ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

DECO2ARBit

Comparison of commercial and new developed adsorbent materials for pre-combustion CO_2 capture by pressure swing adsorption

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TCCS-6
Trondheim, Norway
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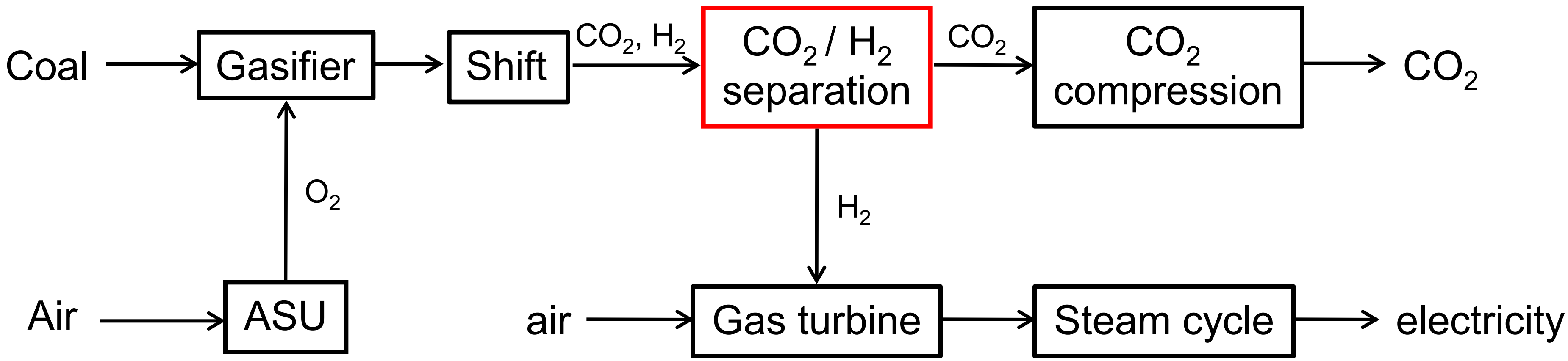
CO_2 capture in an IGCC power plant



CO_2 capture in an IGCC power plant

Pressure	35 bar
CO_2 fraction	40%
H_2 fraction	60%

→ **CO_2 / H_2 separation** →

CO_2 to storage:

CO_2 purity	> 95%
Capture	> 90%
Pressure	110 bar

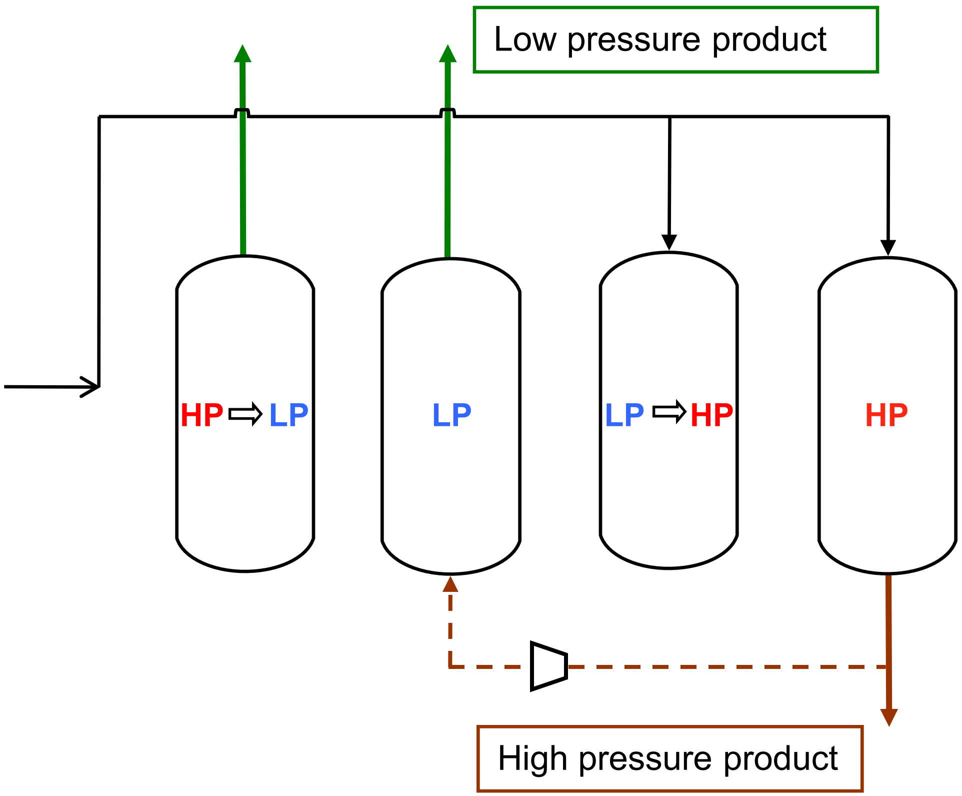
H_2 to gas turbine:

H_2 purity	≈ 94%
Pressure	≈ 25 bar

CO_2 / H_2 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 advaced cycles more steps are applied, e.g.:

- Pressure equalization
- Purge with other than product
- Cocurrent blowdown
- …

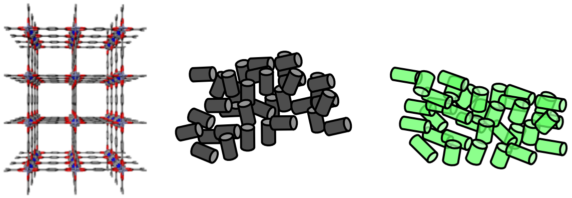
Steps can be combined in multiple ways

➡ Complex process design

Approach

Materials

Commercial and new materials



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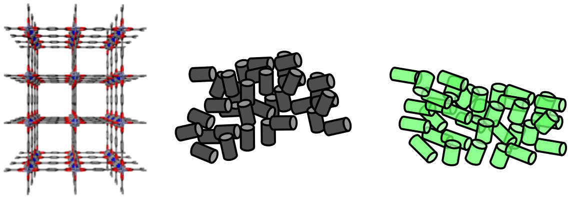
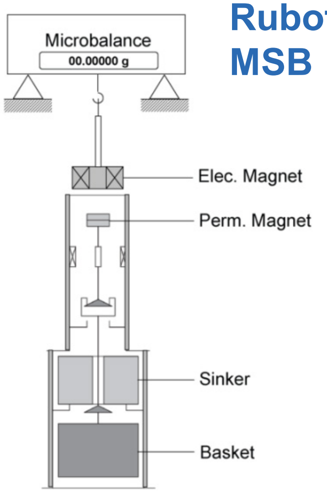


Static experiments

Rubotherm MSB



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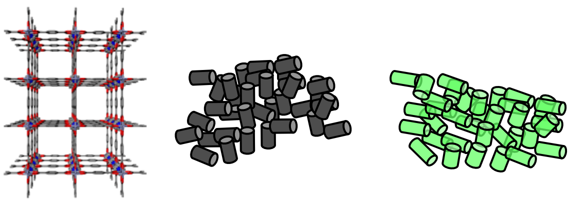

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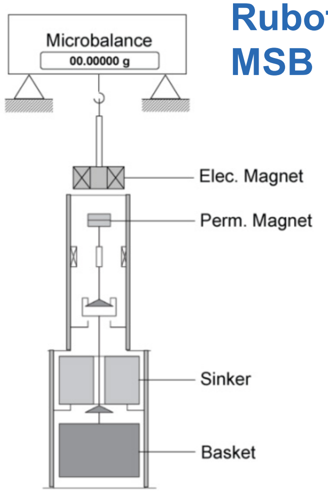

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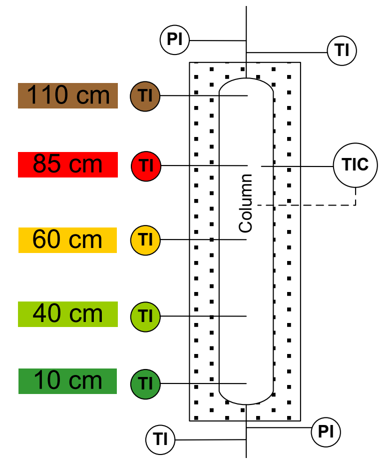

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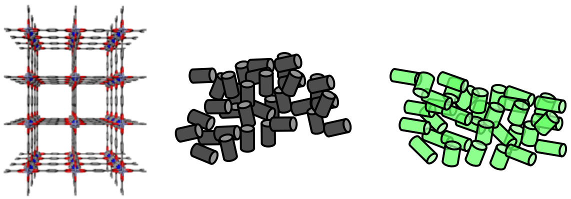
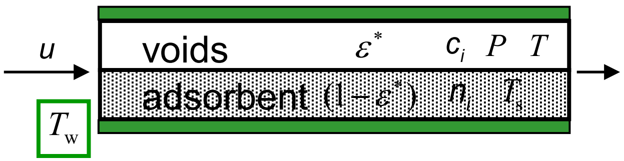


Process modeling

Mass, energy and momentum balances, Isotherms & EOS



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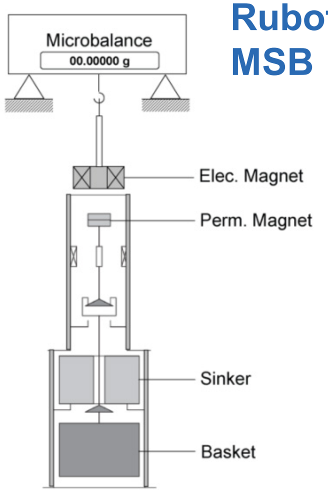

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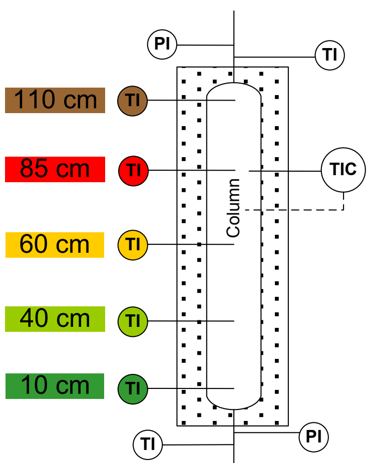

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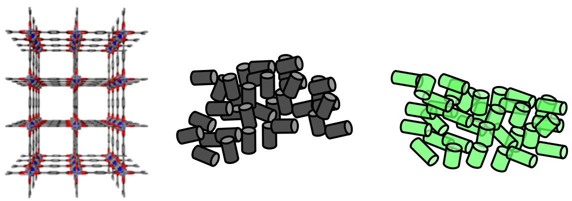

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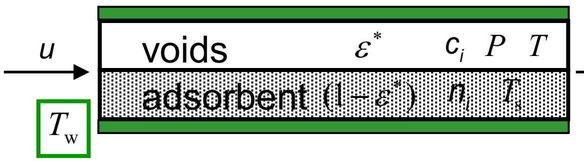

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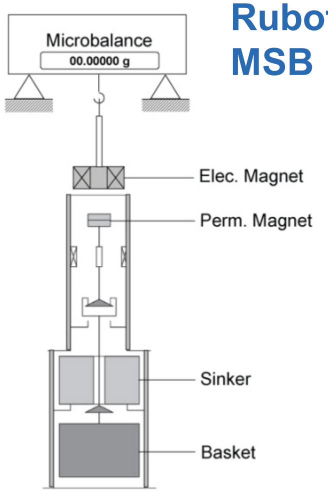

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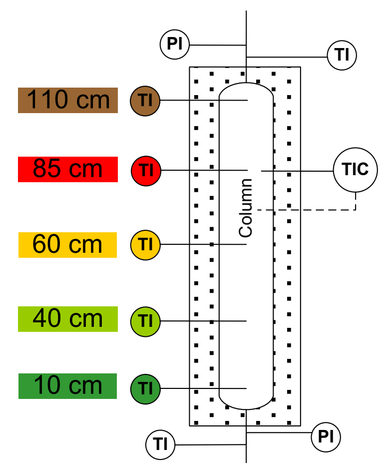

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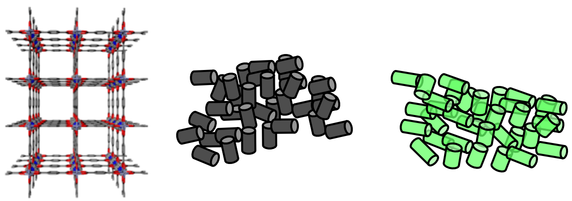

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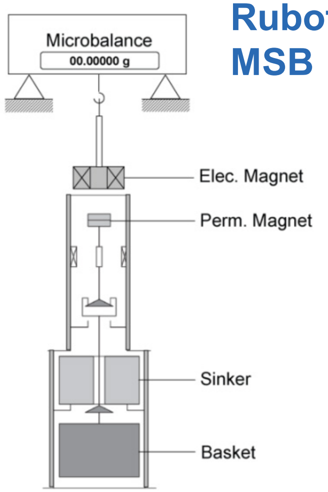

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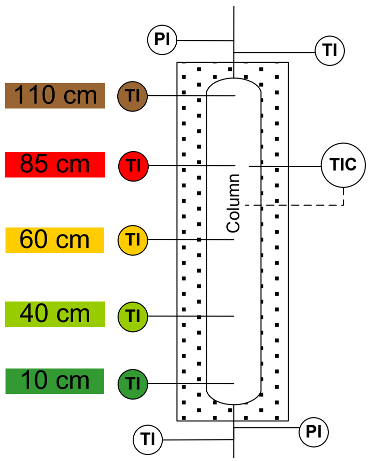
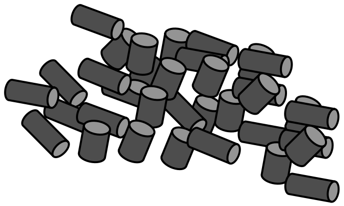


Adsorbent materials

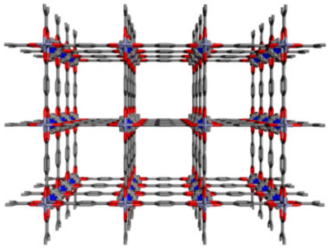
Commercial material

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



New adsorbent material (SINTEF)

- **USO-2-Ni MOF (Ni_2(1.4-bdc)$_2$(dabco)·4DMF·0.5H_2O)**
- **Mesoporous silica MCM-41**



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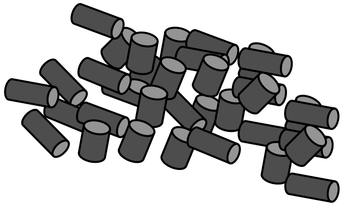

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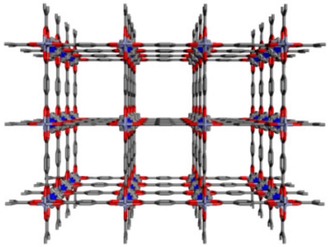


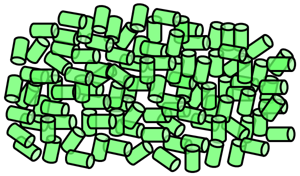
→ New materials synthesized as **powder**

→ 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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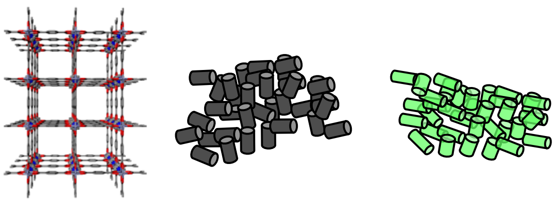

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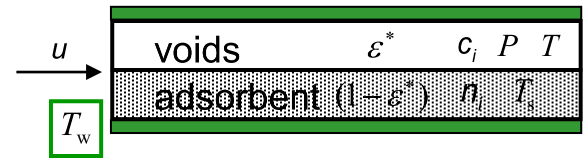

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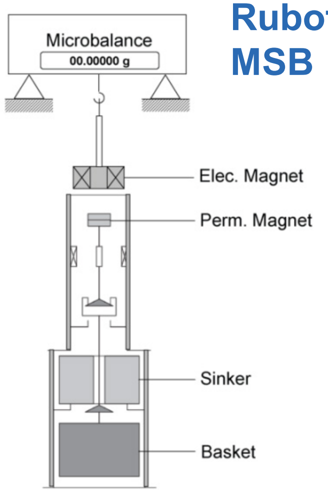

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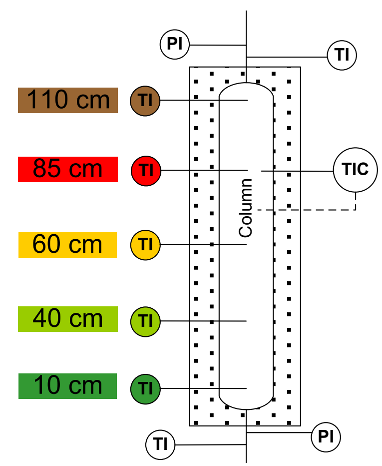
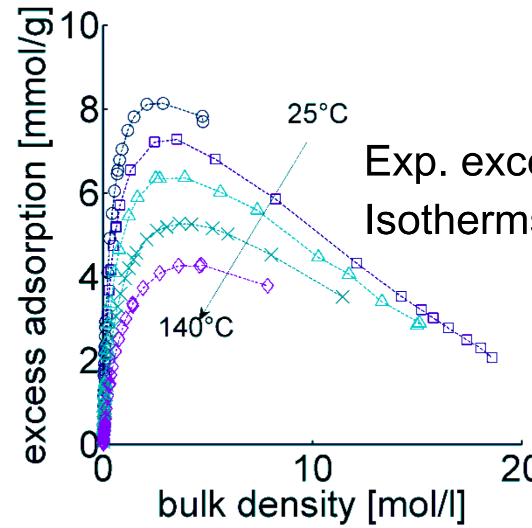


Equilibrium measurements

Isotherm measurements using Rubotherm MSB

		CO_2	H_2	N_2	Mix
AC	*T*	25-140°C	25-65°C	25-140°C	25°C
	p	0.1-210 bar	0.1-140 bar	0.05-200 bar	5-120 bar
MOF	*T*	25-140°C	25-65°C	-	-
	p	0.1-125 bar	1-115 bar	-	-
MCM-41	*T*	25-140°C	In progress	-	-
	p	0.2-154 bar		-	-



Exp. excess Isotherms

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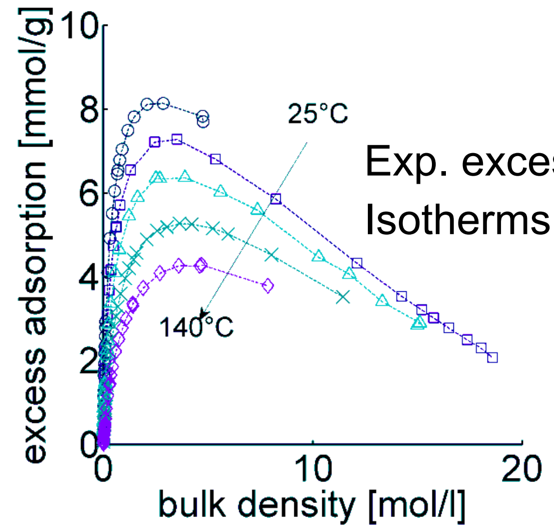
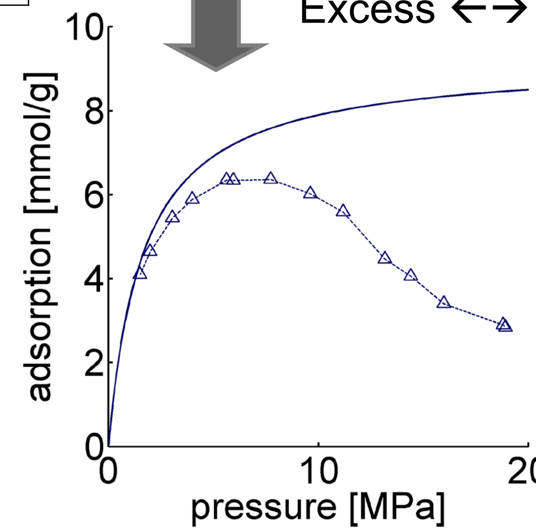
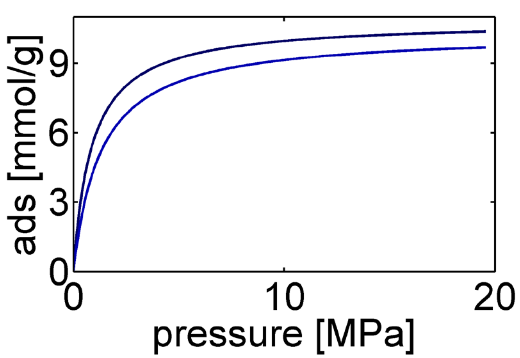


Exp. excess Isotherms

Excess ←→ Absolut



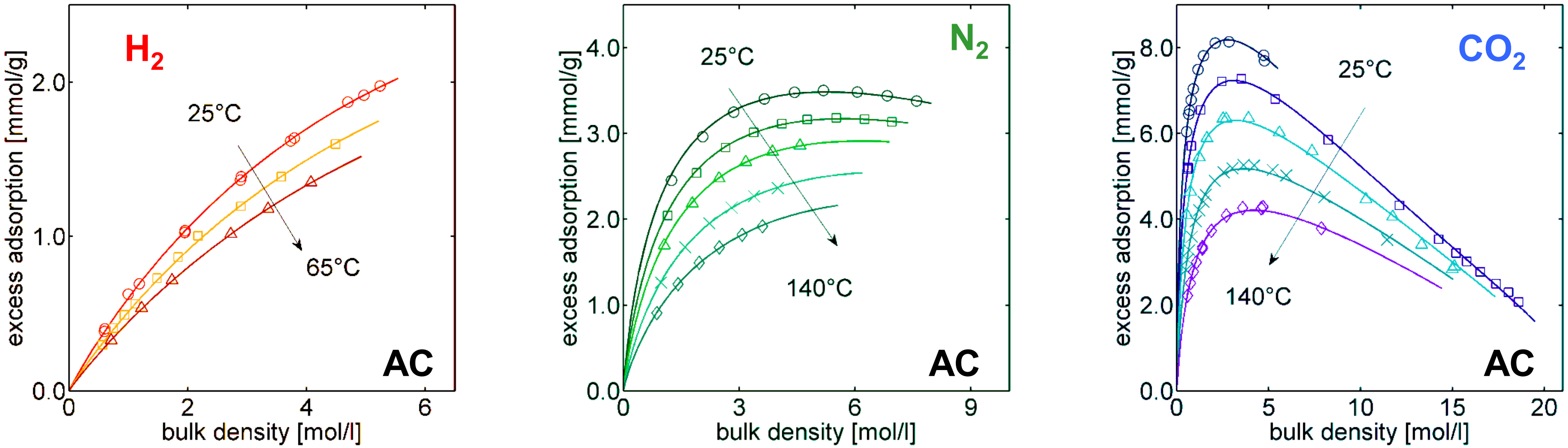
Mathematical description of adsorption equilibrium



Selection Isotherm eq.

Parameter Fitting

AC: pure component isotherms



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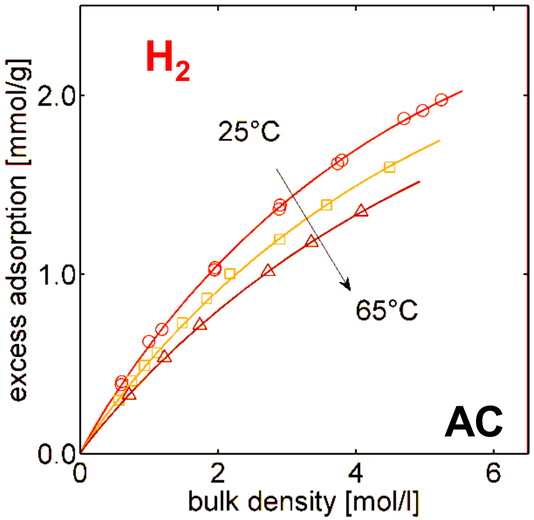
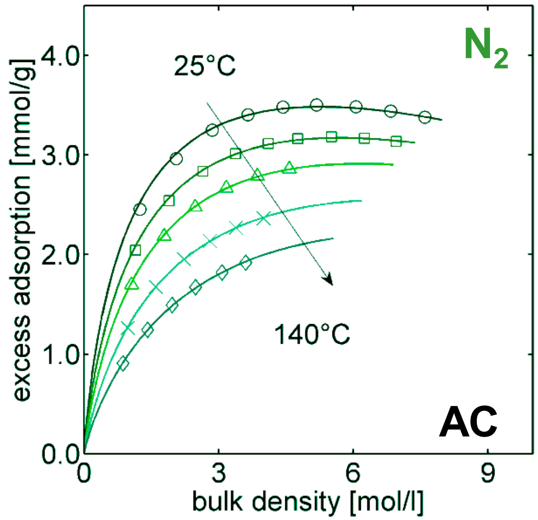
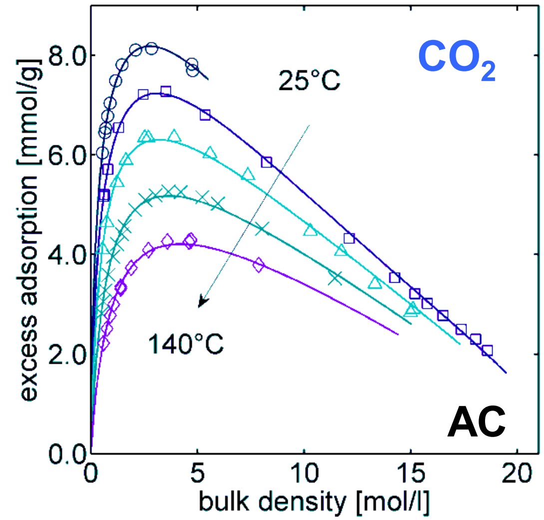
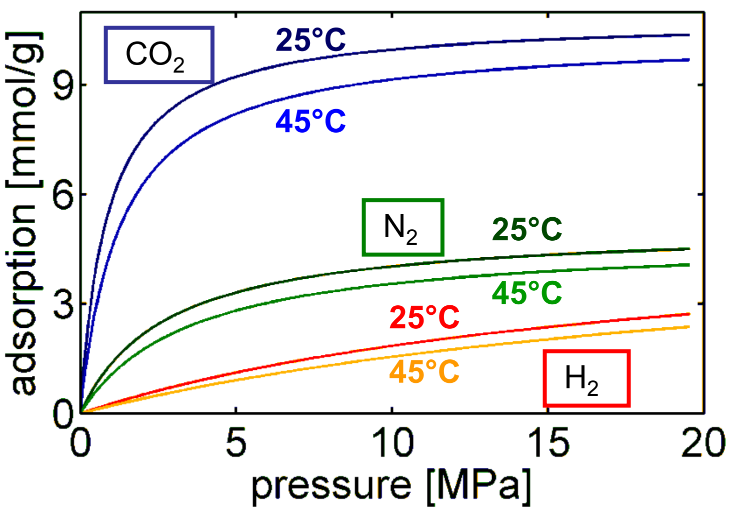






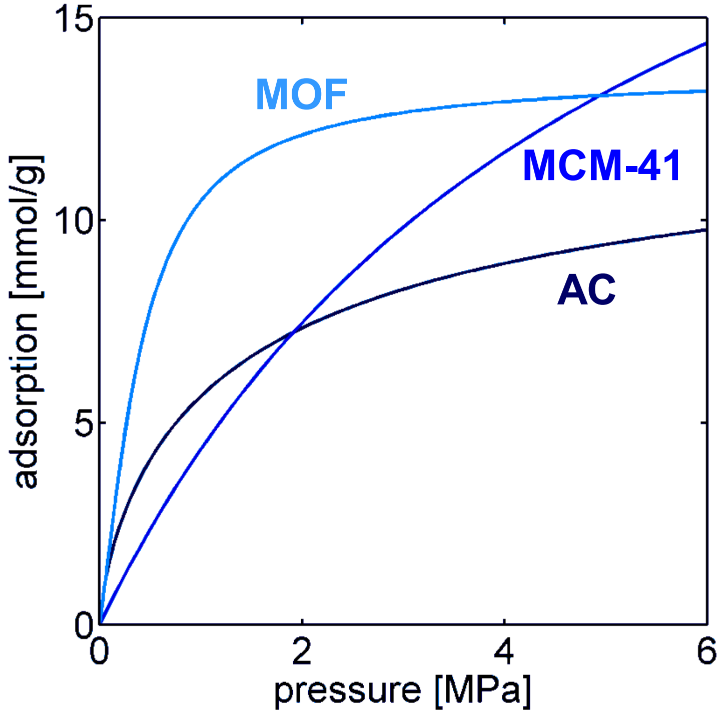


Isotherm parameters used for:

- 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

CO_2 isotherms at 25°C



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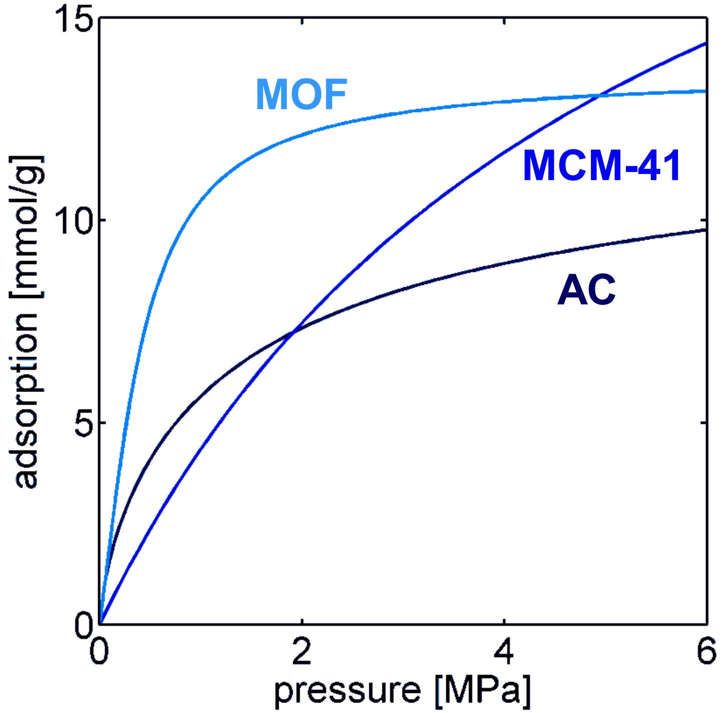
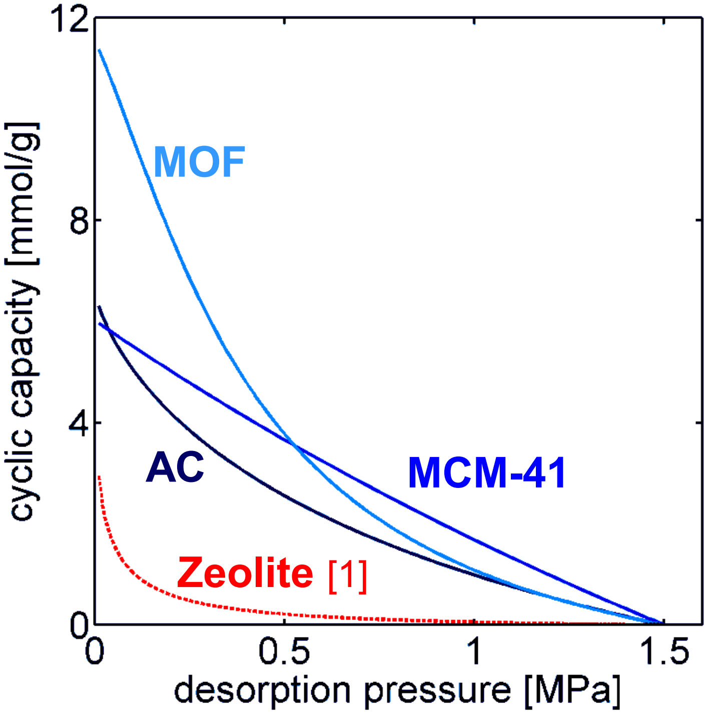


Cyclic capacity
p_{Ads} = 1.5 MPa, p_{Des} varying



[1] Xiao et al., *Adsorption* 14 (2008)

Approach

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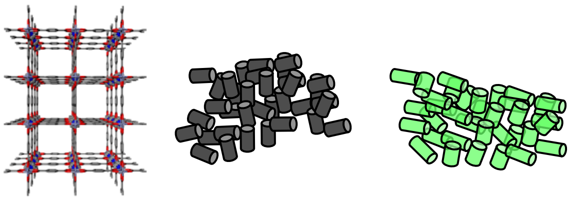

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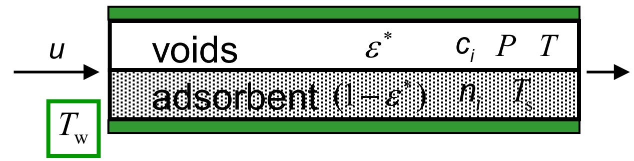

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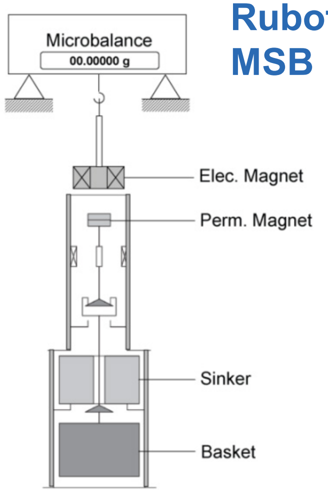

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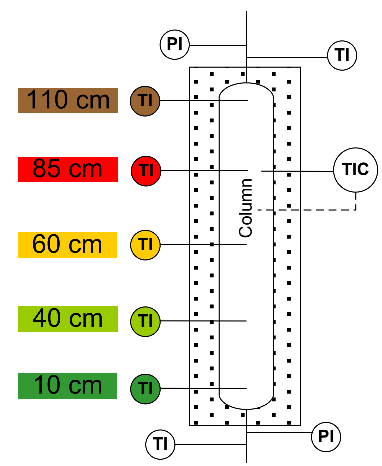
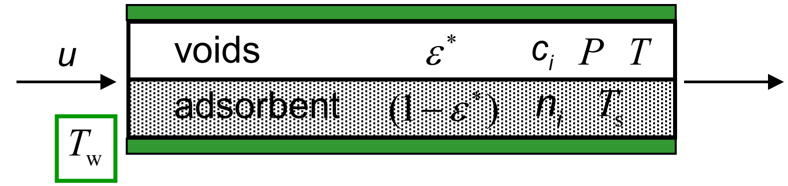


Model equations of an adsorption column



1. Mass balances species *i*

$$\underbrace{\frac{\partial c_i}{\partial t} + \nu \frac{\partial n_i}{\partial t}}_{\text{Accumulation}} + \underbrace{\frac{1}{\varepsilon^*}\frac{\partial (u c_i)}{\partial z}}_{\text{Convection}} - \underbrace{\frac{\varepsilon}{\varepsilon^*} D_{\mathrm{Li}} \frac{\partial}{\partial z}\left(\frac{\partial c_i}{\partial z}\right)}_{\text{Dispersion}} = 0$$

Accumulation Convection Dispersion

$$\frac{\partial n_i}{\partial t} = k_i a_{\mathrm{p}} \left(n_i^* - n_i\right)$$

Linear driving force

2. Energy balances

$$\underbrace{\frac{\partial T_{\mathrm{s}}}{\partial t}}_{\text{Acc}} = \underbrace{\frac{1}{C_{\mathrm{s}}} \sum_{j=1}^{n} \left(-\Delta H_j\right) \frac{\partial n_j}{\partial t}}_{\text{Heat of adsorption}} + \underbrace{\frac{h_{\mathrm{s}} a_{\mathrm{p}}}{C_{\mathrm{s}}} \left(T - T_{\mathrm{s}}\right)}_{\text{Exchange gas - solid}}$$

Acc Heat of adsorption Exchange gas - solid

$$\frac{\partial T}{\partial t} + \nu\gamma \frac{\partial T_{\mathrm{s}}}{\partial t} + \frac{1}{\varepsilon^*}\frac{\partial (uT)}{\partial z} - \frac{\nu}{C_{\mathrm{g}}} \sum_{j=1}^{n} \left(-\Delta H_j\right) \frac{\partial n_j}{\partial t} + \frac{2h_{\mathrm{L}}}{r_i \varepsilon^* C_{\mathrm{g}}} \left(T - T_{\mathrm{w}}\right) - \frac{\varepsilon}{\varepsilon^*} \frac{K_{\mathrm{L}}}{C_{\mathrm{g}}} \frac{\partial}{\partial z}\left(\frac{\partial T}{\partial z}\right) = 0$$

Accumulation Convection Heat of adsorption Exchange wall Dispersion

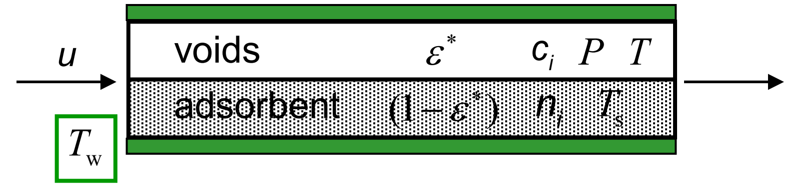
3. Constitutive equations

1. Non linear adsorption isotherm:

   $$n_i^* = n_i^*(p, T, y_{\mathrm{i}})$$

2. Equation of State: *Ideal gas law*
3. Pressure: *Ergun equation*

Model equations of an adsorption column



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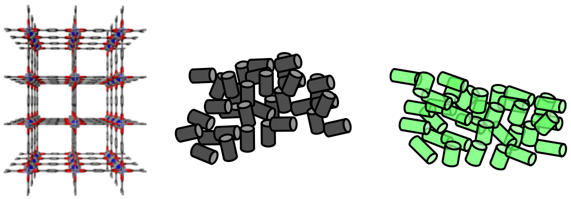

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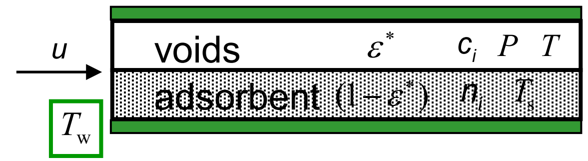

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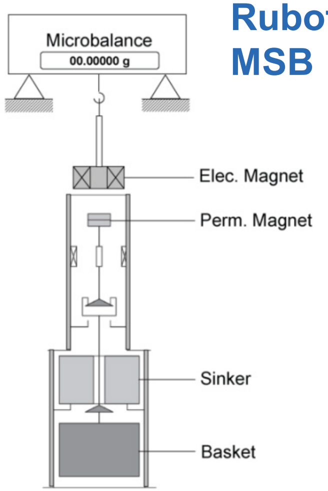

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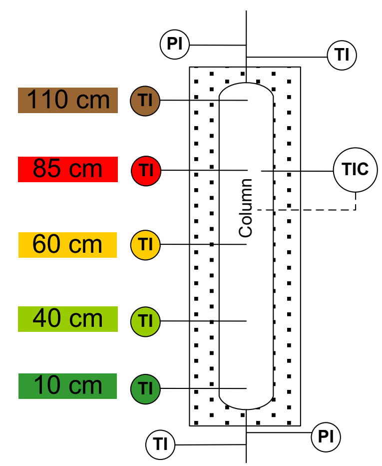
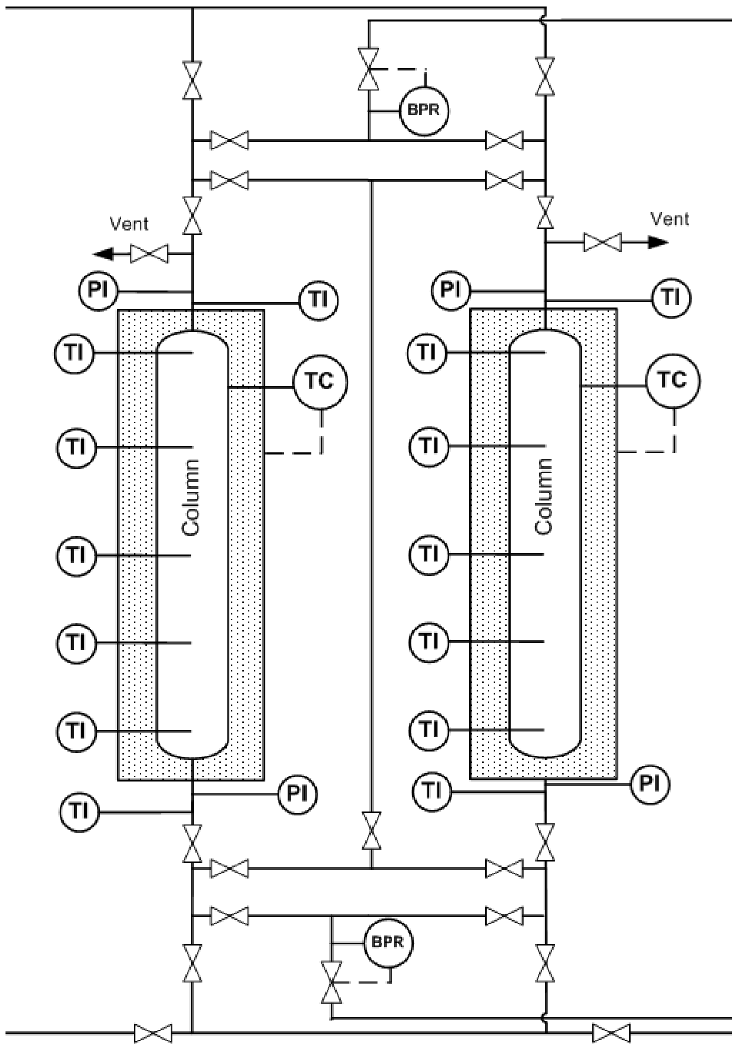


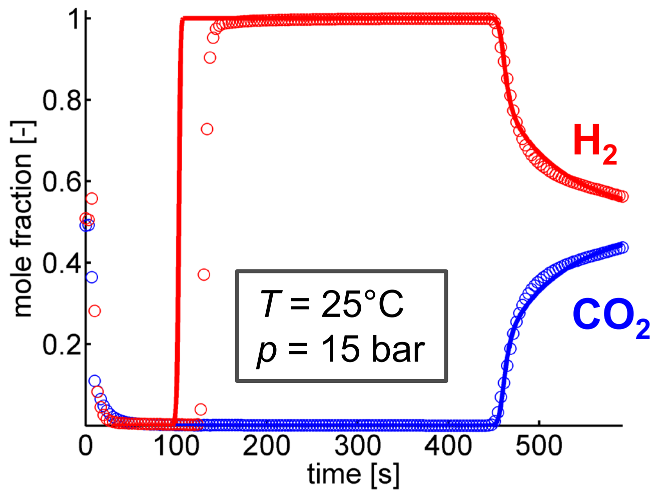
Experimental setup: 2-column Lab PSA

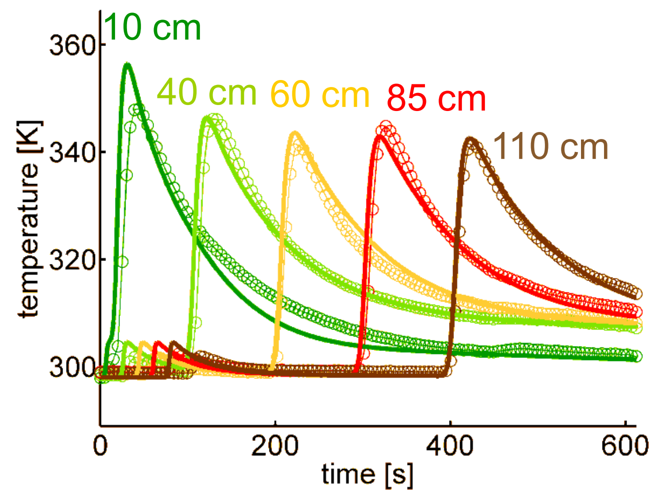


- → Breakthrough experiments
- → PSA cycles including *p* equalization
- → Fully automated
- → Premixed gases
- → Column insulation and heating
- → *p* and *T* measurements
- → Product streams online analyzed by MS

Breakthrough and PSA experiments

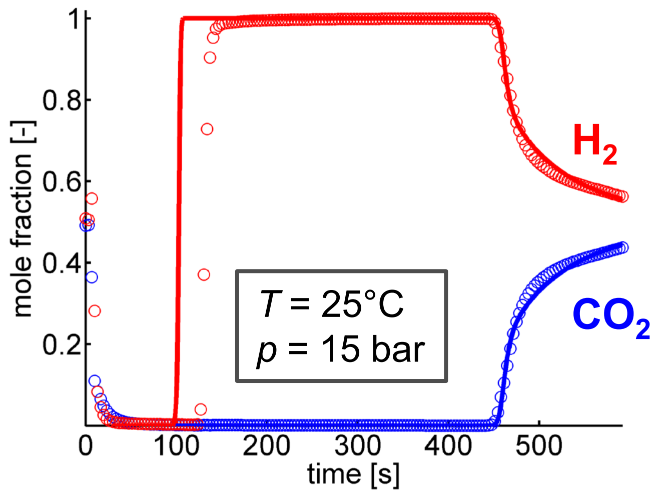
Breakthrough experiments
→ Fit the missing model parameters

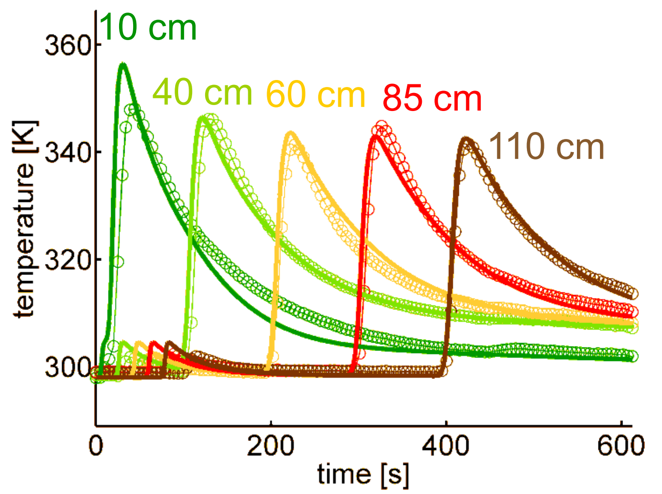




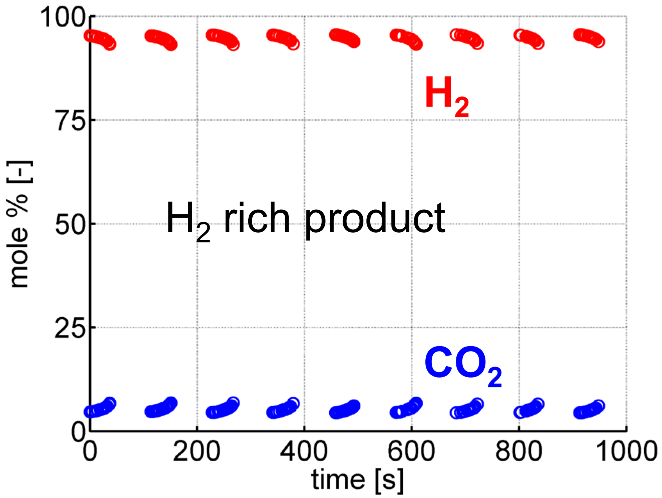
Breakthrough and PSA experiments

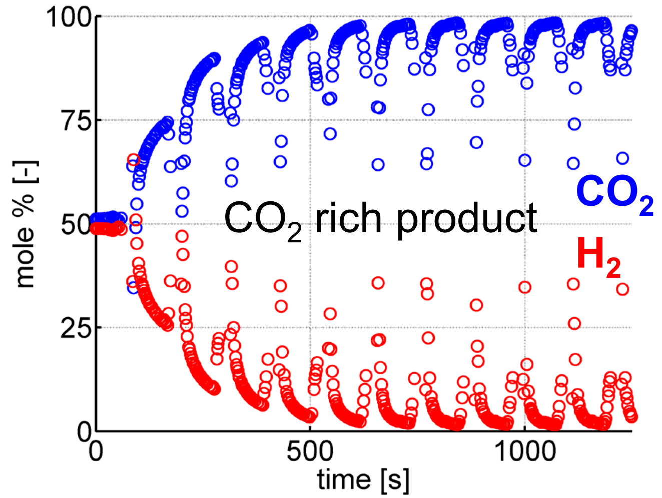
Breakthrough experiments
→ Fit the missing model parameters





PSA experiments
→ Validate the PSA simulation tool
→ Exp. testing of full PSA cycles

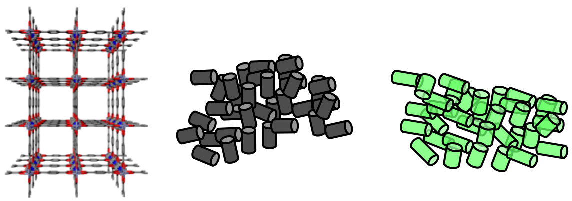




Approach

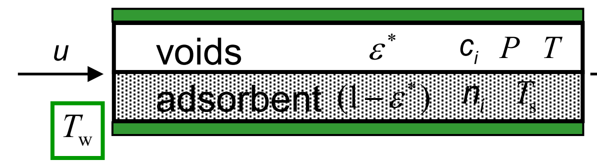
Materials

Commercial and new materials



Process modeling

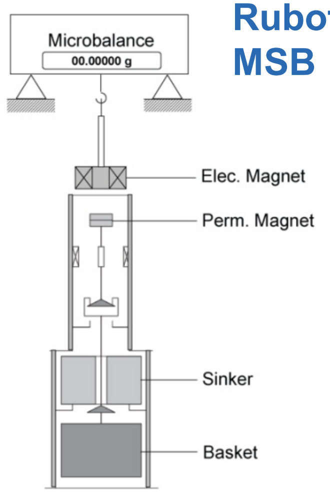
Mass, energy and momentum balances, Isotherms & EOS



Model-based Process Design

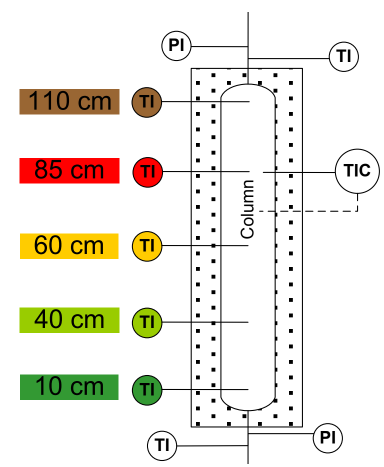
Static experiments

Rubotherm MSB

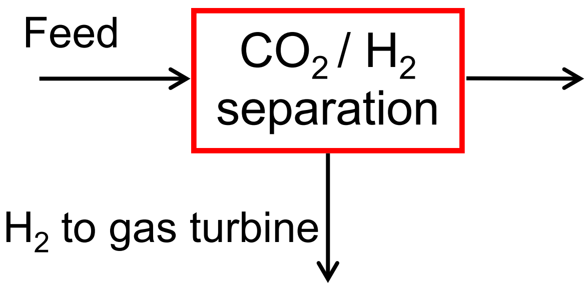


Dynamic experiments

Two column PSA setup



Process Design criteria

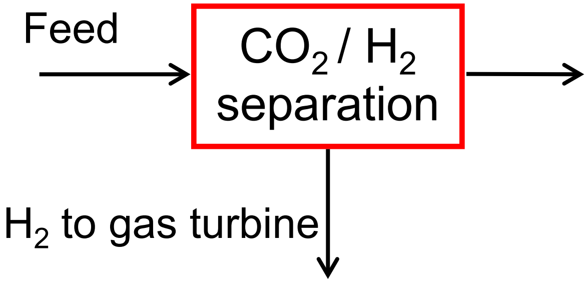


CO_2 to storage:

CO_2 purity	> 95%
Capture	> 90%
Pressure	110 bar

- Specifications & boundary conditions: CO_2 purity and capture rate
  - purge with the feed
  - co-current blowdown
- Minimize energy penalty (compression costs):
  - no repressurization
  - increase CO_2 desorption pressure
- Investments cost:
  - max. 3 *p*-equalization steps

Process Design criteria



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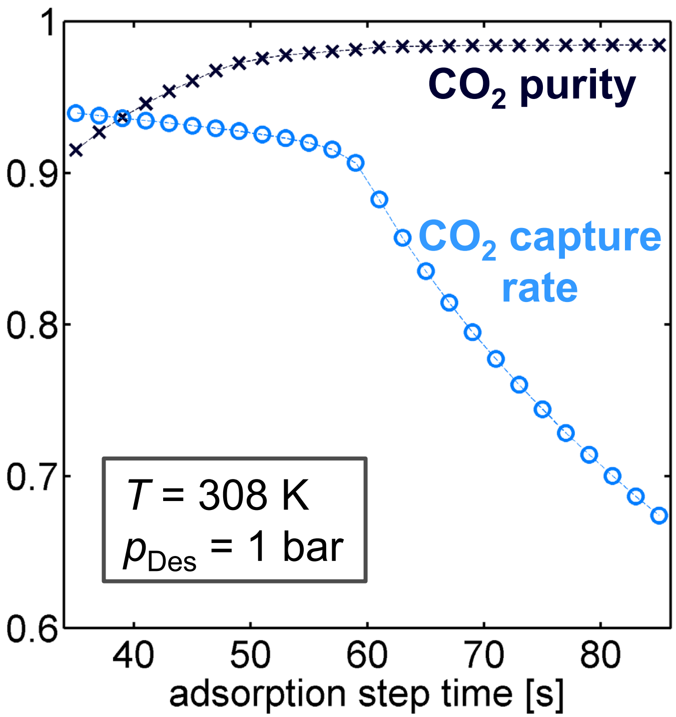
  - increase CO_2 desorption pressure
- Investments cost:
  - max. 3 *p*-equalization steps

→ For fixed material, T and p_{Des}: process performance dependent on t_{ads}, t_{blow} & t_{purge}

Influence of the adsorption step time (AC)

→ Change of time of the adsorption step

→ Time of blowdown and purge step already optimized



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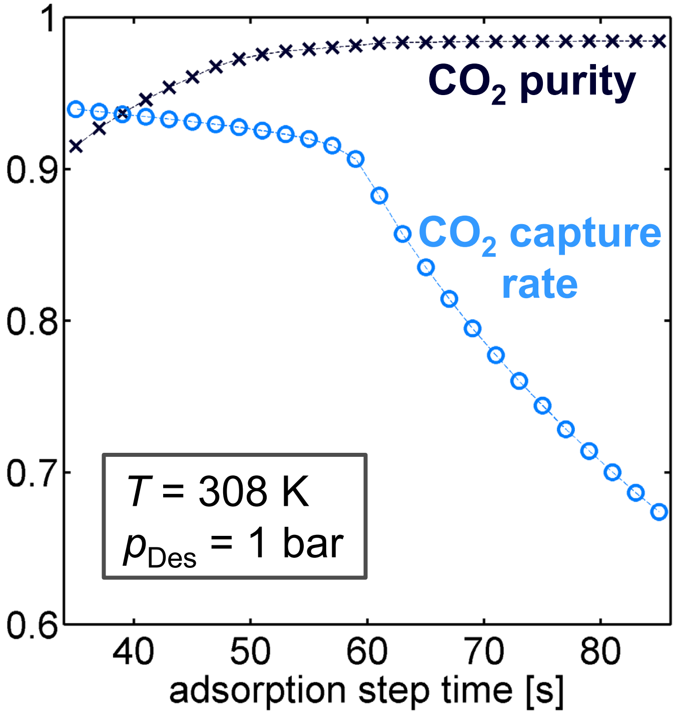
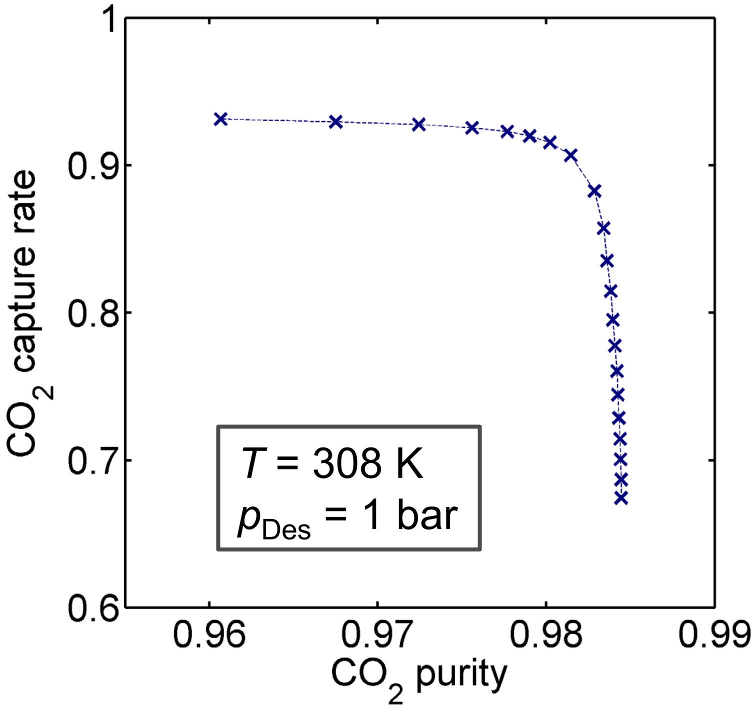


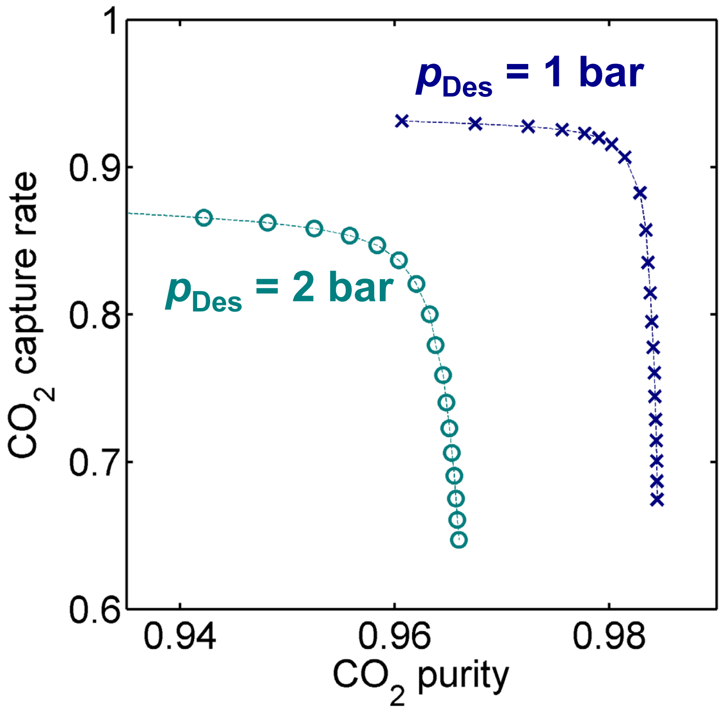
→ Trade-off

→ Better shown as pareto front



AC comparison: process conditions

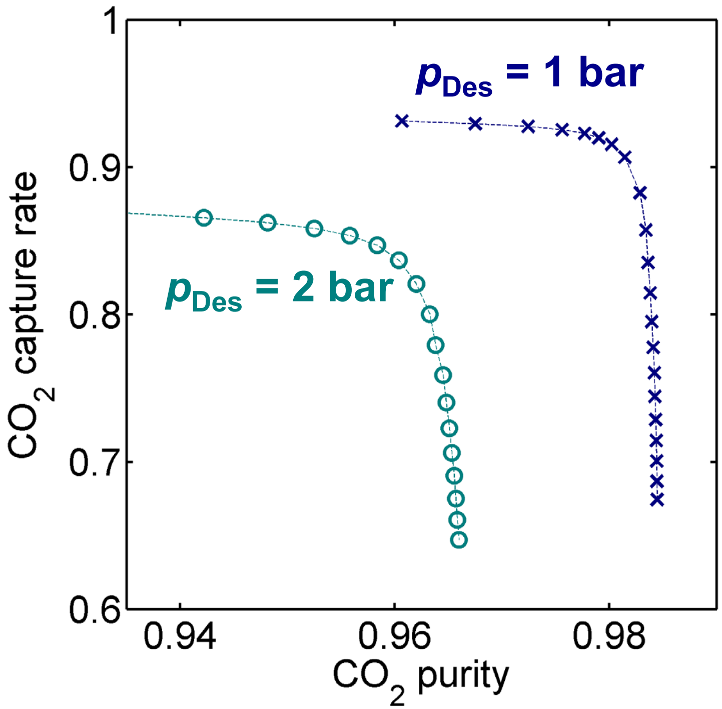
- Different desorption pressures
- T = 308 K

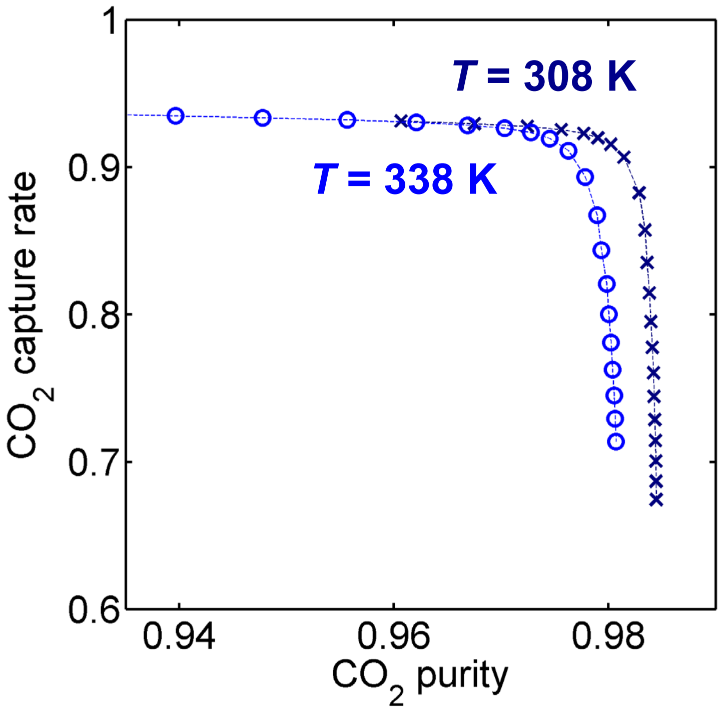


AC comparison: process conditions

- → Different desorption pressures
- → T = 308 K

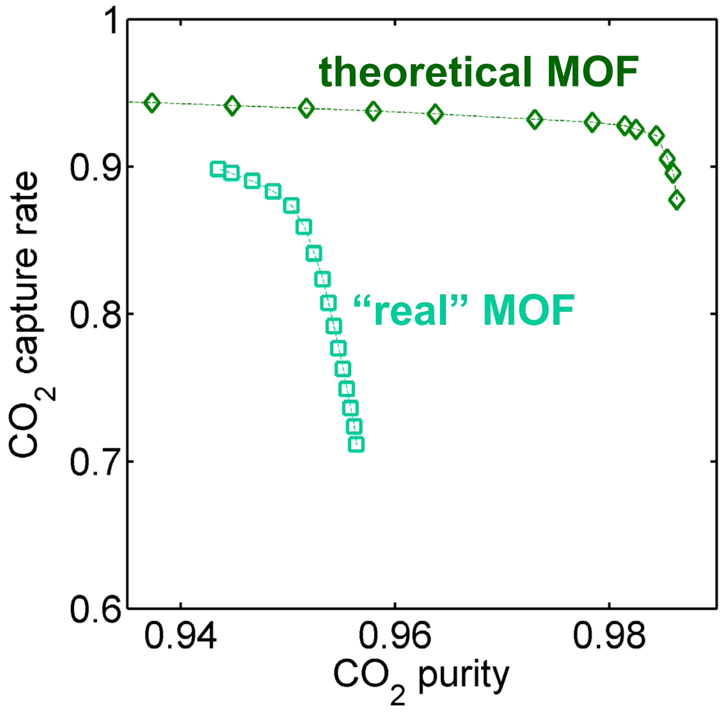
- → Different process temperatures
- → p_{Des} = 1 bar





Comparison: AC ←→ MOF

- → MOF with "real" physical properties compared to theoretical MOF
- → T = 308 K, p_{Des} = 1 bar



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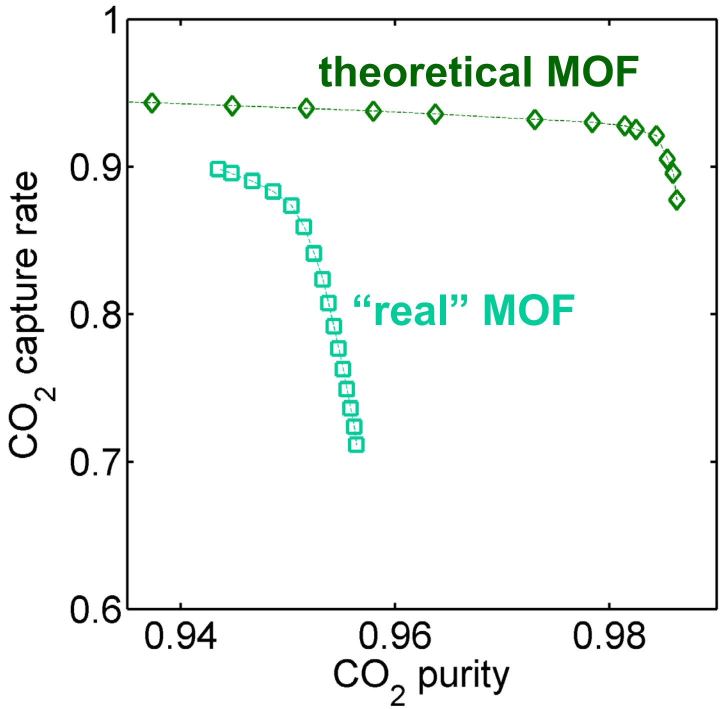
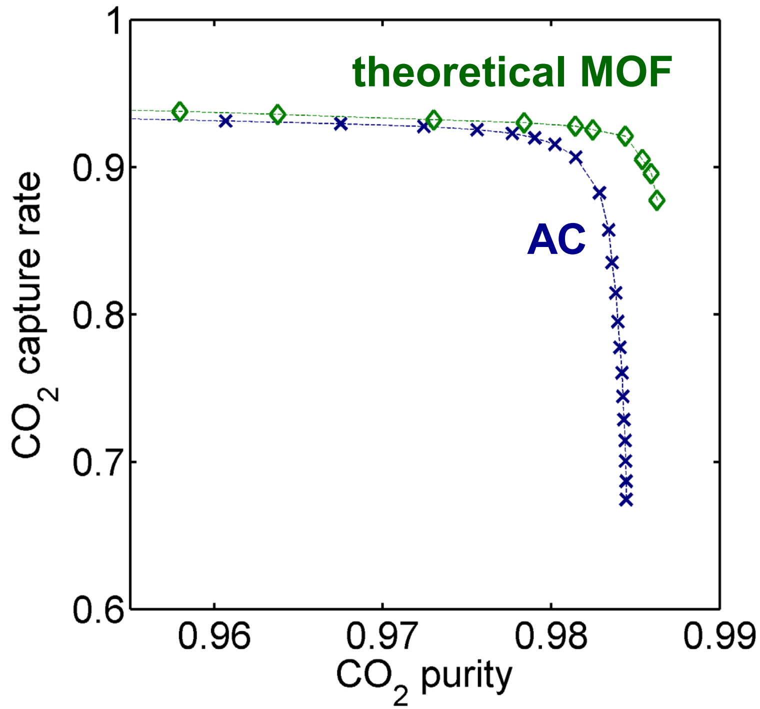


- → Theoretical MOF compared to AC
- → T = 308 K, p_{Des} = 1 bar



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