixed beds.
- Rapid adsorption cycles possible with zeolite 13X.
- Not yet experimentally demonstrated with amine sorbents.

Cycle times of ~25 seconds possible!
RTSA Representation on Isotherm

Isotherm representation of RTSA cycle

35C, CO2, dry
Dual-mode isotherm fit
Adjusted from 45C data on HAS-3 using a \( \Delta H = -55 \) kJ/mol

RTSA Qualitative Cycle

Flue gas $\text{CO}_2/\text{N}_2$ → Cooling water + sorption enthalpy

1 → 2’:
- 35 C → 73.5 C

Cold water

1 → 2:
- 74.5 C

Hot water: $74.5 \, ^\circ\text{C}$

2’ → 3:
- 73.5 C → 120 C

Interstitial gas

3 → 4:
- 120 C → 35 C

Hot water: 120 C → 35 C

4 → 1:
- 35 C → 73.5 C

Near-pure $\text{CO}_2$

Cooling water

$\text{N}_2$ sweep

1 → 2:
- 73.5 C → 120 C

Hot water: 130 C

$\text{N}_2$ sweep

3 → 4:
- 35 C → 73.5 C

Cooling water

$\text{N}_2$ sweep

2’ → 3:
- 73.5 C → 120 C

Near-pure $\text{CO}_2$
• Fiber sorbents show rapid (<10 second) CO$_2$ uptakes

• Fibers can be repeatedly thermally cycled with no loss in capacity or physical damage

• External boundary layers can be removed via close fiber packing ($\varepsilon \sim 0.3$)

• Low pressure drops (< 1.5 psig) at high superficial velocities (~ 1 m/s)

Using carefully timed heating and sweep cycles, a pure CO$_2$ product can be made.

82 mol% (1/2" module), expected

41 mol% (3/8" module), measured

18 mol% (1/4" module), measured

Larger modules should result in near-pure CO$_2$ product streams.
Cost Summary (Analysis performed by Trimeric Corp.)

Assumed installed fiber costs were $30/m² life of 3 years.

<table>
<thead>
<tr>
<th>Total O&amp;M Costs</th>
<th>MM$/year</th>
<th>57.87</th>
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</thead>
<tbody>
<tr>
<td>Averaged annual cost of fiber replacement</td>
<td>MM$/year</td>
<td>24.07</td>
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<table>
<thead>
<tr>
<th>RTSA</th>
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<tbody>
<tr>
<td>Cost of CO2 Capture</td>
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<tr>
<td>Total Annual Cost of CO2 Capture</td>
<td>MM$/year</td>
<td>176.6</td>
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<tr>
<td>CO2 captured</td>
<td>ton/year</td>
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<tr>
<td></td>
<td>tonne/year</td>
<td>3,939,000</td>
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<tr>
<td>Cost of CO2 Capture</td>
<td>$/ton</td>
<td>40.7</td>
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<tr>
<td></td>
<td>$/tonne</td>
<td>44.8</td>
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</table>

Impact of CO2 Capture on Plant Efficiency

| Change in Net Plant Efficiency | % | -7.3 |

RTSA System Cost Estimate

Total Purchased Cost $130.9MM

Escalation Factor = 1.249
### DOE Technoeconomic Metrics – Sensitivity

- **Sensitivity to fiber cost and fiber life**

<table>
<thead>
<tr>
<th></th>
<th>Base Case</th>
<th>70% Fiber Costs</th>
<th>130% Fiber Costs</th>
<th>50% Fiber Life</th>
<th>200% Fiber Life</th>
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<tbody>
<tr>
<td>Cost of CO₂ Capture</td>
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<td>Annual Capital Charge</td>
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<td>/tonne</td>
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<td>17</td>
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Summary & Future Work

• Rapid Temperature Swing Adsorption enabled by a new contactor combined with solid amine sorbents.

• Cycle allows effective recovery of heat of sorption and sensible heat of module through integration of modules in different phases of operation.

• Preliminary Technoeconomic analysis indicates promise: $37 to $50/tonne
  • Relatively low parasitic load (1.25 escalation factor)
  • Capital cost sensitive to fiber life and base fiber costs

• Synthesize amines, spin fibers, and construct benchscale modules (0.5”x3’ 150 fibers)
• Model single fiber through the cyclic behavior and validate against benchscale
• Optimize sorbent, fiber and module parameters to maximize heat recovery
• Refine Technoeconomic model with experimental parameters
Acknowledgements

**Funding**

DOE Award #: DE-FE0007804  
Algenol Biofuels  
GE  
Southern Company

**People**

Dr. Ron Chance – Algenol Biofuels  
Dr. Ying Dai – hollow fiber spinning  
Dr. Yanfang Fan – experimental system design and testing  
Dr. Fateme Rezaei – sorbent synthesis and fiber modeling  
Ms. Jayashree Kalyanaraman – fiber modeling  
Ms. Grace Chen – sorbent synthesis & characterization / fuel gas upgrading

Program officer Barbara Carney – NETL, DOE