Pressure Swing Adsorption: Design and Optimization for Pre-Combustion Carbon Capture

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Research Objectives

- Demonstrate methods for optimal Pressure Swing Adsorption (PSA) process synthesis

- Design **cost effective** PSA cycle for $\text{H}_2$-$\text{CO}_2$ separation in IGCC power plant

Simplified IGCC Flowsheet
Pressure Swing Adsorption (PSA)

• Gas separation utilizing differences in adsorption phenomena

• Adsorption at high pressure, desorption at low pressure

• Numerous industrial examples
  – \( \text{H}_2 \) purification in refineries
  – \( \text{O}_2 \) concentration for medical use
Optimal Cycle Synthesis

Discrete variables make this too computationally expensive to solve

“Parts Box” of Steps

Adsorption  
Pressure Equalization  
Desorption  
Heavy Product Purge  
And many more…
PSA “Superstructure”

Only use continuous variables to model generic PSA cycle

α  Bottom Reflux Fraction
β  Top Reflux Fraction
φ  Feed Fraction
$P_{\text{ads}}$  Adsorption Pressure
$P_{\text{des}}$  Desorption Pressure

H₂ to Turbine

CO₂ preferentially adsorbs

CO₂ desorbs

Feed from WSR, $\varphi(t)$

CO₂ to Pipeline
PSA Model: Transport Equations

Momentum (Ergun Equation)

\[- \frac{\partial P}{\partial x} = \frac{150\mu(1 - \epsilon_b)^2}{d_p^2\epsilon_b^3} v + \frac{1.75}{d_p} \left( \frac{1 - \epsilon_b}{\epsilon_b^3} \right) \left( \sum_i M^i_w C_i \right) v|v| \]

\[v_j(t, x) \leftarrow \begin{cases} \max(0, v_j(t, x)) & \text{if } j = 1 \text{ (co-cur. bed)} \\ \min(0, v_j(t, x)) & \text{if } j = 2 \text{ (counter-cur. bed)} \end{cases} \]

Energy

\[0 = \left( \epsilon_t \sum_i C_i (C^i_{pg} - R) + \rho_s C_{ps} \right) \frac{\partial T}{\partial t} - \rho_s \sum_i \Delta H^i_{ads} \frac{\partial q_i}{\partial t} + \frac{\partial (vh)}{\partial x} + UA(T - T_w) \]

Material

\[\epsilon_b \frac{\partial C_i}{\partial t} + (1 - \epsilon_b) \rho_s \frac{\partial q_i}{\partial t} + \frac{\partial (vC_i)}{\partial x} = D_i \frac{\partial^2 C_i}{\partial x^2} \quad i = 1...N_c \]
PSA Model: Adsorption

Linear Driving Force

\[ \frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i) \quad i = 1 \ldots N_c \]

Dual-Site Langmuir Isotherm

\[ q_i^* = \frac{q_1^s b_{1i} P_i}{1 + \sum_j b_{1j} P_j} + \frac{q_2^s b_{2i} P_i}{1 + \sum_j b_{2j} P_j} \quad i = 1 \ldots N_c \]

where

\[ q_{mi}^s = k_{mi}^1 + k_{mi}^2 T \quad b_{mi} = k_{mi}^3 \exp(k_{mi}^4 / T) \quad m = 1, 2 \]

Thermodynamics: Ideal Gas Law

Take away: complex non-linear PDAE model
Sample Simulation Results

**N₂ Loading on Sorbent**

- **Trace Component**

**CO₂ Concentration in Gas Phase**

- **Primary Component**
Optimization Methodology

Minimize specific energy (kWh/tonne CO₂ captured)

Optimization Algorithm

PSA Superstructure

- PSA Bed Model
- Connectivity Equations
- Compressor and Turbine Model
- Valve Equations
- Cyclic Steady-State Constraint

3 approaches to accommodate cyclic-steady state constraint
1. Periodic Boundary Conditions

5 Slot PSA Cycle

Constraint linking initial and final bed state variables

\[ z_0 - z(t_f) = 0 \]

+ exact and smooth \( \rightarrow \) derivative based optimization algorithms
- large problem \( (z_0 \text{ and } u_i \text{ optimization variables}) \)
- expensive derivatives (from direct sensitivity equations)
2. Direct Substitution

5 Slot PSA Cycle

\[ \begin{bmatrix} u_1 & u_2 & u_3 & u_4 & u_5 \end{bmatrix} \]

Repeat direct substitution until \[ |z_0 - z(t_f)| < \epsilon \]

+ “natural”… mimics process start-up
+ simple implementation
+ medium size problem ($z_0$ not optimization variables)
- not smooth \( \rightarrow \) derivative free optimization
3. Fixed Horizon

5 Slot PSA Cycle

Repeat direct substitution a fixed number of times (M)

+ exact and smooth $\rightarrow$ derivative based optimization algorithms
+ medium size problem ($z_0$ *not* optimization variables)
- expensive objective function and constraint evaluations
- expensive derivatives (from adjoint sensitivity equations)
Implementation Details

• IPOPT for derivative based formulations (1, 3)
  – First derivatives from sensitivity equations
  – Second derivatives approximated with LBFGS

• BOBYQA for direct substitution (2)
  – DFO code based on quadratic approximation to objective function
  – Accommodates variable bounds
Case Study 1

• Common far starting point
• DFO approach terminates at a much poorer solution
  – Local minima?
• Some challenges with gradient-based convergence
  – Terminate due to resource limits or integrator failure
  – Noisy first derivatives, approximate second derivatives

<table>
<thead>
<tr>
<th>Approach</th>
<th>Obj. Func kWh/tonne CO₂</th>
<th>CPU Time/Iter h:mm:ss</th>
<th>Iter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Periodic Bnd. Cnd. (1)</td>
<td>89.63</td>
<td>0:08:49</td>
<td>187</td>
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<tr>
<td>Derivative Free (2)</td>
<td>146.42</td>
<td>0:04:46</td>
<td>566</td>
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<td>Fixed Horizon (3)</td>
<td>98.46</td>
<td>0:20:41</td>
<td>397</td>
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</table>
## Case Study 2

### Part A: Two Components (CO₂, H₂)

<table>
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<tr>
<th>Approach</th>
<th>Obj. Func kWh/tonne CO₂</th>
<th>CPU Time/Iter h:mm:ss</th>
<th>Iter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Periodic Bnd. Cnd. (1)</td>
<td>83.51</td>
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<td>Derivative Free (2)</td>
<td>114.21</td>
<td>0:03:28</td>
<td>1215</td>
</tr>
<tr>
<td>Fixed Horizon (3)</td>
<td>86.46</td>
<td>0:21:09</td>
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</tbody>
</table>

### Part B: Five Components (CO₂, H₂, CH₄, N₂, CO)

<table>
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<tr>
<th>Approach</th>
<th>Obj. Func kWh/tonne CO₂</th>
<th>CPU Time/Iter h:mm:ss</th>
<th>Iter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Periodic Bnd. Cnd. (1)</td>
<td>89.37</td>
<td>1:00:15</td>
<td>470</td>
</tr>
<tr>
<td>Derivative Free (2)</td>
<td>109.04</td>
<td>0:11:29</td>
<td>2500+</td>
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<tr>
<td>Fixed Horizon (3)</td>
<td>86.81</td>
<td>1:27:52</td>
<td>260</td>
</tr>
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</table>

- Common near starting point
- DFO approach terminates at an infeasible solution
Adjoint sensitivity computationally adventitious for large systems
Designed Cycle

Legend: CO₂ Sorbent Loading

Best 5 Component Solution
86.8 kWh/tonne CO$_2$ captured

3.2 MPa

H$_2$ to Turbine

13.0 kWh/tonne

< 2.8 MPa

α Bottom Reflux Fraction
β Top Reflux Fraction
φ Feed Fraction
$P_{ads}$ Adsorption Pressure
$P_{des}$ Desorption Pressure

5.1 MPa

Feed from WSR, φ(t)

-35.4 kWh/tonne

12.6 kWh/tonne

> 0.02 MPa

15 MPa

CO$_2$ to Pipeline

99.9 kWh/tonne

Top Reflux β(t)

Bottom Reflux α(t)
Technology Comparison

Economic Metric: Cost of Electricity

<table>
<thead>
<tr>
<th>IGCC without Carbon Capture*</th>
<th>IGCC with Selexol Carbon Capture*</th>
<th>IGCC with PSA Carbon Capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ 76 / MWh</td>
<td>$ 106 / MWh</td>
<td>$ 103 - 109 / MWh</td>
</tr>
</tbody>
</table>

Goal: $ 83 / MWh

- Results are with **activated carbon**
- Future work: consider advanced sorbents

*Cost and Performance Baseline for Fossil Energy Plants Vol 1: Bit. Coal and Nat. Gas to Elec., NETL (2010)*
Conclusions

• Compared three PSA optimization formulation

• Developed novel application of adjoint sensitivity equations to PSA optimization

• Demonstrated potential cost competitiveness of PSA for H$_2$-CO$_2$ separation in IGCC power plant with an activated carbon sorbent
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Optimization Convergence

Valve closes when \( P < P_{\text{ads}} \)
Solution insensitive to \( \beta \) and \( P_{\text{ads}} \)

\[ \begin{align*}
\alpha & \quad \text{Bottom Reflux Fraction} \\
\beta & \quad \text{Top Reflux Fraction} \\
\phi & \quad \text{Feed Fraction} \\
P_{\text{ads}} & \quad \text{Adsorption Pressure} \\
P_{\text{des}} & \quad \text{Desorption Pressure}
\end{align*} \]