Novel Process That Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process

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Hollow fiber sorbent spinning
Sorbent dispersed in polymer solution

Spinneret
Fiber collection 50 m/min
Module make-up

Quench bath

AR Sujan, RP Lively et al., Ind. Eng. Chem. Res. 2018, 57(1)
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Swing capacity and cycle time are key for driving down capital costs of adsorption-based CO$_2$ capture systems!

Key question: Can we increase swing capacity by 10x and reduce cycle time by 5x to dramatically drive down adsorbent costs?

Capital cost of RTSA system for NETL 550 MW$_e$ baseline: ~$1B

Costs dominated by costs of adsorbent

Swing capacity [mmol/gfiber] vs. Total cost of CO$_2$ capture [$/tCO_2$]

Rapid thermal swing adsorption

RP Lively et al., U.S. Patent 8,409,332  WJ Koros, U.S. Patent 8,658,041
RP Lively, WJ Koros et al., Int. J. Greenhouse Gas Control 2012, 10(1)
Y Fan, CW Jones et al., Int. J. Greenhouse Gas Control 2014, 21, 61-71
Rapidly cycled pressure swing adsorption using MOFs

Cycle times of ~20 seconds are common for industrial RCPSA (>5x faster than RTSA)

JM Simmons, T Yildirim et al., Energ. Env. Sci., 2011, 4(6), 2177-2185
Rapidly cycled pressure swing adsorption using MOFs

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Pressure Swing Adsorption

Sub-Ambient $\Delta N_{\text{CO}_2}$

$\sim 40$ mol/kg

CO$_2$ Uptake (mol/kg)

Pressure (bar)

Temperature (K)

$\Delta P = 1.9$ bar

Pads = 2.0 bar

Pdes = 0.1 bar

Pdes = 0.2 bar

Pdes = 0.3 bar

Pdes = 0.5 bar

Pdes = 1.0 bar

Rapidly cycled pressure swing adsorption using MOFs

Cycle times of ~20 seconds are common for industrial RCPSA (>5x faster than RTSA)

How to economically achieve these pressurized, sub-ambient conditions?

Enabling 10 mol/kg swing capacities via flue gas pretreatment

**Air Liquide Sub-Ambient Membrane System**  
**Sub-Ambient Adsorption System**

Key parameters: swing capacity & selectivity

D Hasse, S Kulkarni et al., *Energy Procedia*, 2013, 37, 993-1003
MIL-101(Cr) emerged as a promising candidate

Low cost ligands (benzene dicarboxylate)
Relatively low cost metal centers (chromium nitrate)
Scale-up is straight forward (70% yield on large batches)
Water stable

\[ \Delta N_{CO_2} \text{ (mol/kg)} \]

\[ P_{ads} = 2.0 \text{ bar} \]
\[ P_{des} = 0.1 \text{ bar} \]
\[ P_{des} = 0.2 \text{ bar} \]
\[ P_{des} = 0.3 \text{ bar} \]
\[ P_{des} = 0.5 \text{ bar} \]
\[ P_{des} = 1.0 \text{ bar} \]

\[ T \text{ (K)} \]

Manufacturing MIL-101(Cr) fiber sorbents

Dope
Bore fluid

Spinninget

Dope
Bore fluid

Water quench bath
Take-up drum

~50 wt% MOF
73-80 vol% MOF
PSA separation of simulated flue gas mixtures

Pressurization

Feed

Evacuation

Blow-down
PSA separation of simulated flue gas mixtures

- **Graph 1:**
  - Graph shows the concentration of gases with time.
  - The x-axis represents time (seconds), ranging from 0 to 1500.
  - The y-axis represents the concentration ratio of gas to initial concentration.

- **Graph 2:**
  - Graph shows the fraction of gas in the outlet with time.
  - The x-axis represents time (seconds), ranging from -50 to 300.
  - The y-axis represents the fraction of gas in the outlet.
  - Different lines represent different gases: N2, CO2.

- **Text:**
  - Fiber sorbents were cycled in CO2/N2 for 4 weeks (~4000 cycles).

Georgia School of Chemical & Tech Biomolecular Engineering
Stability to acid gases

CO₂ Isotherms on SO₂ Exposed MIL-101(Cr)

Fiber sorbents stable to aggressive acid gas exposures
Issues with heat effects

50K increase in temperature during adsorption

Sorbent-loaded porous polymer matrix

Sorption/desorption enthalpy

Phase Change Material

Impermeable microcapsule

µPCM

Fiber Module

SJA DeWitt, RP Lively et al., PCT US18/48110; WO 2019/09908
Issues with heat effects

Concept of Phase Change Material for PSA Heat Management

SJA DeWitt, RP Lively et al., PCT US18/48110; WO 2019/09908
“Passive” thermal management via microPCM capsules

“Passive” thermal management via microPCM capsules
"Passive" thermal management via microPCM capsules

MIL-101(Cr) at 243 K, cyclic steady state simulations

Inclusion of thermal modulation pushes Pareto front into the "attractive" zone for post-combustion CO₂ capture
Process economics – from molecular models to PSA simulation to flowsheet analysis

Prediction of binary isotherms from CoreMOF database

Pareto fronts from PSA optimizer

Flowsheet optimization for each material
Process economics – from molecular models to PSA simulation to flowsheet analysis

- Cost of Capture ($/tonne CO₂)
- Productivity (mol/kg*sec)

- Fiber sorbent cost:
  - 14.44%
  - 9.63%
  - 75.94%

- Total capex: $216M (25% of RTSA)
Accomplishments and outcomes

• Developed a “template” flowsheet for any sub-ambient pressure-driven CO₂ capture process
• Created multi-scale workflow for process-driven material screening and selection for adsorption processes
• Scaled-up two different MOFs (MIL-101(Cr) and UiO-66) to >1 kg scale
• Fabricated MOF fiber sorbents with integrated, passive thermal management
• Constructed two PSA minipilot systems (~500 grams of CO₂/day productivity)
• Humid acid gas stability of MOFs, PSA, and fiber sorbents demonstrated
• Capital and operating cost estimation for sub-ambient PSA CO₂ capture

Papers and Patents


1 submitted, 5 to be submitted Fall 2019
Conclusions and perspectives

Key question: Can we increase swing capacity by 10x and reduce cycle time by 5x to dramatically drive down adsorbent costs?

• Combining RCPSA cycles with appropriate metal-organic frameworks in sub-ambient conditions results in highly productive adsorption systems (i.e., ~30 tonne CO₂/tonne adsorbent-day)

• Significant “real world” complexities exist, but hollow fiber sorbent platform provides solutions to many of these (scalability, transport limitations, etc.)

• Costs in the range of $40-$50/tonne CO₂ at sequestration pressures may be achievable using these materials in this process concept, but significant work remains. Advantages of small size, material stability to flue gas conditions, and modularity are important.
https://lively.chbe.gatech.edu