Development of cyclic adsorption process for CO$_2$ capture: Process modeling and optimization

Marx D., Joss L., Hefti M., Gazzani M., Mazzotti M.

Institute of Process Engineering, ETH Zurich
Adsorption-based capture processes

Separation from pressurized syngas

<table>
<thead>
<tr>
<th>Pressure</th>
<th>30-60 bar</th>
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<tbody>
<tr>
<td>CO₂ fraction</td>
<td>10-40%</td>
</tr>
<tr>
<td>H₂ fraction</td>
<td>30-60%</td>
</tr>
<tr>
<td>CO, O₂, N₂, H₂O...</td>
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Adsorption-based separation:

- Very high purity of the less retained component
- Very low energy requirement
- Non-volatility of the sorbent

Pressure Swing

Δ ads

P adsorption

P desorption

Pressure Swing

H₂

CO₂ + impurities

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Adsorption-based capture processes

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<tr>
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<tr>
<td>$\text{CO, O}_2, \text{N}_2, \text{H}_2\text{O}$...</td>
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$\text{H}_2$ separation from $\text{CO}_2$ fraction 10-40%

$\text{H}_2$ fraction 30-60%

PSA

$\Delta \text{ads}$

Pressure Swing

$P_{\text{desorption}}$  $P_{\text{adsorption}}$
Adsorption-based capture processes

Separation from pressurized syngas
- Pressure: 30-60 bar
- CO₂ fraction: 10-40%
- H₂ fraction: 30-60%
- CO, O₂, N₂, H₂O...

Post-combustion capture
- Pressure: 1 bar
- CO₂ fraction: 6-15%
- N₂ fraction: 85-94%
- H₂O, O₂,...

**PSA**

**TSA**

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<tr>
<th>Temps</th>
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<th>Δ ads</th>
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<tr>
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Adsorption-based capture processes

Motivation:
• Heat recovery from low grade heat sources and no need of compression energy make temperature-based swing adsorption attractive for CO₂ post-combustion capture.
• Gentle separation typical of adsorption process is complemented by low primary energy demand.
## Talk outline

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Talk outline

Approach for robust process design:

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- Schell et al., *Adsorption* 2012, 18, 49-65
- Casas et al., *Adsorption* 2012, 18, 143-161
- Marx et al., *Adsorption* 2014, 20, 493-510
Material characterization and selection

Pure-component CO₂ isotherms

Zeolite ZSM-5

Zeolite 13-X

Isotherm model
- Sips model

\[ n = n_\infty \frac{(bp)^c}{1 + (bp)^c} \]

Multi-component N₂-CO₂ isotherms

Binary isotherms
- Extended Sips

\[ n_i = \frac{n_i^\infty (b_i P_i)^{c_i}}{1 + \sum_j (b_j P_j)^{c_j}} \]
### Approach for robust process design

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<td><img src="image" alt="Lab pilot diagram" /></td>
<td><img src="image" alt="Process design diagram" /></td>
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- **Equilibria**: Rubotherm MSB
- **Fixed bed**: [Diagram](image)
- **Modeling**: Mass and energy balances, Isotherms, EOS
- **Lab pilot**: Experimental validation
- **Process design & Optimization**: AC, MOF, Mix, Cycle I, Cycle II, Energy, Productivity

References:
- Schell et al., *IEC&R 2013*, 52, 8311-8322
- Marx et al., *IEC&R 2015*, 54, 6035-6045
- Marx et al., *in preparation*
## Modeling: equations

### 1. Mass balances species \( i \)

\[
\varepsilon_t \frac{\partial c_i}{\partial t} + \rho_b \frac{\partial n_i}{\partial t} + \frac{\partial (uc_i)}{\partial z} - \varepsilon_b \frac{\partial}{\partial z} \left( D_L c \frac{\partial y_i}{\partial z} \right) = 0
\]

- **Accumulation**
- **Convection**
- **Dispersion**

\[
\frac{\partial n_i}{\partial t} = k_i a_p (n_i^* - n_i)
\]

**Linear driving force**

### 2. Energy balances

\[
\frac{\partial T_w}{\partial t} = \frac{2\pi}{C_w a_w} \left( h_L R_i (T - T_w) - h_w R_o (T_w - T_{amb}) \right)
\]

- **Acc**
- **Exchange column - wall**
- **Exchange wall - outside**

\[
\left( \varepsilon_t C_g + \rho_b C_s + \rho_b C_{ads} \right) \frac{\partial T}{\partial t} - \varepsilon_t \frac{\partial p}{\partial t} + u C_g \frac{\partial T}{\partial z} - \rho_b \sum_{j=1}^{n} \left( - \Delta H_j \right) \frac{\partial n_j}{\partial t} + \frac{2h_L}{R_i} (T - T_w) - \varepsilon_b \frac{\partial}{\partial z} \left( K_L \frac{\partial T}{\partial z} \right) = 0
\]

- **Accumulation**
- **Convection**
- **Heat of adsorption**
- **Exchange column - wall**
- **Conductivity**

### 3. Constitutive equations

1. **Non linear adsorption isotherm:**
   \[ n_i^* = n_i^* (p, T, y_i) \]

2. **Equation of State: ideal gas**

3. **Pressure: **Ergun equation**
Modeling: equations

1. Mass balances species $i$

$$
\varepsilon \frac{\partial c_i}{\partial t} + \rho_b \frac{\partial n_i}{\partial t} + \frac{\partial (uc_i)}{\partial z} - \varepsilon_b \frac{\partial \rho_b}{\partial z} \left( \varepsilon_c \frac{\partial y_i}{\partial z} \right) = 0
$$

$$
\frac{\partial n_i}{\partial t} = k_i a_p (n_i^* - n_i)
$$

Linear driving force

2. Energy balances

$$
\frac{\partial T_w}{\partial t} = \frac{2\pi}{\varepsilon C_w a_w} \left( h_L R_i (T - T_w) - h_w R_o (T_w - T_{amb}) \right)
$$

3. Constitutive equations

1. Non linear adsorption isotherm:

$$
n_i^* = n_i^* (p, T, y_i)
$$

Mass transfer CO$_2$

$$
k_{CO2} = 0.1 \text{ s}^{-1}
$$

Mass transfer N$_2$

$$
k_{N2} = 0.5
$$

Internal heat transfer

$$
h_L = 33 \text{ W}
$$

Internal heat transfer, static

$$
h_L^0 = 22
$$

External heat transfer,

$$
h_W = 220
$$
**Modeling: validation**

| Column length | 1.2 [m] |
| Internal radius | 12.5 x 10^{-3} [m] |
| External radius | 15.0 x 10^{-3} [m] |
| Heat capacity wall | 4 x 10^6 [J / Km] |
| 13X material density | 2359 [kg/m^3] |
| Particle density | 1085 [kg/m^3] |
| Bed density | 652 [kg/m^3] |
| Particle diameter | 1.6-2.0 x 10^{-3} [m] |
| Heat capacity sorbent | 920 [J / Kkg] |

**Rig modifications for TSA experiments**
- 2 jacketed columns
- 2 thermostats (Hüber Kältmachinenbau, DE)
- Automatic valves at inlet/outlet of the jacket

**Main features gas piping**
- 5 thermocouples along the column
- 2 mass flow controllers for feeding control
- Mass spectrometer for product analysis
Modeling: validation

Different comparisons between model and test rig results were carried out:

1. Breakthrough experiments
2. Heating (material regeneration) and cooling steps
3. Whole TSA cycle
Modeling: validation

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Modeling: validation

Different comparisons between model and test rig results were carried out:
1. Breakthrough experiments
2. Heating (material regeneration) and cooling steps
3. Whole TSA cycle

Simplest TSA cycle for CO₂ extraction:
3-steps
1. Feeding and adsorption of CO₂
2. Heating for material regeneration
3. Cooling for column preparation

Feed:
CO₂-N₂ binary (12%-88%), fixed flow rate
Modeling: validation

Different comparisons between model and test rig results were carried out:
1. Breakthrough experiments
2. Heating (material regeneration) and cooling steps
3. Whole TSA cycle

CO₂ purity > 90%

Waste (N₂)

Dry feed

CO₂

Adsorption tₐₐ₅s Heating tₜₐ₅ Heat Cooling tₐ₉s

Considered simulated cycle for validation

T°C100125150

Experimental results for same cycle parameters

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## Approach for robust process design

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### Equilibria

- Mass and energy balances
- Isotherms
- EOS

### Fixed bed

- Rubotherm MSB

### Modeling

- Joss et al., *IEC&R* 2015, 54, 3027-3038
- Joss et al., *in preparation*

### Lab pilot

- Experimental validation

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Separation Processes Laboratory

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Process synthesis: boundary conditions

Assumptions:
- Binary CO$_2$+N$_2$ (12%-88%) mixture entering the capture section
- Energy for drying: 8 MJ$_{th}$/kg$_{H2O}$

* Perry's Chemical Engineers' Handbook
Process synthesis: boundary conditions

Assumptions:
- Binary CO₂+N₂ (12%-88%) mixture entering the capture section
- Energy for drying: 8 MJ_th/kgH₂O

* Perry's Chemical Engineers' Handbook
Process synthesis: cycle design

**Cycle A**

- 3-steps cycle
- CO$_2$ is produced as the bed heated up
- Simplest configuration
- Lowest number of variables
## Process synthesis: cycle design

### Cycle A
- Dry feed
- Adsorption
- Rinse
- Heating
- Purge

### Cycle B
- CO₂ (N₂)
- CO₂

### Diagram
- 5 steps cycle
- CO₂ is produced as the bed heated up
- CO₂ rich recycle enhances purity and productivity
- Make use of recycled N₂ to push CO₂ out
- Increased number of variables
Process synthesis: cycle design

<table>
<thead>
<tr>
<th>Cycle A</th>
<th>Cycle B</th>
<th>Cycle C</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Waste $(N_2)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO$_2$</td>
</tr>
<tr>
<td>Dry feed</td>
<td></td>
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</tr>
<tr>
<td>Adsorption</td>
<td>Heat 1</td>
<td>Heat 2</td>
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- 4 steps cycle
- First heating step to collect impure CO$_2$, which is then recycled to the feed
- Second heating step to produce the pure CO$_2$ product
Process synthesis: heuristic comparison

- Lowest separation performance

Rinse-purge combination:
- Purity and recovery enhancement
Additional step is fast:
- Improved specific productivity
Compared to Cycle A, we should obtain an improvement in all indexes

Dedicate heating time for evacuation:
- Best purity among A, B and C
- Improved recovery compared to A
Additional step is slow:
- Reduced productivity and higher energy consumption
Process synthesis: separation performance

Recovery-Purity pareto curves can be established by varying the cycle times

\[
\text{Recovery} = \frac{n_{CO_2,\text{product}}}{n_{CO_2,\text{feed}}}
\]

\[
\text{Purity} = y_{CO_2,\text{product}}
\]
Process synthesis: separation performance

Recovery-Purity pareto curves can be established by varying the cycle times

**Cycle A**: 3-steps cycle:

- $t_{ads}$, $t_{heat}$ and $t_{cool}$
Process synthesis: separation performance

Recovery-Purity pareto curves can be established by varying the cycle times

**Cycle B:** 5-steps cycle
\[ t_{\text{ads}}, t_{\text{heat}}, t_{\text{cool}}, t_{\text{purge}} = t_{\text{rinse}} \]
Process synthesis: separation performance

Recovery-Purity pareto curves can be established by varying the cycle times

**Cycle C**: 4-steps cycle
- $t_{\text{ads}}$, $t_{\text{heat1}}$, $t_{\text{heat2}}$, $t_{\text{cool}}$

Cycle C outperforms A and B in term of separation performance.
Energy consumption-Productivity pareto curves are also established when varying cycle times. Simulations with \((R,P) < (0.8,0.8)\) are not considered.

\[
\text{Energy consumption} = \frac{Q_{TSA}}{m_{CO_2, prod}}
\]

\[
\text{Productivity} = \frac{m_{CO_2, prod} / t_{cycle}}{\rho_{bed} V_{col}}
\]
Energy consumption-Productivity pareto curves are also established when varying cycle times.
Process synthesis: energy and productivity

Energy consumption-Productivity pareto curves are also established when varying cycle times.

\[(R,P) = (0.8, 0.8)\]
Energy consumption-Productivity pareto curves are also established when varying cycle times.

Cycle B outperforms A and C in term of energy and productivity for a given separation target.
Process design for CO$_2$ capture

\[(R,P) = (0.9, \text{maxP}=0.93)\]
Process improvement

**Process optimization**
- Mixed Integer Non-Linear
- Many degrees of freedom
- Multi-objective
- Control
- Economics

**Materials**
- Synthesis & engineering
- Working capacity
- Stability to H₂O
- Formulation
- Characterization

**Process design**
- Modeling
- Cycle configuration
- Scheduling
- Column/module design
- Energy integration
Process improvement

**Process optimization**

---

**Challenges:**
- Multi-objective optimization of two conflicting objectives (energy-productivity)
- Noisy and non-smooth objective function because of the PDE solver
- Computational time of each function evaluation is considerable
- Purity and recovery are non-linear constraints

**Implemented algorithm:**
- Model-based, derivative-free algorithm:
  revised version of the Multilevel Coordinate Search (MCS) algorithm
Process improvement

Process optimization

New feasible points are obtained:
- pareto front moves towards higher productivity.
- Minimum energy consumption is slightly affected.
Process improvement

**Materials**

Mg$_2$(dobdc) (Mg-MOF-47): high CO$_2$ capacity, high selectivity, potential for TSA

Simulated counter-current heat exchanger:

Low grade heat stream $T_{in}$

$T_5 > T_4 > T_3 > T_2 > T_1$

Specific Energy Consumption, [MJ/kg$_{CO_2}$]

Amines

- Optimized with Z-13X
- Optimized with MOF

Heat integration

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Conclusions

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Marx et al., *Adsorption* 2014, 20, 493-510  
Joss et al., *IEC&R* 2015, 54, 3027-3038
Conclusions

- A good commercial material for CO$_2$ capture with a TSA process is already available.
- Separation performance is very promising; cycles can be tuned according to requirements.
- Careful cycle synthesis and selection are needed to obtain the best trade-off between energy consumption and productivity.
- Optimization, new materials and heat integration make the TSA a promising solution for 2$^{nd}$ generation CO$_2$ post-combustion capture.

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Backup slides
Breakthrough experiments on 13X

Concentration and temperature profiles for the breakthrough experiment with an initial temperature of 25°C, a feed composition of \( y_{\text{CO}_2} = 0.12 \), and a feed flow rate of 300 cm³/s.
Heating and cooling

The full length of the steps was 1800 s for the heating step and 1200 s for the cooling step. Along with the temperatures measured in the bed (symbols) and the corresponding simulation results (lines), the measured temperature of the heat exchange fluid at the jacket inlet and outlet is shown using dots.
Pure component equilibria

**Zeolite ZSM-5**

**P/T conditions**
- Pressure: up to 10bar
- Temperature range: 25 - 140°C

**Zeolite 13-X**

**CO₂**

**N₂**
Pure component equilibria

Zeolite ZSM-5

P/T conditions
- Pressure: up to 10 bar
- Temperature range: 25 - 140°C

Isotherm model
- Sips model
  \[ n = n^\infty \frac{(bp)^c}{1 + (bp)^c} \]
  
  \[ n^\infty = n^\infty (T) \]
  \[ b = b (T) \]
  \[ c = c (T) \]

Zeolite 13-X
Pure component equilibria

Zeolite ZSM-5

P/T conditions
- Pressure: 1-10 bar
- Temperature range: 25 and 45°C

Zeolite 13-X

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Pure component equilibria

Zeolite ZSM-5

P/T conditions
- Pressure: 1-10 bar
- Temperature range: 25 and 45°C

Binary isotherms
- Extended Sips

\[ n_i = n_i^\infty \left( \frac{b_i P_i}{1 + \sum_j (b_j P_j)^{c_j}} \right)^{c_i} \]

Zeolite 13-X

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Simulated counter-current heat exchanger:

\[ T_5 > T_4 > T_3 > T_2 > T_1 \]

Trade-off between CAPEX and OPEX

Recovered heat, [MJ/kg CO₂]

Number of columns, \( N_{\text{col}} \)

\( N_{\text{steps}} = 5 \)
Comparison with existing plants

TSA productivity is converted to volume based
- Factor 2 assumed when moving from tonne\textsubscript{zeolite} to m\textsuperscript{3}

Boundary Dam productivity: approximately 13 kg\textsubscript{CO\textsubscript{2}}/(m\textsuperscript{3}h)
using:

$\text{CO}_2$ capacity: 3000 t/day
$\text{CO}_2$ absorber 11 x 11 x 54 m
$\text{CO}_2$ desorber 8 x 43 m