Comparison of commercial and new developed adsorbent materials for pre-combustion CO$_2$ capture by pressure swing adsorption

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CO$_2$ capture in an IGCC power plant

Coal $\rightarrow$ Gasifier $\rightarrow$ Shift $\rightarrow$ CO$_2$ / H$_2$ separation $\rightarrow$ CO$_2$ compression $\rightarrow$ CO$_2$

Air $\rightarrow$ ASU $\rightarrow$ Gas turbine $\rightarrow$ Steam cycle $\rightarrow$ electricity

Coal $\rightarrow$ CO$_2$, H$_2$ $\rightarrow$ CO$_2$ $\rightarrow$ CO$_2$ compression

Air $\rightarrow$ O$_2$ $\rightarrow$ H$_2$
CO₂ capture in an IGCC power plant

Pressure 35 bar
CO₂ fraction 40%
H₂ fraction 60%

CO₂ / H₂ separation

CO₂ to storage:
CO₂ purity > 95%
Capture > 90%
Pressure 110 bar

H₂ to gas turbine:
H₂ purity ≈ 94%
Pressure ≈ 25 bar

CO₂ / H₂ separation by PSA promising
PSA cycle possibilities

- Classical Skarstorm cycle used to produce high purity high $p$ product (e.g. H$_2$)
- consists of 4 basic steps:
  - Pressurization with Feed
  - Adsorption
  - Countercurrent blowdown
  - Purge with high pressure product

In more advanced cycles more steps are applied, e.g.:
- Pressure equalization
- Purge with other than product
- Cocurrent blowdown
- ...

Steps can be combined in multiple ways
Approach

Materials

Commercial and new materials
Approach

Materials

Commercial and new materials

Static experiments

Rubotherm

MSB

Microbalance

Elec. Magnet

Perm. Magnet

Sinker

Basket
Approach

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Rubotherm
MSB

Dynamic experiments

Two column PSA setup

Materials

Commercial and new materials

Static experiments

Rubotherm
MSB

Dynamic experiments

Two column PSA setup
**Approach**

### Materials

**Commercial and new materials**

![Microbalance](image)

- Rubotherm
- MSB

### Static experiments

- *Rubotherm*
- *MSB*

### Dynamic experiments

**Two column PSA setup**

- 110 cm
- 85 cm
- 60 cm
- 40 cm
- 10 cm

### Process modeling

**Mass, energy and momentum balances, Isotherms & EOS**

\[
\begin{align*}
  u & \quad \varepsilon^* \\
  \text{voids} & \quad c_i, P, T \\
  \text{adsorbent} & \quad (1 - \varepsilon^*) \\
  T_w & \quad n, I_i
\end{align*}
\]
Approach

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Rubotherm MSB

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Model-based Process Design

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Two column PSA setup

Process modeling

Mass, energy and momentum balances, Isotherms & EOS

\[ u \]

\[ \text{voids} \quad \varepsilon^* \quad c, P, T \]

\[ T_w \]

\[ \text{adsorbent} (1 - \varepsilon^*) \quad n, T_i \]
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Adsorbent materials

Commercial material

- **Activated carbon AC AP3-60, Chemviron, Germany**

New adsorbent material (SINTEF)

- **USO-2-Ni MOF** \((\text{Ni}_2(1.4\text{-bdc})_2(\text{dabco})\cdot4\text{DMF}\cdot0.5\text{H}_2\text{O})\)
- **Mesoporous silica MCM-41**
Adsorbent materials

Commercial material
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- Mesoporous silica MCM-41

→ New materials synthesized as powder
→ For process application: formulation as pellets crucial
→ No well established method
→ 4 Different formulation methods investigated
→ Particle size: 35 -70 mesh
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Rubotherm MSB

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Two column PSA setup
# Equilibrium measurements

Isotherm measurements using Rubotherm MSB

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>H₂</th>
<th>N₂</th>
<th>Mix</th>
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<tbody>
<tr>
<td><strong>AC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>25-140°C</td>
<td>25-65°C</td>
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<tr>
<td>$p$</td>
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<td>0.05-200 bar</td>
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</tr>
<tr>
<td>$T$</td>
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<td>In progress</td>
<td>-</td>
<td>-</td>
</tr>
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Equilibrium measurements

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Mathematical description of adsorption equilibrium

Parameter Fitting

Selection Isotherm eq.

Excess ↔ Absolut
AC: pure component isotherms
AC: pure component isotherms

Isotherm parameters used for:
- Absolute adsorption
- Heat of adsorption (Clausius Clapeyron)
- Prediction of binary adsorption, e.g.:
  - Empirical binary isotherm (e.g. Langmuir)
  - IAST
- Cyclic capacity → evaluation of suitability
Comparison: pure component isotherms

CO₂ isotherms at 25°C
Comparison: pure component isotherms

CO₂ isotherms at 25°C

Cyclic capacity
\[ p_{\text{Ads}} = 1.5 \text{ MPa}, \ p_{\text{Des}} \text{ varying} \]

Approach

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Commercial and new materials

Static experiments
Rubotherm MSB

Model-based Process Design

Process modeling
Mass, energy and momentum balances, Isotherms & EOS

Dynamic experiments
Two column PSA setup

110 cm
85 cm
60 cm
40 cm
10 cm
Model equations of an adsorption column

1. Mass balances species $i$

\[
\frac{\partial c_i}{\partial t} + \frac{\partial n_i}{\partial t} + \frac{1}{\varepsilon^*} \frac{\partial (uc_i)}{\partial z} - \frac{\varepsilon}{\varepsilon^*} D_i \frac{\partial}{\partial z} \left( \frac{\partial c_i}{\partial z} \right) = 0
\]

Accumulation
Convection
Dispersion

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

Linear driving force

2. Energy balances

\[
\frac{\partial T_s}{\partial t} = \frac{1}{C_s} \sum_{j=1}^{n} \left( -\Delta H_j \right) \frac{\partial n_j}{\partial t} + \frac{h_s a_p}{C_s} (T - T_s)
\]

Acc
Heat of adsorption
Exchange
gas - solid

\[
\frac{\partial T}{\partial t} + \nu \frac{\partial T_s}{\partial t} + \frac{1}{\varepsilon^*} \frac{\partial (uT)}{\partial z} - \frac{\nu}{C_g} \sum_{j=1}^{n} \left( -\Delta H_j \right) \frac{\partial n_j}{\partial t} + \frac{2h_L}{r_i \varepsilon^* C_g} (T - T_w) - \frac{\varepsilon}{\varepsilon^*} D_L \frac{\partial}{\partial z} \left( \frac{\partial T}{\partial z} \right) = 0
\]

Accumulation
Convection
Heat of adsorption
Exchange wall
Dispersion

3. Constitutive equations

1. Non linear adsorption isotherm:

\[ n_i^* = n_i^* (p, T, y_i) \]

2. Equation of State: Ideal gas law

3. Pressure: Ergun equation
Model equations of an adsorption column

1. Mass balances species $i$

$$\frac{\partial c_i}{\partial t} + \nu \frac{\partial n_i}{\partial t} + \frac{1}{\varepsilon^*} \frac{\partial (uc_i)}{\partial z} - \frac{\varepsilon}{\varepsilon^*} D_{Li} \frac{\partial}{\partial z} \left( \frac{\partial c_i}{\partial z} \right) = 0$$

$$\frac{\partial n_i}{\partial t} = k_i a_p \left(n_i^* - n_i\right) \quad \text{Linear driving force}$$

2. Energy balances

$$\frac{\partial T_s}{\partial t} = \frac{1}{C_s} \sum_{j=1}^{n} \left( -\Delta H_j \right) \frac{\partial n_j}{\partial t} + \frac{h_s a_p}{C_s} (T - T_s)$$

$$\frac{\partial T}{\partial t} + \nu \gamma \frac{\partial T_s}{\partial t} + \frac{1}{\varepsilon^*} \frac{\partial (uT)}{\partial z} - \frac{\nu}{C_g} \sum_{j=1}^{n} \left( -\Delta H_j \right) \frac{\partial n_j}{\partial t} + \frac{2h_L}{r_i \varepsilon^* C_g} (T - T_w) - \frac{\varepsilon}{\varepsilon^*} K_L \frac{\partial}{\partial z} \left( \frac{\partial T}{\partial z} \right) = 0$$

3. Constitutive equations

1. Non linear adsorption isotherm:

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- Commercial and new materials

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**Static experiments**

- Rubotherm MSB

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**Process modeling**

- Mass, energy and momentum balances, Isotherms & EOS

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**Dynamic experiments**

- Two column PSA setup

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**Model-based Process Design**
Experimental setup: 2-column Lab PSA

- Breakthrough experiments
- PSA cycles including $p$ equalization
- Fully automated
- Premixed gases
- Column insulation and heating
- $p$ and $T$ measurements
- Product streams online analyzed by MS
Breakthrough and PSA experiments

- Breakthrough experiments
- Fit the missing model parameters

\[ T = 25^\circ C \]
\[ p = 15 \text{ bar} \]
Breakthrough and PSA experiments

Breakthrough experiments

→ Fit the missing model parameters

PSA experiments

→ Validate the PSA simulation tool

→ Exp. testing of full PSA cycles

Breakthrough experiments

$T = 25^\circ C$

$p = 15$ bar

H$_2$ rich product

CO$_2$ rich product
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Process Design criteria

**CO₂ to storage:**

- **CO₂ purity**: > 95%
- **Capture**: > 90%
- **Pressure**: 110 bar

**Specifications & boundary conditions:**
- CO₂ purity and capture rate
- Purge with the feed
- Co-current blowdown

**Minimize energy penalty (compression costs):**
- No repressurization
- Increase CO₂ desorption pressure

**Investments cost:**
- Max. 3 p-equalization steps
Process Design criteria

**CO₂ to storage:**
- CO₂ purity > 95%
- Capture > 90%
- Pressure 110 bar

**Feed**
- Specifications & boundary conditions: CO₂ purity and capture rate
  - purge with the feed
  - co-current blowdown
- Minimize energy penalty (compression costs):
  - no repressurization
  - increase CO₂ desorption pressure
- Investments cost:
  - max. 3 $p$-equalization steps

\[ \rightarrow \text{For fixed material, } T \text{ and } p_{\text{Des}}: \text{ process performance dependent on } t_{\text{ads}}, t_{\text{blow}} \text{ & } t_{\text{purge}} \]
Influence of the adsorption step time (AC)

→ Change of time of the adsorption step
→ Time of blowdown and purge step already optimized

\[ T = 308 \, \text{K} \]

\[ p_{\text{Des}} = 1 \, \text{bar} \]
Influence of the adsorption step time (AC)

- Change of time of the adsorption step
- Time of blowdown and purge step already optimized

\[
T = 308 \text{ K} \\
\rho_{\text{Des}} = 1 \text{ bar}
\]

\[
\text{CO}_2 \text{ capture rate}
\]

\[
\text{CO}_2 \text{ purity}
\]

- Trade-off
- Better shown as pareto front
AC comparison: process conditions

- Different desorption pressures
- $T = 308$ K
AC comparison: process conditions

- Different desorption pressures
- $T = 308 \, \text{K}$

- Different process temperatures
- $p_{\text{Des}} = 1 \, \text{bar}$
Comparison: AC $\leftrightarrow$ MOF

- MOF with “real” physical properties compared to theoretical MOF
- $T = 308$ K, $p_{\text{Des}} = 1$ bar
Comparison: AC ↔ MOF

→ MOF with “real” physical properties compared to theoretical MOF

→ $T = 308 \text{ K}, p_{\text{Des}} = 1 \text{ bar}$

→ Theoretical MOF compared to AC

→ $T = 308 \text{ K}, p_{\text{Des}} = 1 \text{ bar}$

![Graph 1: CO₂ capture rate vs. CO₂ purity for theoretical MOF and “real” MOF.](image)

![Graph 2: CO₂ capture rate vs. CO₂ purity for AC and theoretical MOF.](image)
Conclusions

- PSA for pre-combustion very promising because of boundary conditions and process specifications
- Model-based process design beneficial due to various process configurations
- Model parameters have to be determined in a reliable way
- Pareto front to compare different process conditions and materials
- MOF shows promising behavior however material formulation very important for process performance