Contactor Design for Transformational Sorbents: Application to LBNL MOF

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Outline

- Exploiting transformational sorbents: LBNL MOF
- Process Modeling
- CFD Modeling
- Design of Experiments
- Upcoming/Future Works
Exploiting Transformational Sorbents: LBNL MOF

- Complex and highly nonlinear equilibrium and kinetic characteristics
- Need to exploit the step-shaped isotherms
- Limiting mechanism is likely to be heat transfer, possibly along with mass transfer—both strongly depend on contactor type, design, and configuration
- Heat recovery from the hot solid is critical for reducing the energy penalty but can be challenging
- Lack of understanding of mass/heat transfer characteristics and hydrodynamics for different contactor types under various operating regimes
- Multiple spatial and time scales are of interest
- Strong tradeoff between CAPEX and OPEX
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Isotherm Model

- Traditional isotherm models unable to predict experimental data
- Sips isotherms have been successfully used to model CO₂ adsorption on MOFs and activated carbons¹,²
- Modified dual-site Sips isotherm developed taking into account both chemisorption and physisorption

Kinetic Model

- A kinetic model is developed by considering both the physisorption and chemisorption
- Model parameters are estimated using TGA data from LBL

2 - Tzabar, N., Brake, H. Adsorption isotherm and Sips models of nitrogen, methane, ethane, and propane on commercial activated carbons and polyvinylidene chloride. Adsorption. 2016; 22, 901-914
Axial-Flow Fixed Bed Model

- Dynamic, 1-D, non-isothermal model
- Incorporates external and internal mass transfer resistances

Lab-Scale Model Validation
- Lab scale experimental data from LBNL for the powdered material

Model Results

Process Scale
- Temperature swing adsorption (TSA) cycle using an embedded heat exchanger
- Sized to process flue gas from a gross 644 MWe power plant\(^1\)

Key Observation: Breakthrough time can increase by about 4 times for isothermal operation in comparison to adiabatic operation

1 - Fout et al., Cost and Performance Baseline for Fossil Energy Plants Volume 1. 2015. DOI: DOE/NETL-2015/1723.y
• 1-D two-phase pressure-driven non-isothermal dynamic model of a moving bed reactor

• Cooling water used in the adsorber while steam used in the desorber

• An integrated process is set up by including the adsorber, desorber, and heat recovery system

• Heat exchange among gas, solid and with the embedded heat exchanger considered
Techno-Economic Analysis

- Techno-economic analysis using equivalent annual operating cost (EAOC)

\[
EAOC = \text{Capital cost} \left[ \frac{i}{(1 - (1 + i)^{-n}} \right] + \text{Yearly Operating Costs}
\]

\(i = \text{Discount Rate}\)
\(n = \text{Number of Years}\)

- Capital cost evaluated using Aspen Process Economics Analyzer (APEA) and standard correlations\(^1\)

- Operating costs includes process utilities- steam, electricity, and cooling water

- Comparison to a traditional MEA system\(^2\)

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2 - Fout et al., Cost and Performance Baseline for Fossil Energy Plants Volume 1. 2015. DOI: DOE/NETL-2015/1723.y
Basic TSA Process

- No thermal management during adsorption results in sharp temperature spikes and low solid loadings.

Temperature and loading profiles at end of adsorption step for a specific basic TSA process case.
Modified TSA Process

Temperature and loading profiles at end of adsorption step for a specific modified TSA process case:

- Increase in average bed loading: 133%

EAOC ($\text{Million/year}$)

- $25^\circ C$
- $35^\circ C$

MEA Comparison: +7.3%

Solids Temperature (°C)

Solids Loading (mol/kg)

Residence Time (s)

200 250 300 350 400 450 500 550

0 10 20 30 40 50 60

20 25 30 35 40 45 50

0.2 0.4 0.6 0.8 1

0.2 0.4 0.6 0.8 1

0 0.2 0.4 0.6 0.8 1

0 0.2 0.4 0.6 0.8 1

2 2.5 3 3.5 4 4.5 5

0.2 0.4 0.6 0.8 1

CCSI²

National Energy Technology Laboratory

Lawrence Livermore National Laboratory

Los Alamos National Laboratory

Pacific Northwest National Laboratory

West Virginia University

U.S. Department of Energy
Modified TSA Process with Heat Recovery

Heat Recovery

• Utilizing remaining sensible heat at the end of desorption
• MEA systems can achieve about 85% heat recovery which may not be feasible for a gas-solid system

<table>
<thead>
<tr>
<th>Energy Requirements</th>
<th>Basic TSA Process Using Steam</th>
<th>Modified TSA Process with Cold/Hot Water in Integrated HE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensible Heat (MJ/kg CO₂)</td>
<td>0.76</td>
<td>0.39</td>
</tr>
<tr>
<td>Reaction Energy (MJ/kg CO₂)</td>
<td>1.48</td>
<td>1.48</td>
</tr>
<tr>
<td>Total Regeneration Energy (MJ/kg CO₂)</td>
<td>2.24</td>
<td>1.87</td>
</tr>
</tbody>
</table>

*For lowest EAOC cases with practical heat recoveries

MEA Comparison: -9.8%

~35% Heat Recovery (Practical)

85% Heat Recovery

Residence Time (s)

EAOC ($Million/year)
Moving Bed Analysis

- Capital cost uncertainty
  - ±50% to account for uncertainties in the moving bed process equipment

![Diagram of moving bed process equipment]

- Lean Sorbent Loading (mol/kg)
- EAOC ($Million/year)
- ±50% capital cost uncertainty
- MEA Comparison: +3.2%
- MEA Comparison: -13.8%
- MEA Comparison: -30.8%
- 85% Heat Recovery
- 25°C
Techno-economic analysis shows potential to improve when compared to traditional MEA system

- **Fixed bed system**: cooling during adsorption and 35% heat recovery result in similar EAOC as the MEA system
- **Fixed bed system**: cooling during adsorption and 85% heat recovery result in 10% decrease in EAOC compared to the MEA system
- **Moving bed system**: For the nominal cost, about 14% decrease in EAOC compared to the MEA system can be achieved. If the capital cost is lower by 50%, then 30% reduction in EAOC may be possible.
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Multiphase Flow Modeling

Why CFD for MOF?

Efficiency of CO₂ adsorption will depend on overall flow distribution and local inhomogeneity.

- **Micro Scale**: particles in gas (~100’s microns)
- **Meso Scale**: particle clusters (~ mm’s to meters)
- **Device Scale**: large flow structures in a CFB (~10’s meters)

Use MFIX to predict 3-D distributions in volume fraction, temperature and species concentration.

Model the effect of small-scale fluctuations that are too expensive to simulate directly.

1) https://mfix.netl.doe.gov/experimentation/
Chemistry and Mass Transfer

\[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(s) \]

\[ R_{g,CO_2} = - \sum R_{m,CO_2,\alpha} \]

\[ R_{m,CO_2,\alpha} = \varepsilon_m \rho_m \chi_{m,MOF} \frac{dn_\alpha}{dt} \]

\[ \frac{dn_\alpha}{dt} = k_{ov,\alpha}(n^*_\alpha(P,T) - n_\alpha) \quad \alpha = c, p \]

Isotherm model for \( n^*_\alpha(P,T) \) based on WVU sub-model

- dual-Sips isotherm model for chemical/physical adsorption: parameterized with equilibrium data

Mass transfer model for \( k_{ov,\alpha} \) based on WVU sub-model*

- reaction kinetics: term introduced by WVU and parameterized with TGA data
- macropore diffusion resistance: parameterized with breakthrough data (molecular diffusion + Knudsen diffusion)
- gas-film resistance: neglected; looking to incorporate this term (separately like process model as opposed to within LDF)
- micropore diffusion resistance: neglected

*Similar to the Linear Driving Force model of Farooq/Ruthven (1990)
1. Incorporated chemistry, heat (preliminary) and mass transfer into CFD framework for diamine appended MOF: dmpn-Mg₂(dobpdc)

   **Approach: CFD-TFM** that includes adsorption isotherm and kinetics for \( CO_2 \) transfer and corresponding density changes.

2. Verified model with expected sub-model predictions and validated with data from LBNL: equilibrium isotherms, TGA and breakthrough experiments
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Design of Experiments for Sorbent Modeling and Characterization

Problem Statement: What experimental designs maximize useful information collection to:

- Create predictive models of sorbent processes and ultimately reduce uncertainty in technoeconomic optimization.
- Discern between proposed mechanisms to accelerate scientific understanding.

Accomplishments:
- U. Notre Dame joined CCSI² team in May 2019.
- Shared models from WVU to ND, creating software for parameter estimation.

\[
\frac{\partial C_{s,i}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_{ma} \frac{\partial C_{s,i}}{\partial r} \right) + \left( \frac{1 - \varepsilon_p}{\varepsilon_p} \right) \rho_s \frac{\partial q_i}{\partial t}
\]

\[
\frac{1}{D_{ma}} = \tau \left( \frac{1}{D_{k,i}} + \frac{1}{D_{g,i}} \right)
\]

\[
D_{k,i} = C_1 r_{pore} \left( \frac{T_S}{M_{w,i}} \right) C_2
\]

Parameters to be estimated

Local temperature inside particles cannot be measured

DoE → Process → Updated Model Parameters

Process Model
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Upcoming/Future Works

Process Modeling
- Further development of the kinetic model considering species other than CO₂
- Development of the mass transfer and heat transfer model using data from the shaped particles
- Radial flow fixed bed model development and optimization
- Rotary packed bed model development and optimization
- Bubbling/circulating fluidized bed model development and optimization

CFD Modeling
- Simulate/investigate contactor (packed/fluidized) performance under different conditions
- Finish extending to PIC-CFD & investigate $O(m)$ pilot scale adsorber
- Continue model refinement
- Add new sub-models as available: additional species mass transfer (H₂O/N₂)
- Incorporate gas-side mass transfer resistance: separately or part of LDF

Design of Experiments
- Complete identifiability analysis based on existing experimental capabilities
- Compute optimal experimental designs
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