Dynamic Sorption

Adsorption of Polar and Nonpolar Vapors on Selected Adsorbents: Breakthrough Curves and their Simulation

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www.dynamicsorption.com

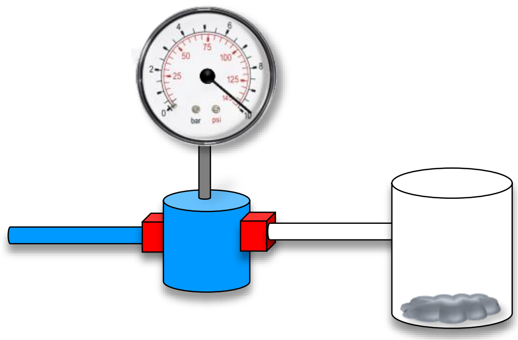
Outline

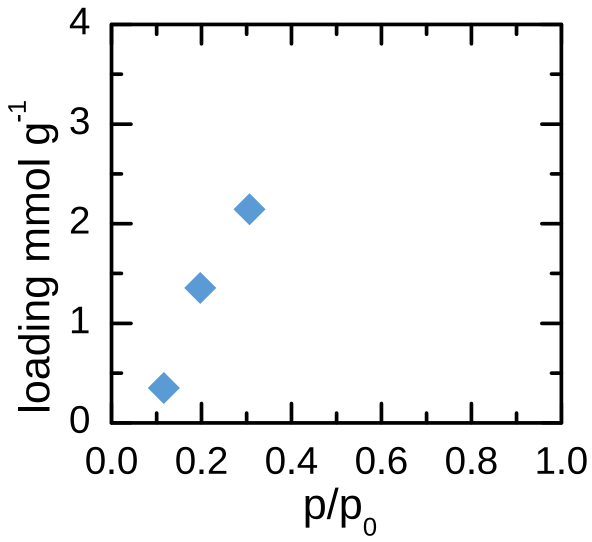
1. **Breakthrough Curve Introduction**
2. **The mixSorb L with Vapor Option**
3. **Breakthrough Curves of Vapors**
   I. Water Breakthrough Curves on Zeolite, Silica Gel
   Regenerability and Heat Output
   II. Toluene Breakthrough Curve
   on Activates Carbon
   III. Ethanol/water Mixture Adsorption
   on Activates Carbon
4. **Modelling**
   I. Simulating Water Breakthrough Curves
   II. Simulating Ethanol Breakthrough Curves

1. Breakthrough Curve Introduction

Static Volumetric Measurements

- Sorption takes place in enclosed chamber
- Pressure is recorded over time
- Pure Gases only





$$n_{\text{ads},i} = n_{\text{dosed},i} - n_{\text{free},i}$$

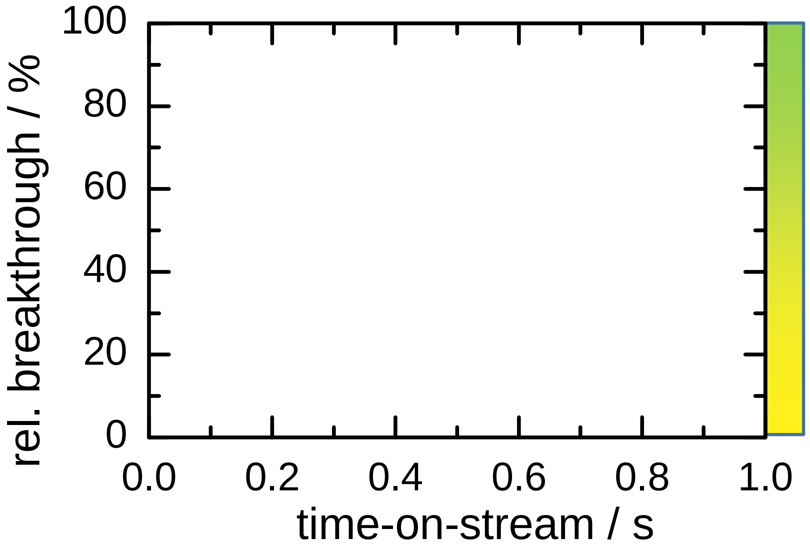
$$n_{\text{dosed},i} = \frac{p_{\text{Dose},i}\, V_{\text{Dose}}}{RT}$$

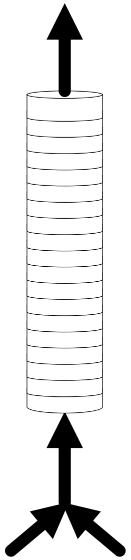
$$n_{\text{free},i} = \frac{p_{\text{Cell},i}\,(V_{\text{Dose}} + V_{\text{Cell}})}{RT}$$

$$n_{\text{ads}} = \sum_{0}^{i} n_{\text{ads},i}$$

Breakthrough Experiment

- Sorption takes place in open system
- Pressure is constant
- Gas Mixtures only
- Outlet composition is recorded over time





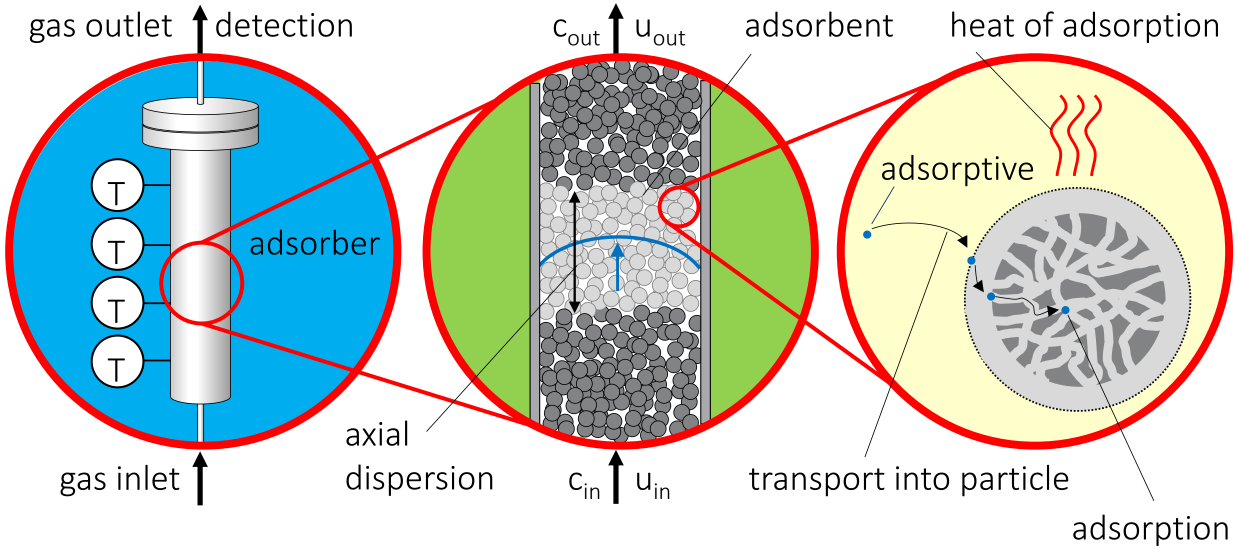
$$n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t)\text{d}t - \int \dot{n}_{\text{out}}(t)\text{d}t$$

$$n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t)\frac{y_{\text{in}}(t)}{V_{\text{m}}}\text{d}t - \int \dot{V}_{\text{out}}(t)\frac{y_{\text{out}}(t)}{V_{\text{m}}}\text{d}t$$

1. Breakthrough Curve Introduction

Breakthrough Curves

- Not all Gas Flow Experiments are Breakthrough Experiments!
- Requirement: **Fixed Adsorber Bed**
  → gas must not pass the sample without **interaction**!



- What is the result of a breakthrough experiment?

  ✓ **Time** until 5 %, 50 % ,… of breakthrough is the **cycle or production time**

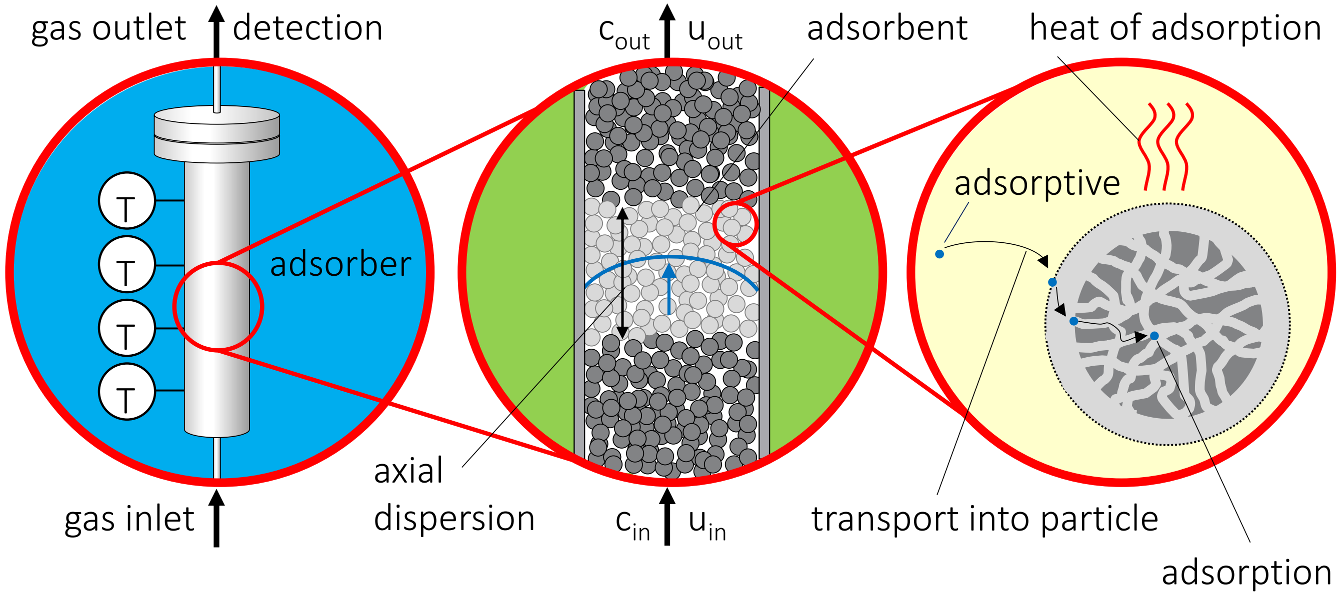
  ✓ **Integration** of the **full curve** gives **saturation capacity** of a gas on the adsorbent (**equilibrium**)

  ✓ **Integration** until cycle time gives **technically usable sorption capacity**

  ✓ **Shape of the curve** contains information about **kinetics/mass transfer**

1. Breakthrough Curve Introduction

Different Scales



Macroscopic

- Size of Adsorber
- Shape of Adsorber

Mesoscopic

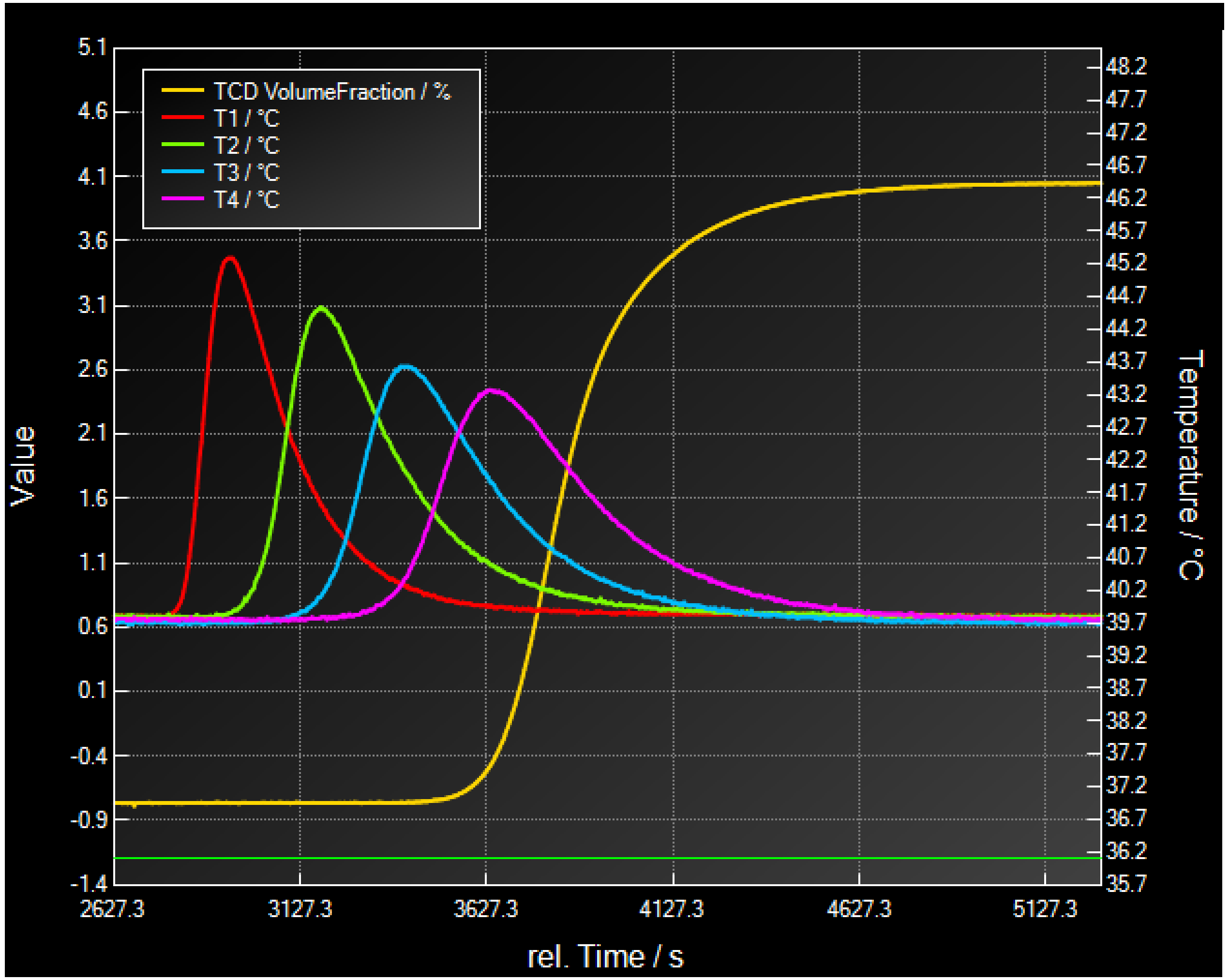
- Nature of the Fixed Bed
- Bed Porosity
- Shape of Particles

Microscopic

- Textural Properties
- Surface Characteristics
- Accessibility

1. Breakthrough Curve Introduction

Resulting Curves



- 40 °C, 2 L min^{-1}
- 5 bar (pressurization with N_2)
- Inlet compositions: **5 % CO_2 in N_2**

- Temperature Maxima Decrease in Flow Direction
  → Increasing Dispersion
- Area under Temperature Curves increases in Flow Direction
  → Transfer of heat through gas flow

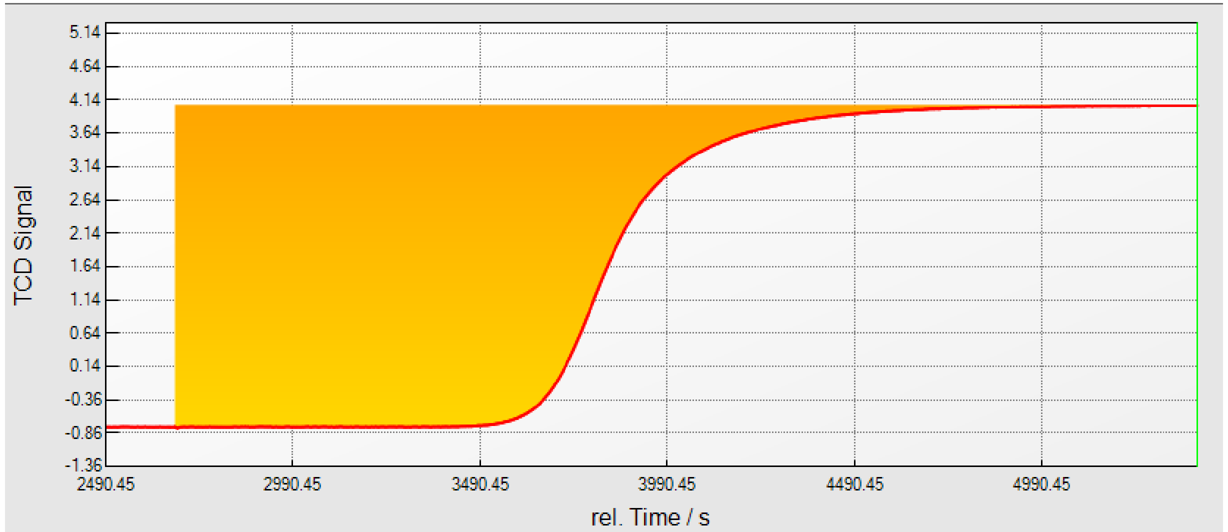
1. Breakthrough Curve Introduction

Calculating Loadings

$$n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t)\text{d}t - \int \dot{n}_{\text{out}}(t)\text{d}t$$

$$n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t)\frac{y_{\text{in}}(t)}{V_{\text{m}}}\text{d}t - \int \dot{V}_{\text{out}}(t)\frac{y_{\text{out}}(t)}{V_{\text{m}}}\text{d}t$$

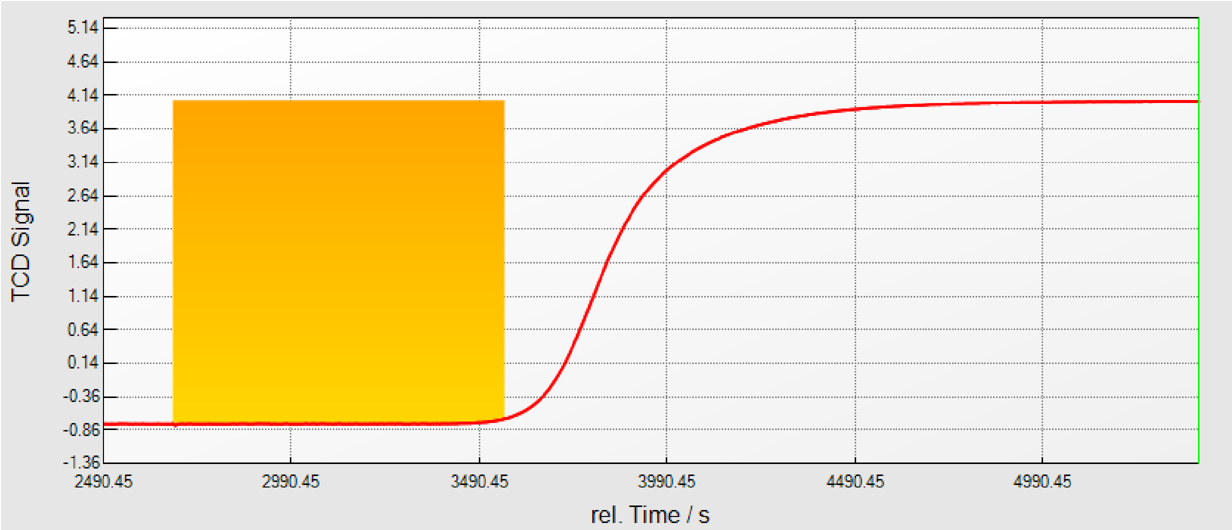
Integrating over the full Curve



Saturation Capacity

dq = 0.611 mmol g^{-1}

Integrating over the Curve to *e.g.* 1 % Breakthrough



Technically Usable Sorption Capacity

dq = 0.445 mmol g^{-1}

2. The mixSorb L Vapor Option

mixSorb L

- Fully automated Breakthrough Analyzer
- **Integrated Gas Mixing – Including Vapors**
- Up to 40 L/min Gas Flow, up to **10 bar**
- Up to **4 mass flow controllers (MFCs)**
- Up to 2 **Evaporators**, each capable to supply vapor mixtures

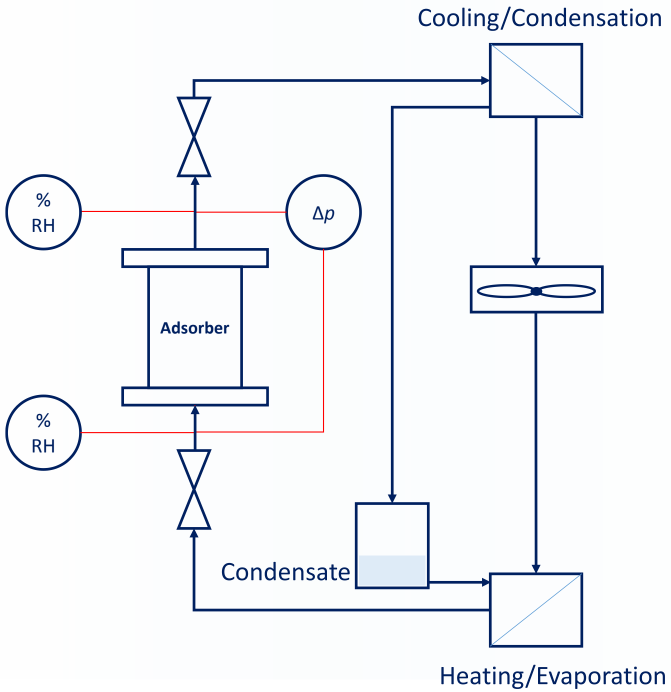
- Monitoring of gas composition by **TCD** at the Outlet or Bypass
- You can attach any additional Analytical Device (e.g. **Mass Spec**) at the **sample port**
- **3P-SIM** Simulation Software

Dynamic orption

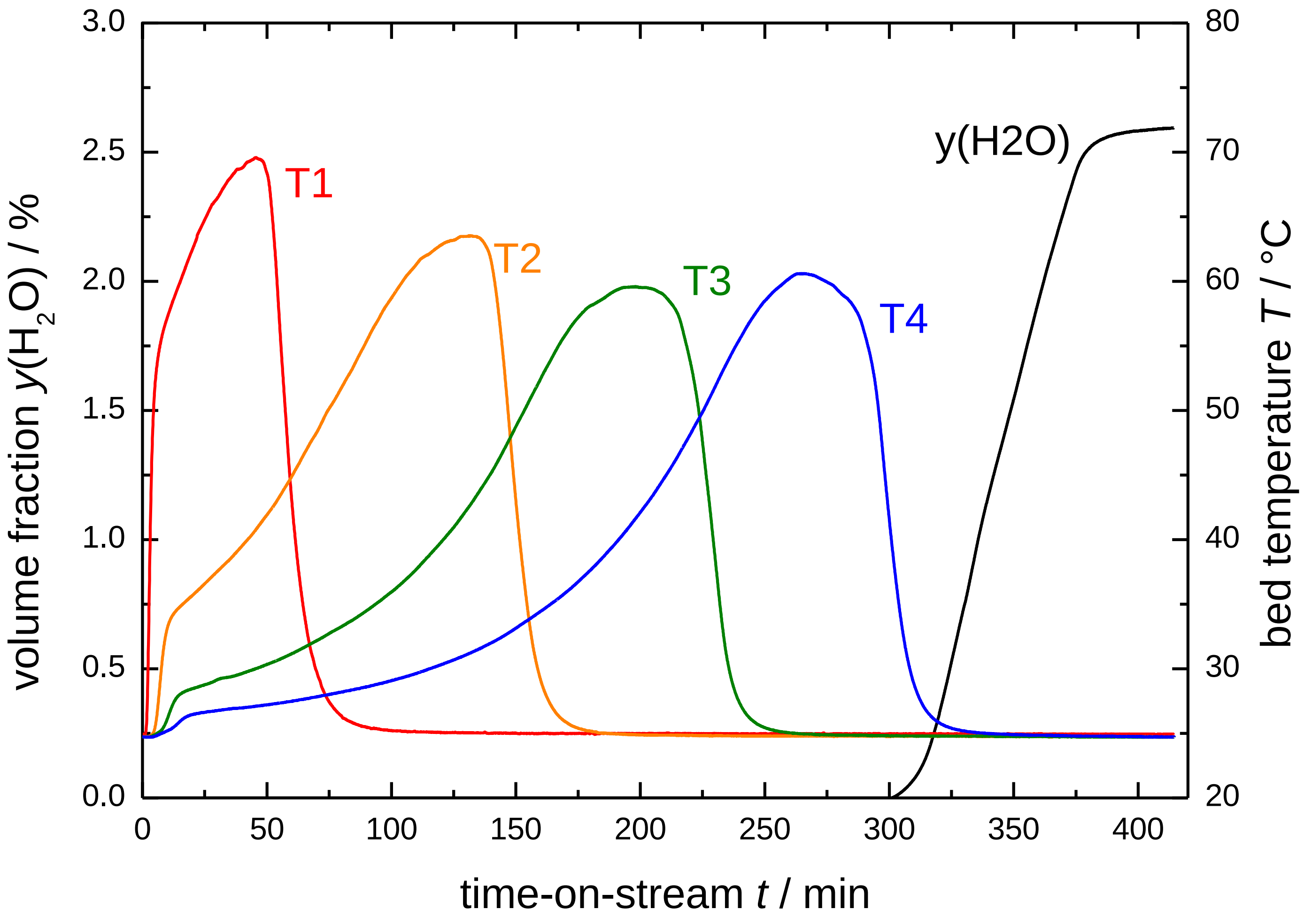
I. Breakthrough Curves of H_2O

- **Drying of process gases**
  - → Important to remove Water and CO2 in Air before Cryogenic Air Separation
    - → Water would plug the piping by freezing.
  - → Air separation with Pressure Swing Adsorption (PSA) on Zeolites
    - → Water has strong affinity to surface

- **Energy Storage**
  - → Adsorption of water vapor → releasing heat of adsorption. Control heat output with **dosing of water**
  - → Regeneration with e.g. thermal **solar energy**
  - → Can be used for cooling as well



Breakthrough Curve of H_2O / N_2 on Zeolite 13X



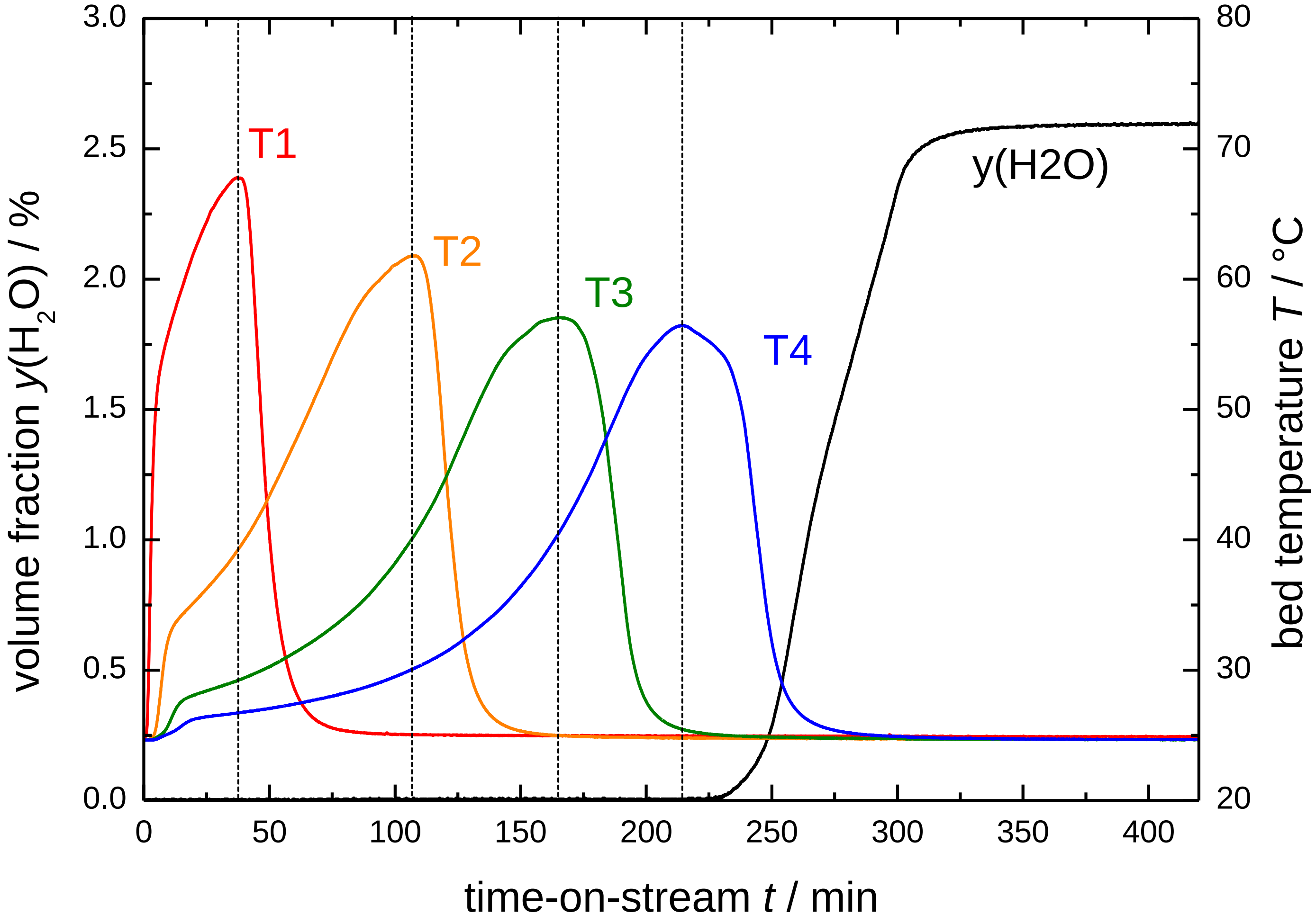
- Experimental conditions of a simple breakthrough experiment after Activation at **400 °C for 4 h**
- 25 °C, Flow rate 4 L min^{-1}
- Pressure: 1 bar
- Standard Adsorber with 80 g of sample
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

→ High temperatures during adsorption

→ Loading: **18.9 mmol g^{-1}**

→ **Regeneration at 130 °C for 3.5 h**

Breakthrough Curve of H_2O / N_2 on Zeolite 13X



- Sample regenerated at **130 °C for 3.5 h**
- Same experimental conditions
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

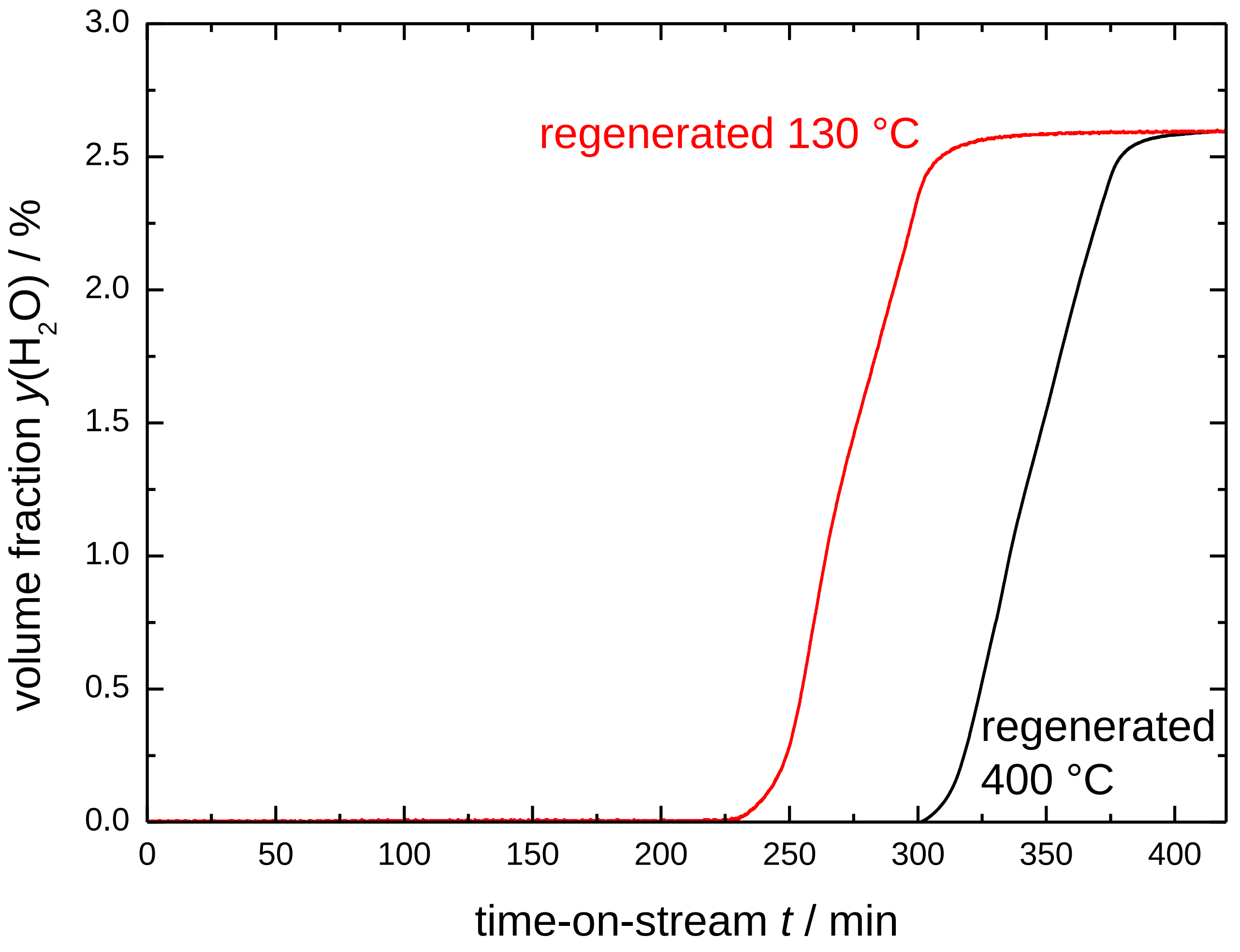
→ Loading: **15.4 mmol g^{-1} → lower**

→ Unsymmetrical temperature profiles

→ Residual loading before experiment not equally distributed

→ Overlay

Breakthrough Curve of H_2O / N_2 on Zeolite 13X



- Loadings:
  18.9 mmol g^{-1} (activated at 400 °C) vs.
  15.4 mmol g^{-1} (regenerated at 130 °C)
- Breakthrough Curve shifted to the left
- Breakthrough curves still have similar shapes

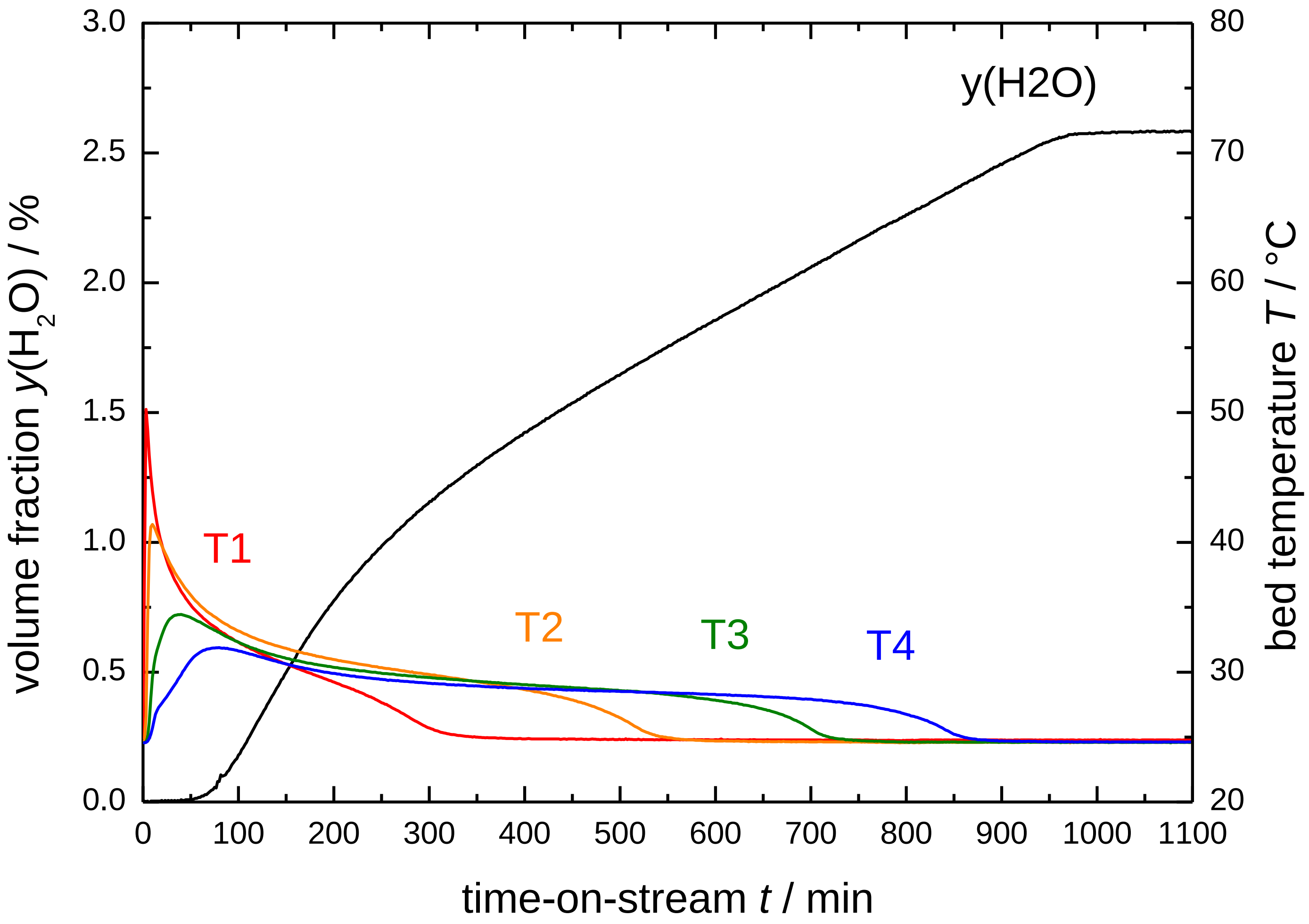
→ Zeolite requires harsh regeneration

→ High temperatures

→ Steep Breakthrough Curves indicate steep isotherms

→ High affinity to water

Breakthrough Curve of H_2O / N_2 on Silica Gel



- Experimental conditions of a simple breakthrough experiment after Activation at **350 °C for 4 h**
- 25 °C, Flow rate 4 L min^{-1}
- Pressure: 1 bar
- Standard Adsorber with 80 g of sample
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

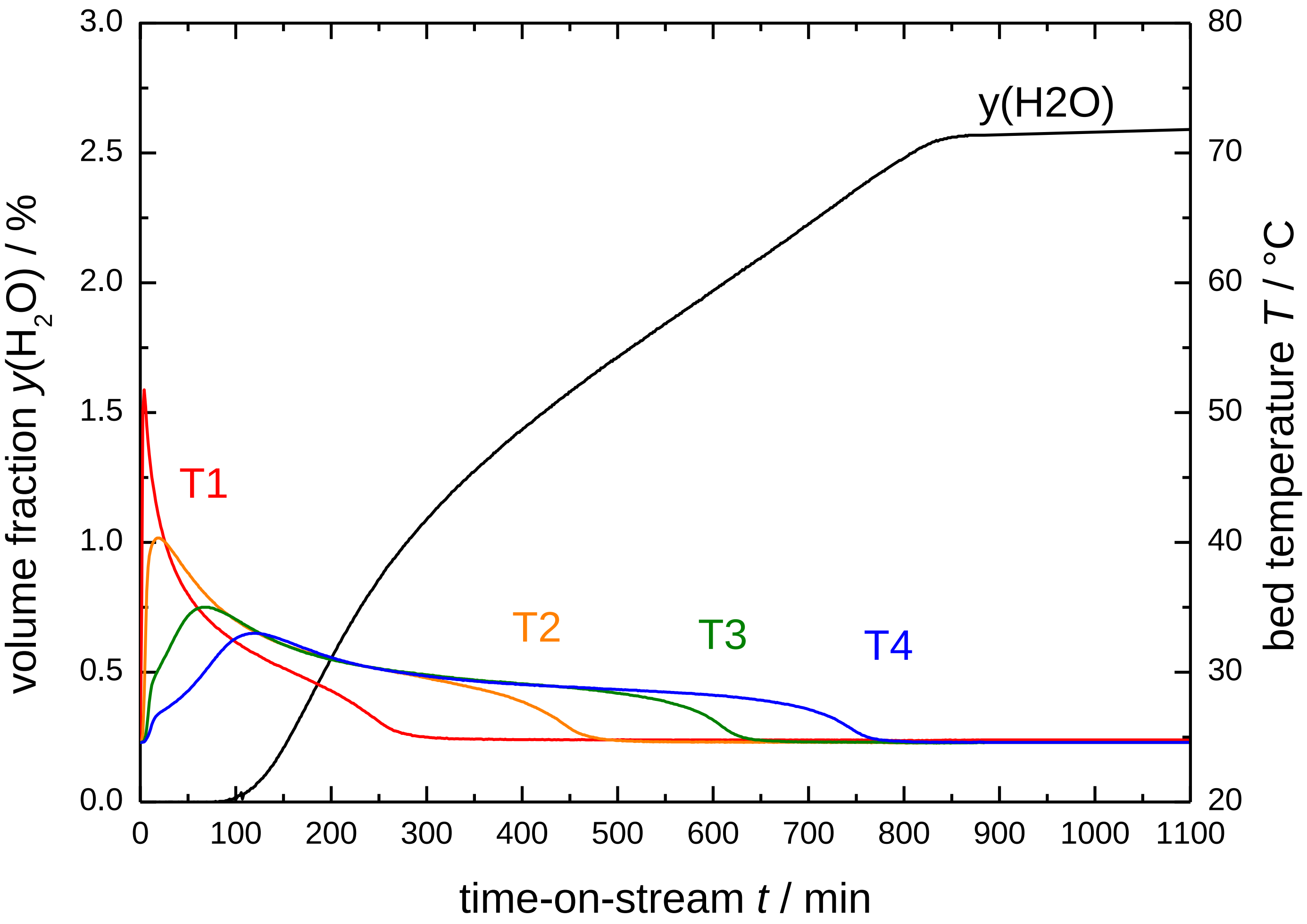
→ Smaller temperatures peaks

→ Much longer measurement

→ Loading: **25.9 mmol g^{-1}**

→ **Regeneration at 130 °C for 3.5 h**

Breakthrough Curve of H_2O / N_2 on Silica Gel



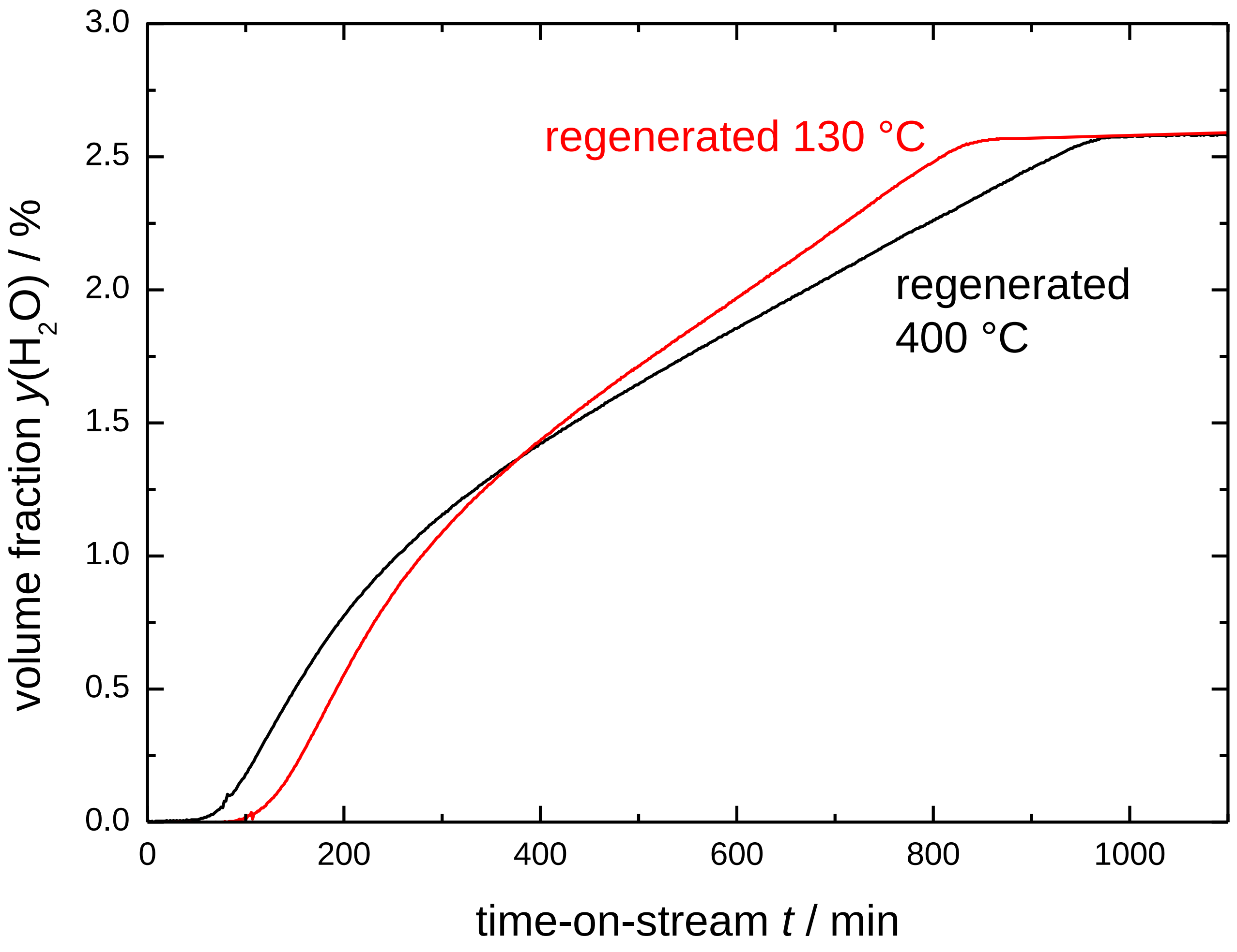
- Sample regenerated at **130 °C for 3.5 h**
- Same experimental conditions
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

→ Loading: **25.1 mmol g^{-1}**
→ **almost identical**

→ Overlay

3. Breakthrough Curve Experiments

Breakthrough Curve of H_2O / N_2 on Silica Gel



- Loadings:
  25.9 mmol g^{-1} (activated at 350 °C) vs.
  25.1 mmol g^{-1} (regenerated at 130 °C)
- Breakthrough Curve changed slope
- Changing surface chemistry until stable in cycles

→ **Regeneration** much **easier**, efficient

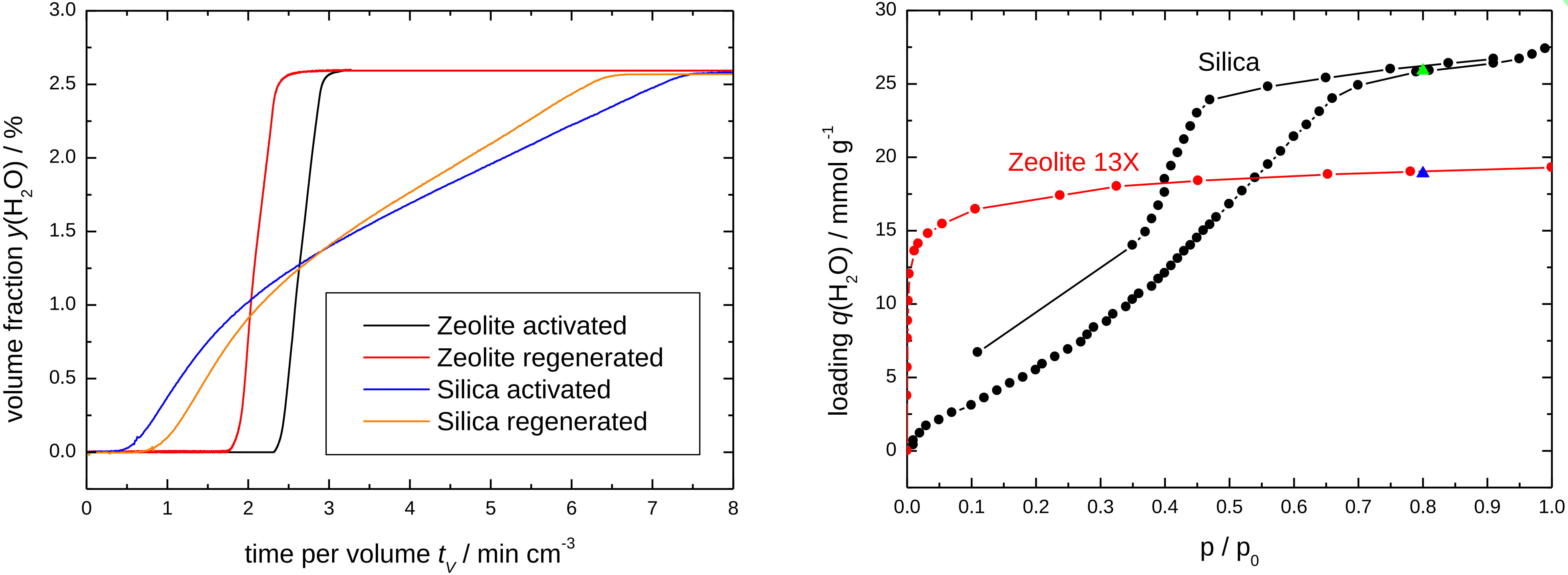
→ No high temperature required

→ Regeneration possible by **Pressure Reduction**

→ **But**: Breakthrough occurs earlier!

3. Breakthrough Curve Experiments

Breakthrough Curve of H_2O / N_2 on Zeolite 13X and Silica Gel



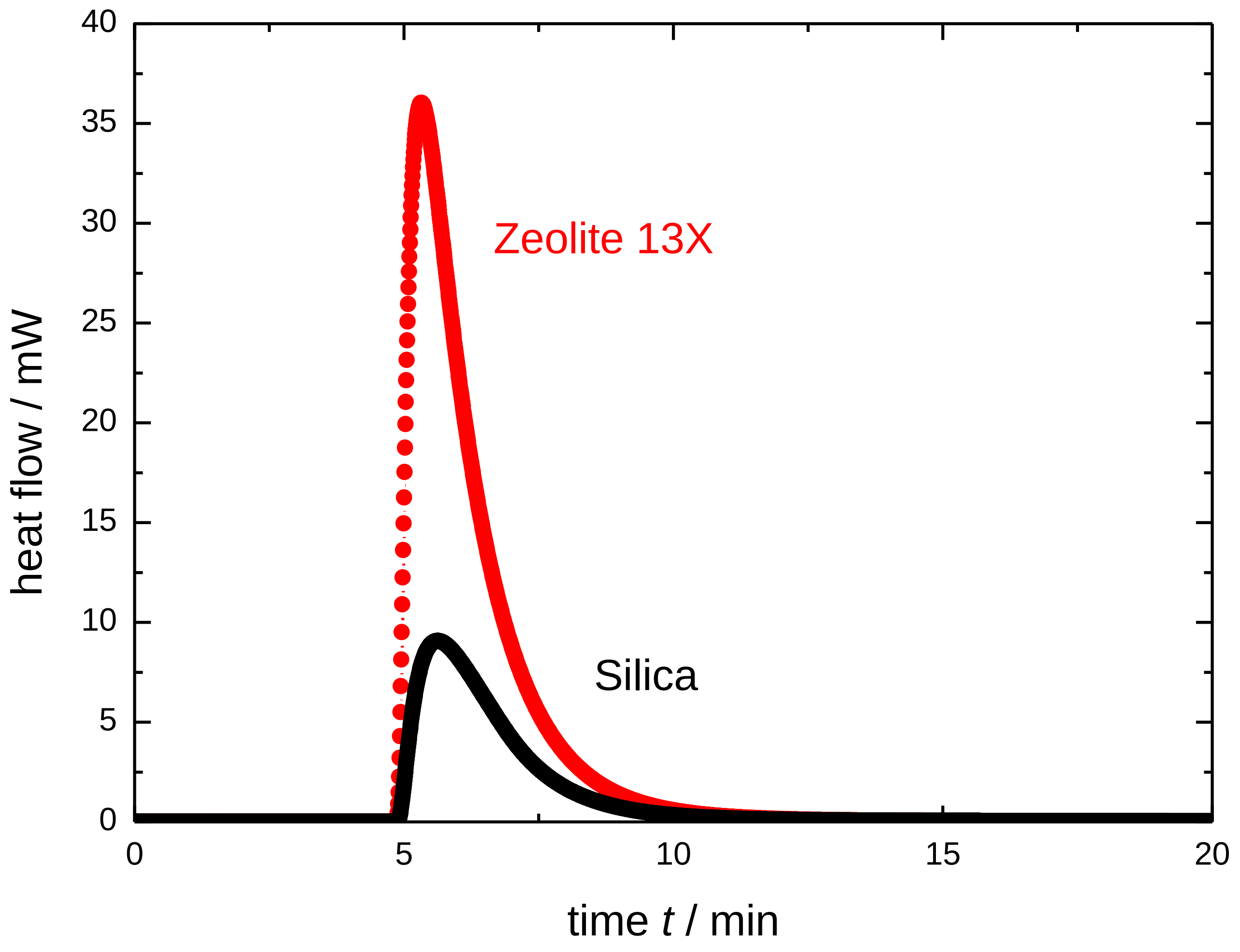
- Materials behave differently in Adsorption/Desorption Cycles
- Good Agreement with Isotherm data (right hand side)

→ **Can we use these curves to get information about stored energy and heating power?**

3. Breakthrough Curve Experiments

Immersion Calorimetry

- Determining the Heat of Adsorption in Liquid Phase



»Enthalpy of Adsorption = Wetting + Condensation«

$$h_A = h_W + h_C$$

Enthalpy of wetting

Zeolite: 550 J g^{-1} (g of Adsorbent)

Silica Gel: 140 J g^{-1}(g of Adsorbent)

Zeolite: 1600 J g^{-1} (g of water)

Silica Gel: 300 J g^{-1} (g of water)

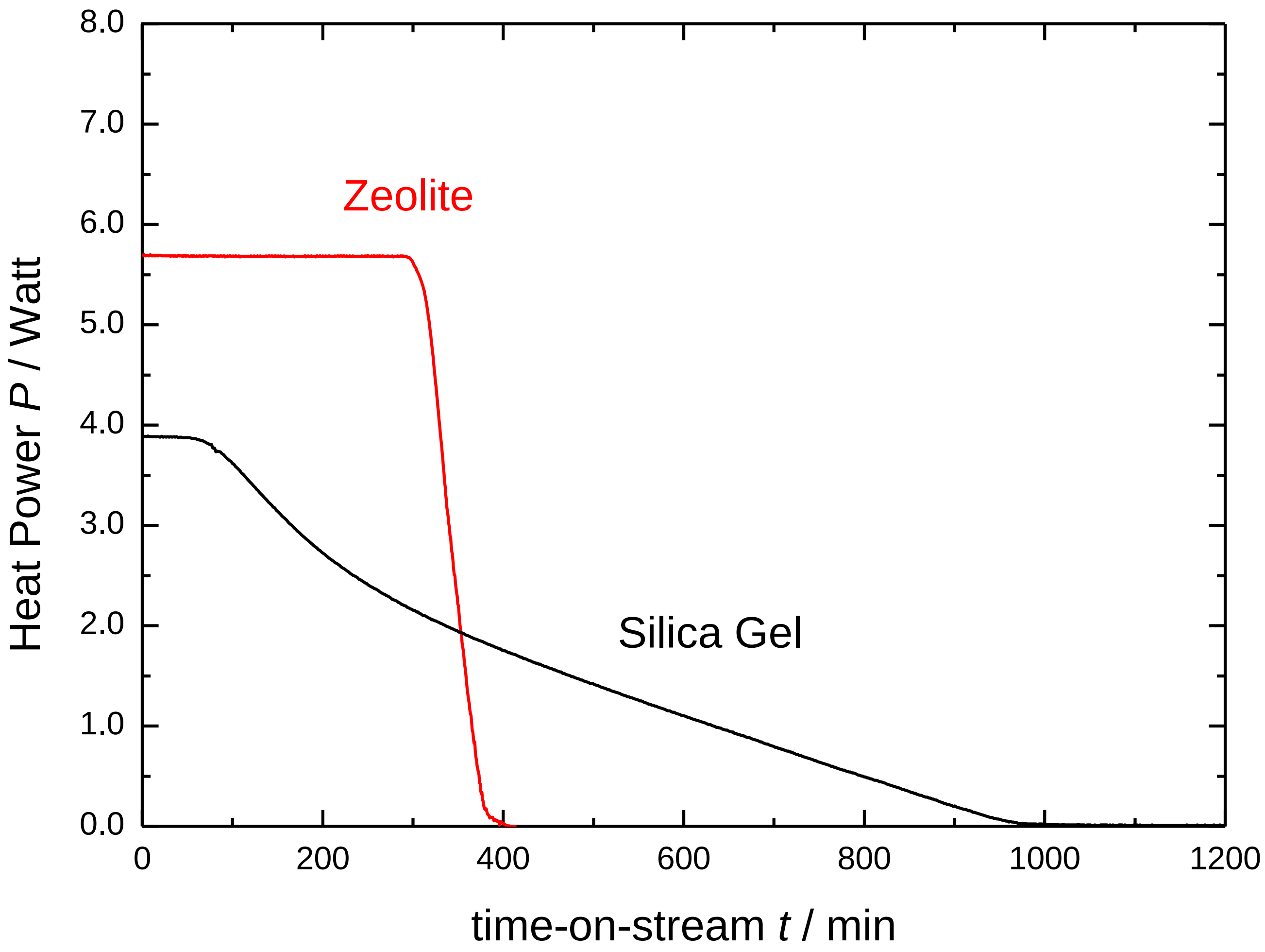
(re-calculated according to water isotherms)

	Zeolite 13X	Silica Gel
h_W / J g^{-1} (H_2O)	1600	300
h_C / J g^{-1} (H_2O)	2500	2500
h_A / J g^{-1} (H_2O)	**4100**	**2800**

3. Breakthrough Curve Experiments

Heat Power Comparison

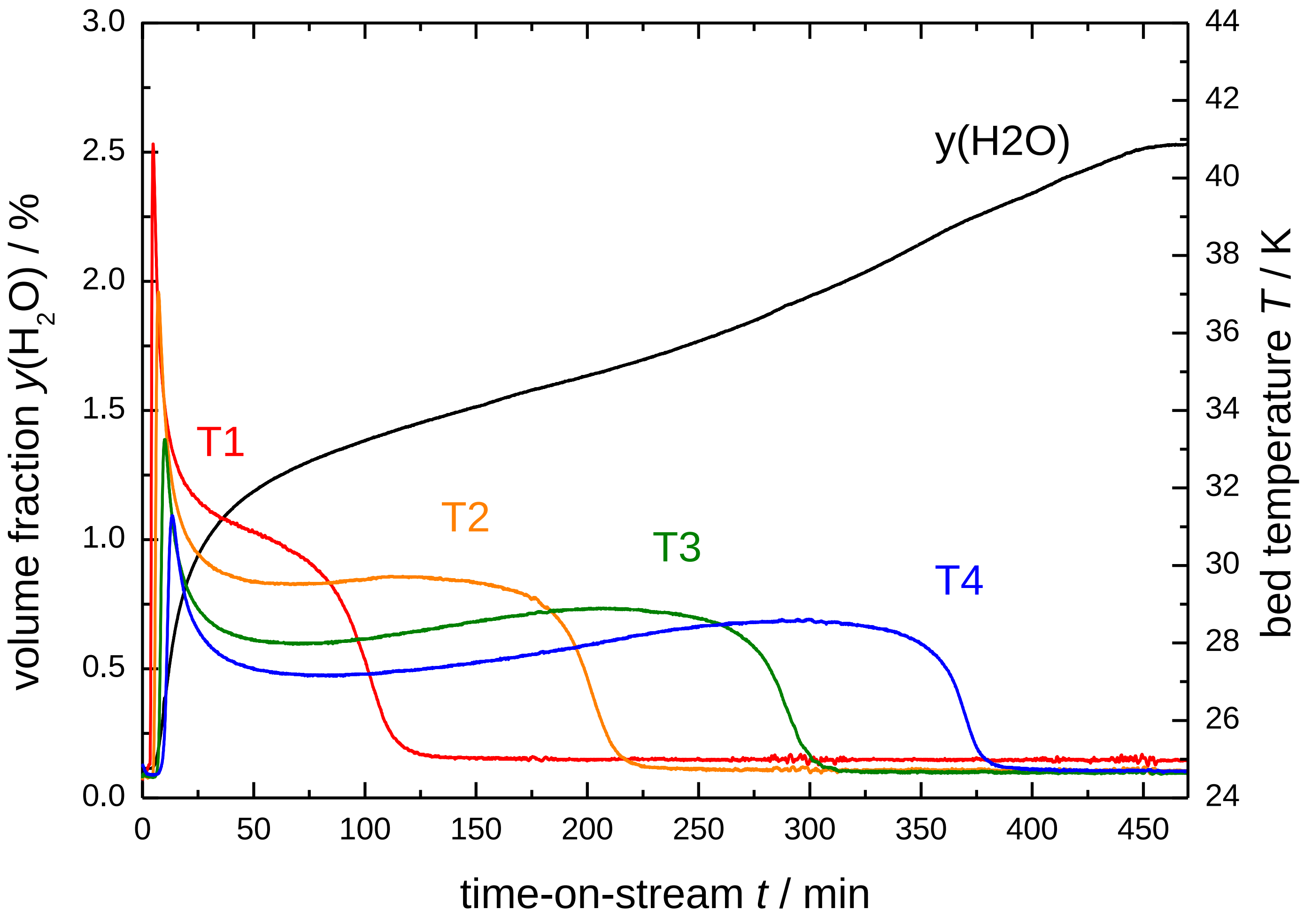
- Comparing the Heating Power during Adsorption



$$P = (1 - \text{rel. Breakthrough}) \times \frac{5\,\frac{\text{g}}{\text{h}}}{3600\,\frac{\text{s}}{\text{h}}} \times h_A$$

- Zeolite: More Heating Power, but over short duration → abrupt drop
- Silica Gel: Less Heating Power, continuously decreasing → longer duration

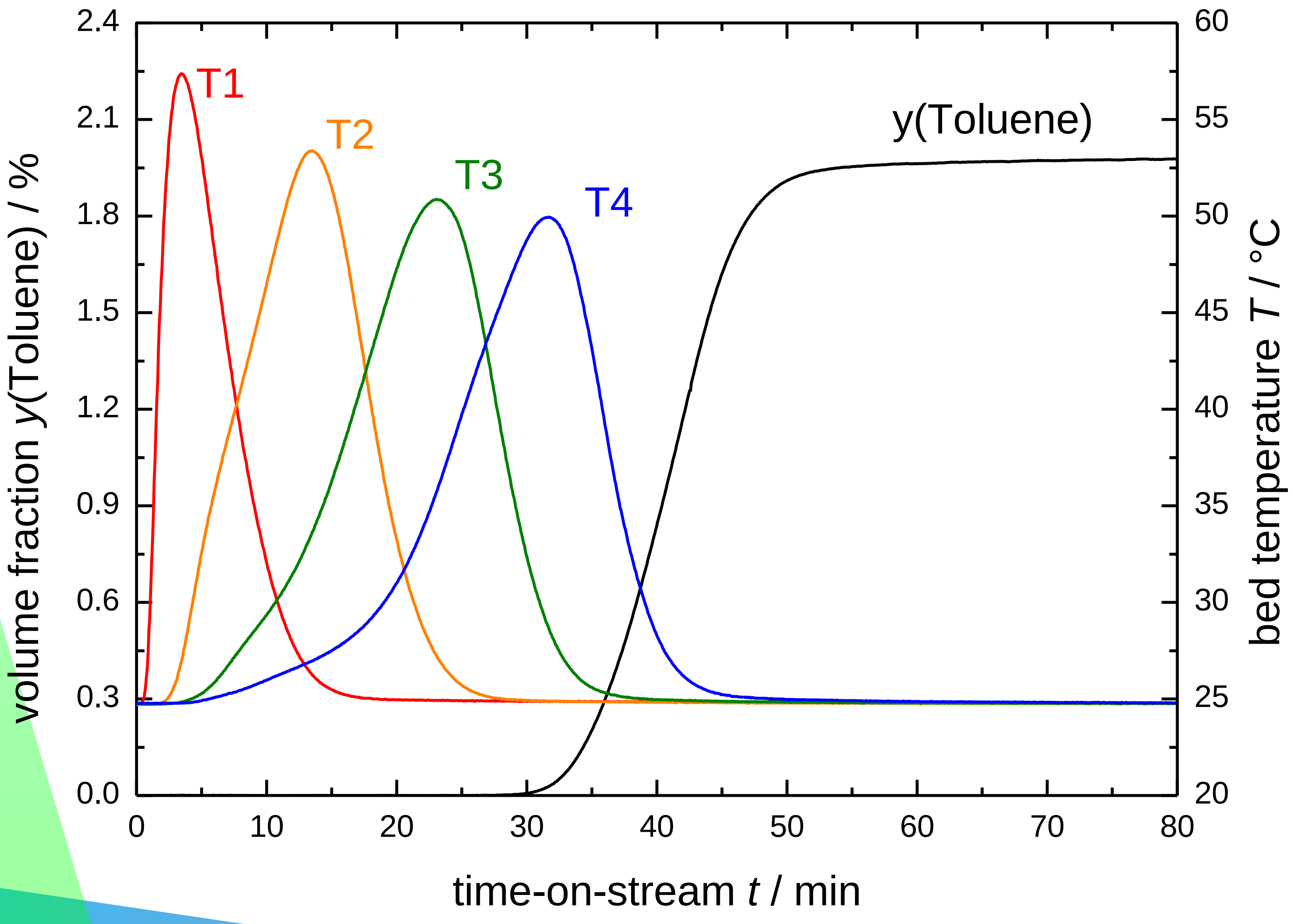
Breakthrough Curve of H_2O / N_2 on Activated Carbon



- 25 °C, 4 L min^{-1}
- 1 bar
- Inlet composition:
  5 g h^{-1} H_2O in N_2
  (volume fraction y(H_2O) = 2.59 %, RH approx. 80%)
- Loading: **10.0 mmol g^{-1}**
- Shape of curves can be explained by **adsorption** and **condensation** in the pores.
- Fast breakthrough due to hydrophobic surface
- Similar to Silica Gel, but Condensation is more pronounced

Dynamic orption

II. Breakthrough Curve of Toluene/N_2



- Activated Carbon D55/1.5
- 25 °C, 4 L min^{-1}
- Inlet composition: **20 g h^{-1}** Toluene in N_2 (volume fraction *y*(Toluene) = **2.0 %, p/p_0= 0.53** (@ 25 °C)

→ Large temperature peaks

→ Steep Breakthrough Curve

→ Loading: **2.1 mmol g^{-1}**

→ More similar to **H_2O/Zeolite** than H_2O/Activated Carbon

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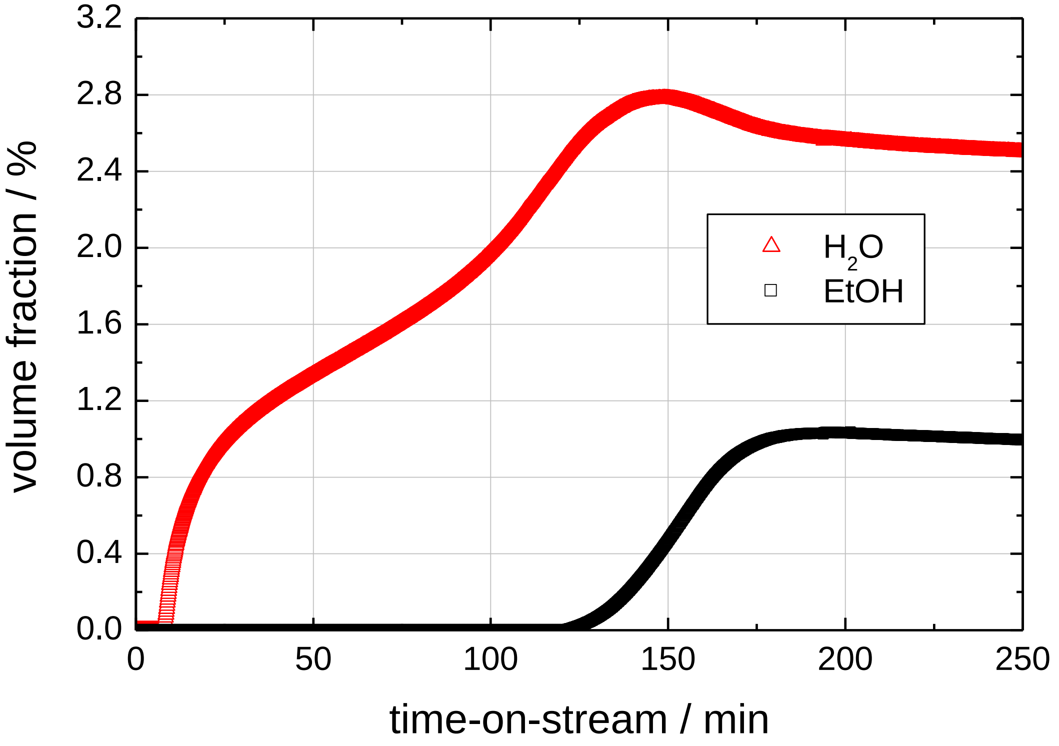
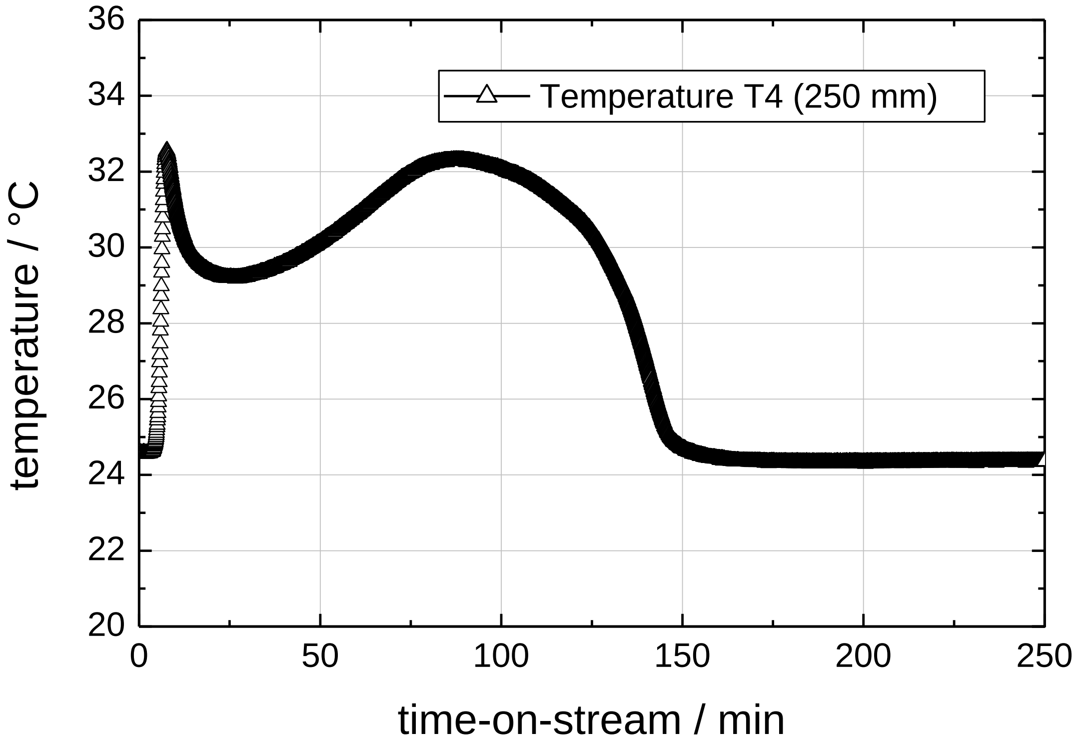
III. Breakthrough Curves of a EtOH/H_2O Mixture in N_2 on Activated Carbon





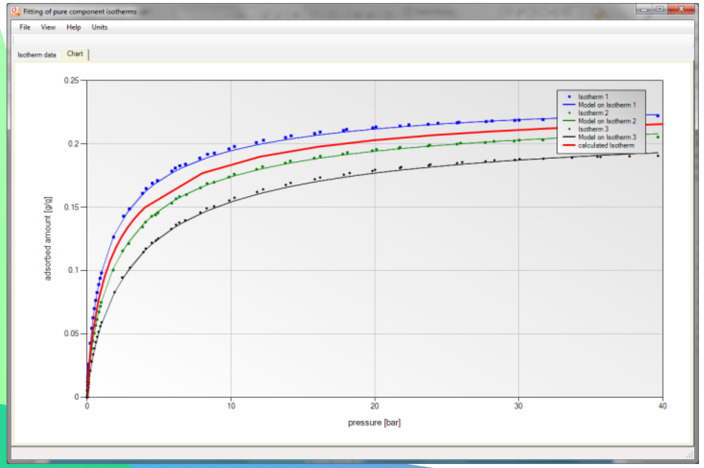
- complex breakthrough due to Type-V/Type-I isotherms
- **roll-up effect** for H_2O due to replacement by EtOH

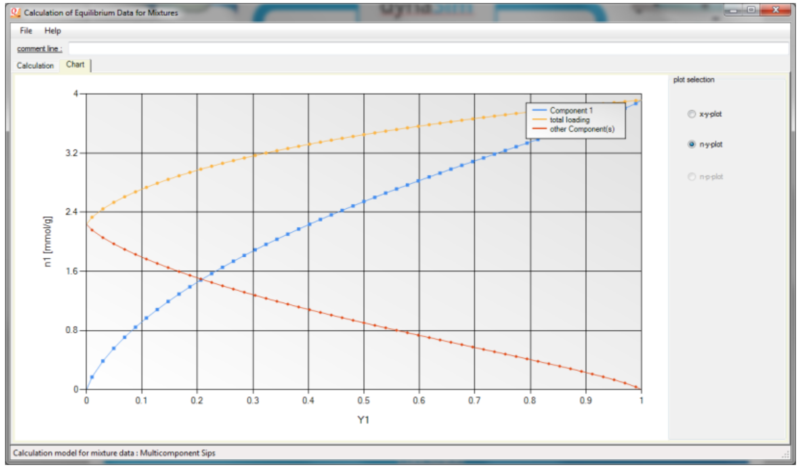
2.5 % H_2O, 1 % EtOH in N_2, Total Flow: 4 Nl min^{-1} T = 25 °C

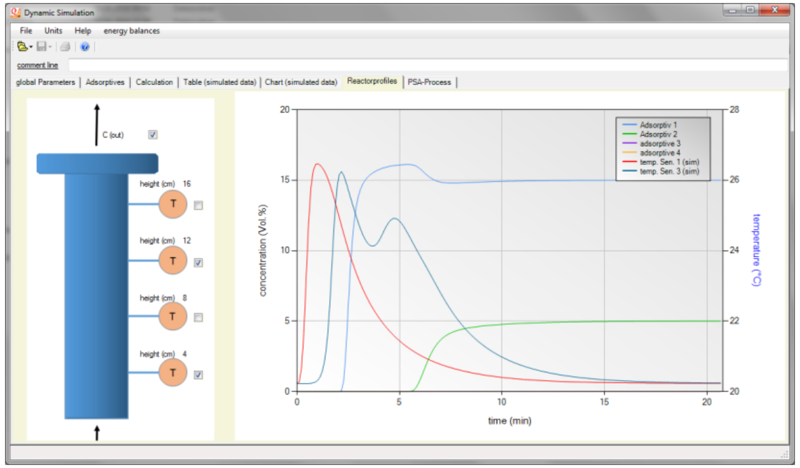
Procedure

3P-SIM

1. Measuring **Breakthrough Curve**
2. Measuring **Pure Component Isotherms**: **1** of each adsorptive for **isothermal** simulations
   3 of each adsorptive for **non-isothermal** simulations
3. Predict **Mixture Adsorption** with IAST or Multi-Component Models
4. Predict Breakthrough Curves based on **Mass- and Energy Balances**
5. Evaluate **mass transfer** by varying $\boldsymbol{k_{LDF}}$ to fit the predicted to the experimental Breakthrough Curves

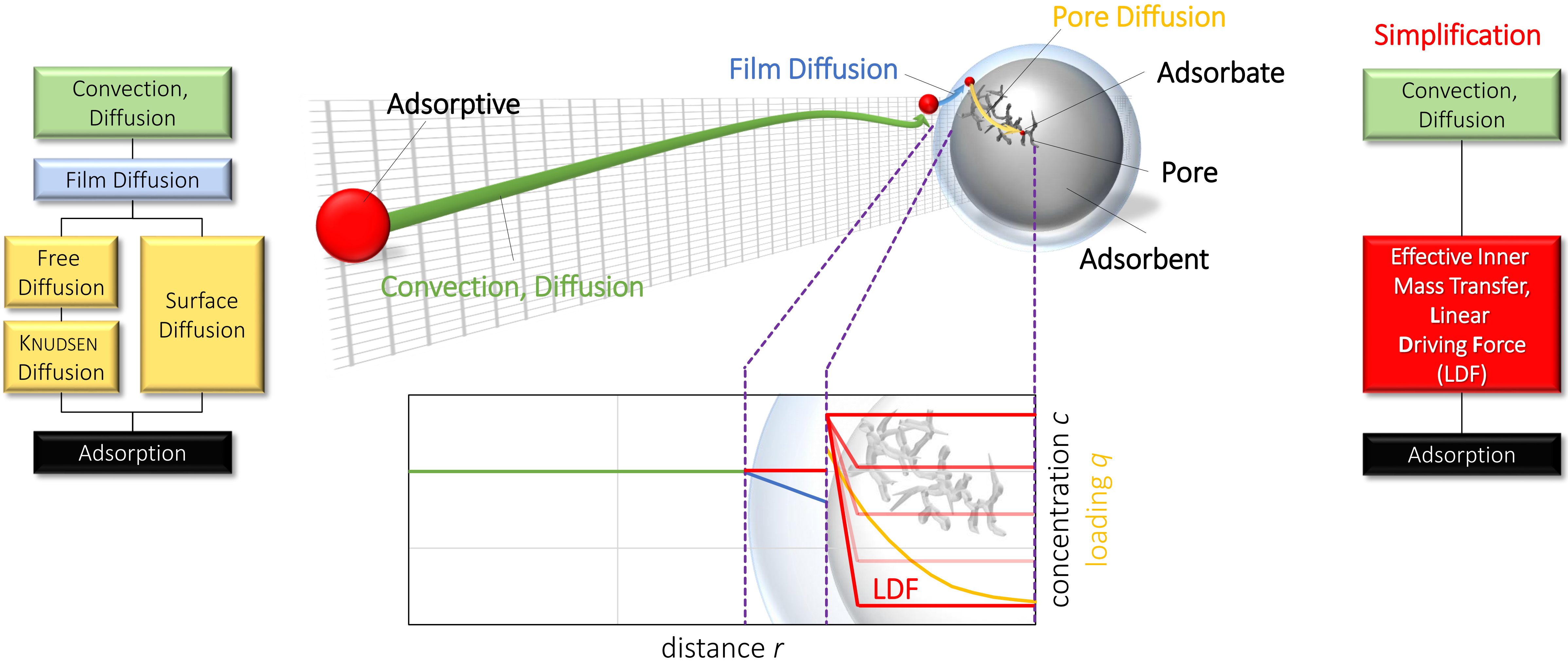






4. Modelling

Mass Transfer coefficient k_{LDF}



W. Kast, *Adsorption aus der Gasphase: Ingenieurwissenschaftliche Grundlagen und technische Verfahren*, 1.Aufl., VCH Wiley Verlag, Weinheim, 1988.

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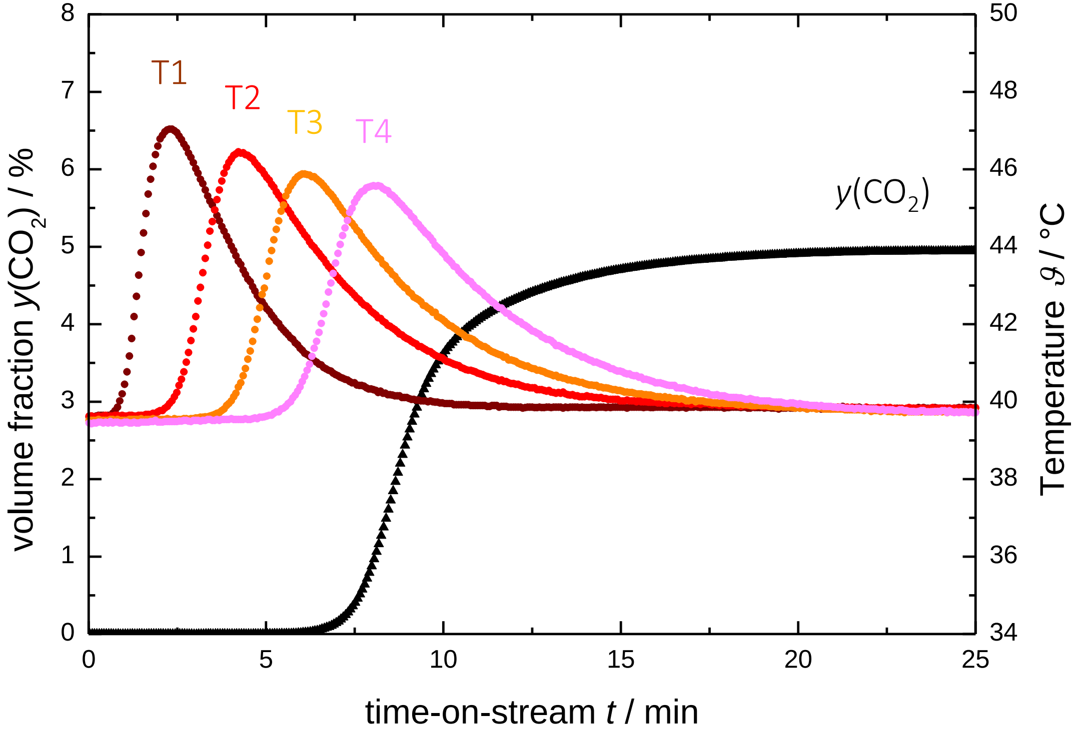
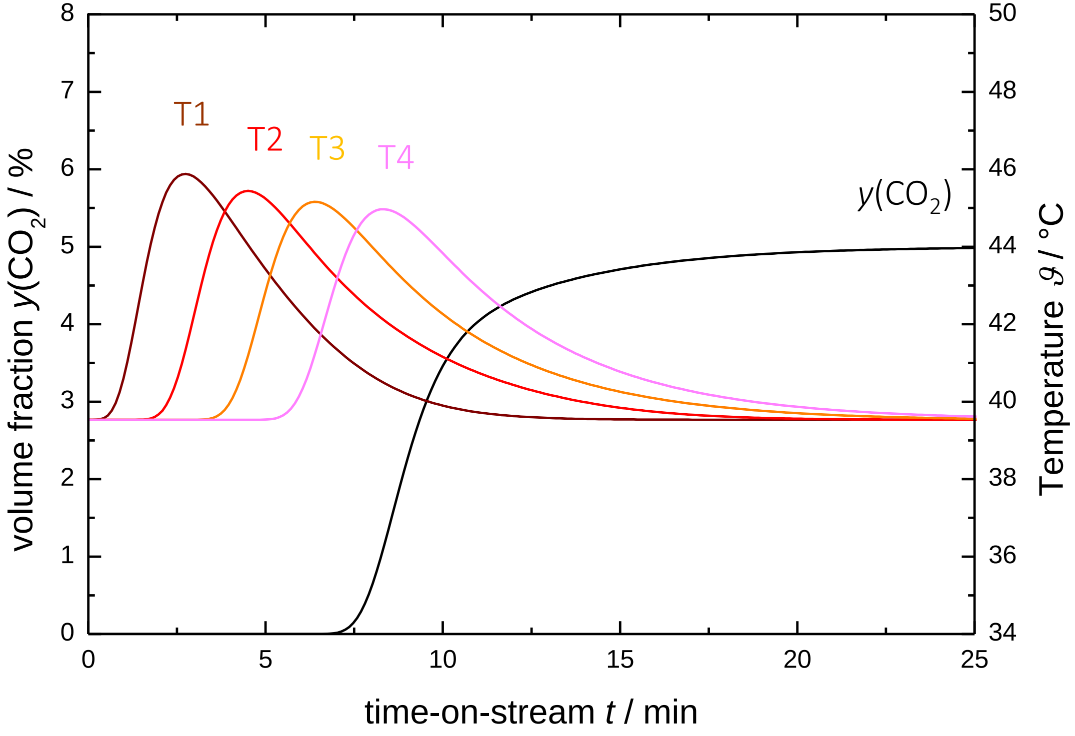
Fitting of Breakthrough Curves + Temperatures

Experiment

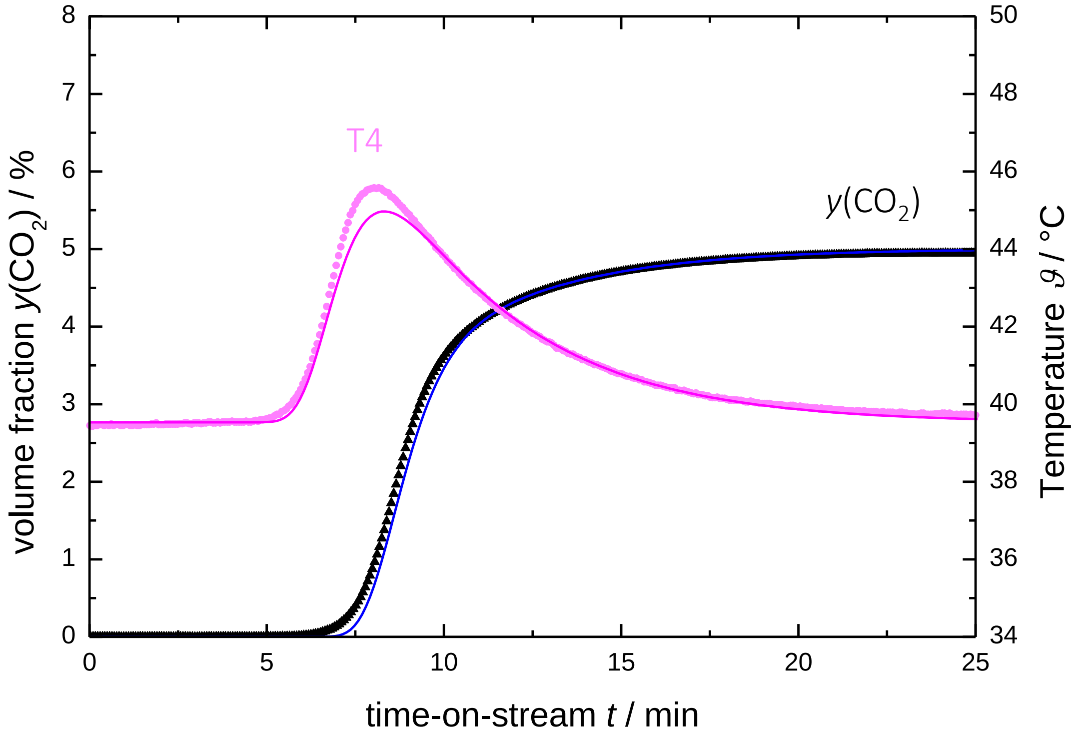


Simulation



- After fitting the k_{LDF} **Mass Transfer Coefficient** → Good Agreement of Experiment and Simulation in a Standard Breakthrough Experiment (5% CO_2 in N_2)
- Course of Volume Fraction and Temperatures is depicted correctly

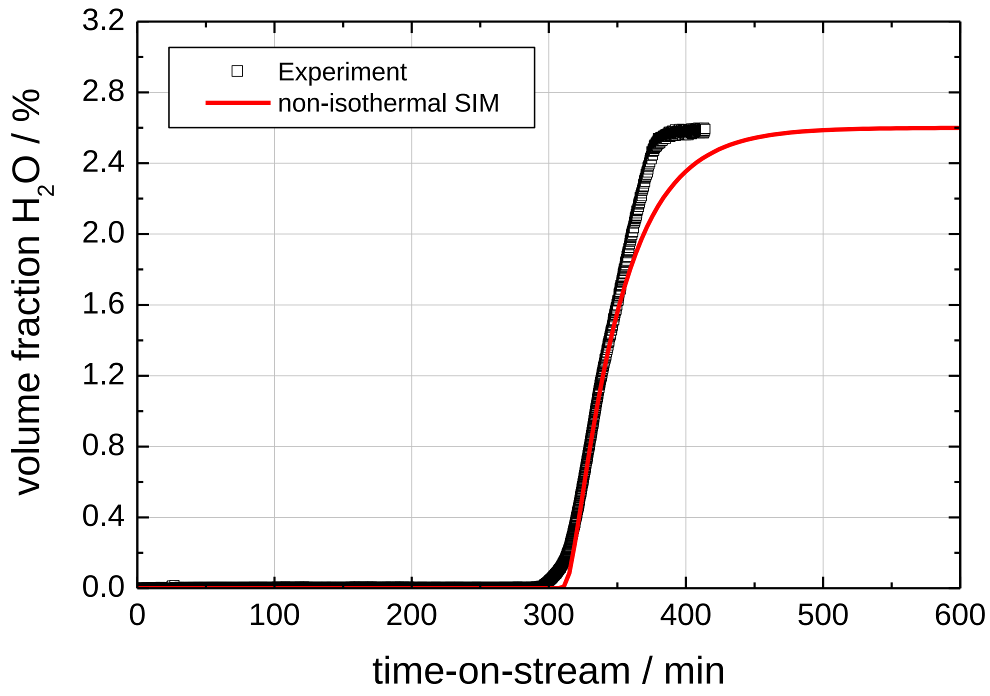
Fitting of Breakthrough Curves + Temperatures

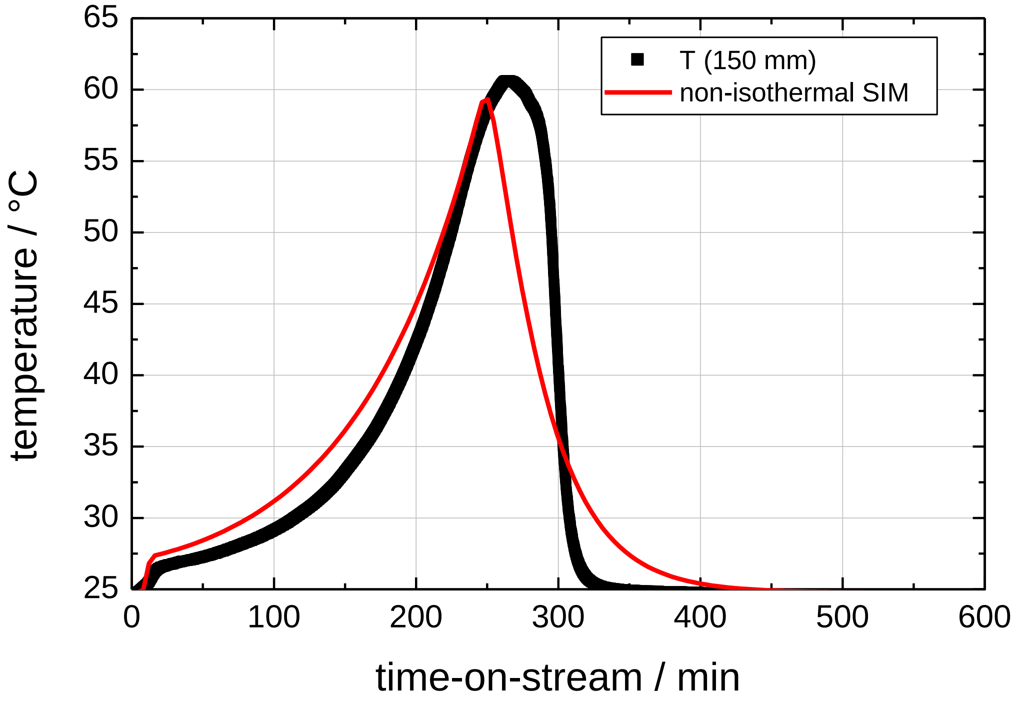


Overlay of Experiment (Points) and Simulation (Line)

- After fitting the k_{LDF} **Mass Transfer Coefficient** → Good Agreement of Experiment and Simulation in a Standard Breakthrough Experiment (5% CO_2 in N_2)
- Course of Volume Fraction and Temperatures is depicted correctly

H_2O on 13XBFK – Modeling with Dual-site Langmuir Sips isotherm model (DSLAI-SIPS)





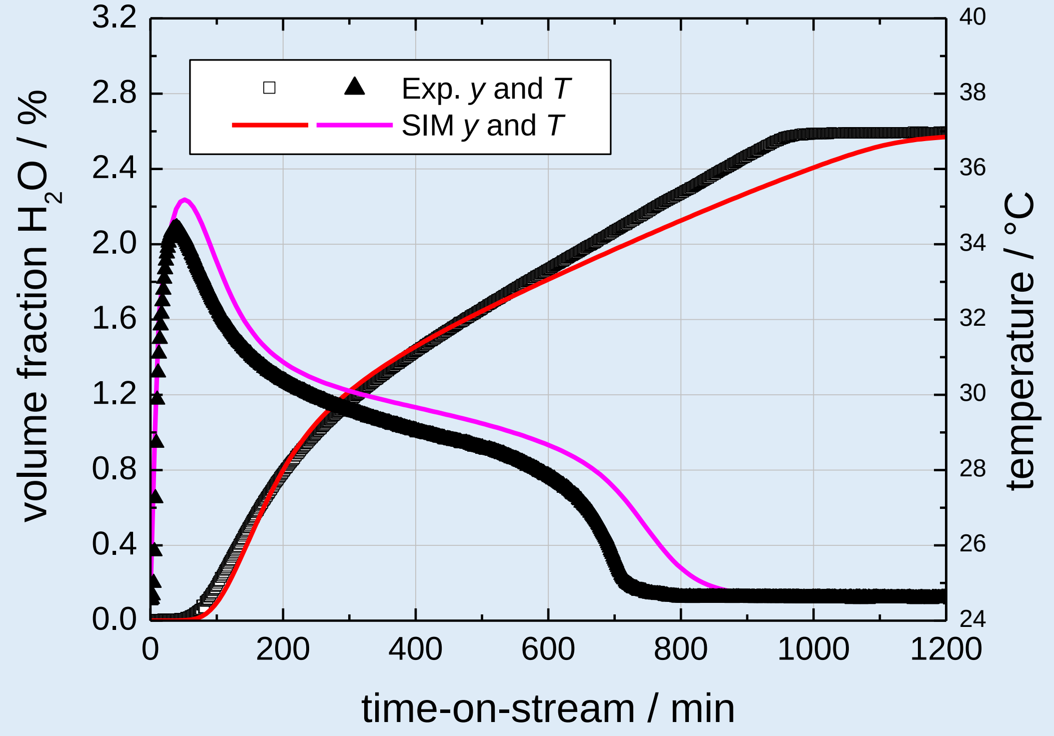
- **Good correlation** between experiment and simulation for **Type I** isotherms
- Heat effects can be simulated by using **non-isothermal** models
- Future Improvements: Using 2D, instead of 1D models (radial discretization)

$$q_{\mathrm{eq}} = q_{\mathrm{max}} \left(\frac{K_1 \cdot p}{1 + K_1 \cdot p} + \frac{(K_2 \cdot p)^t}{1 + (K_2 \cdot p)^t} \right)$$

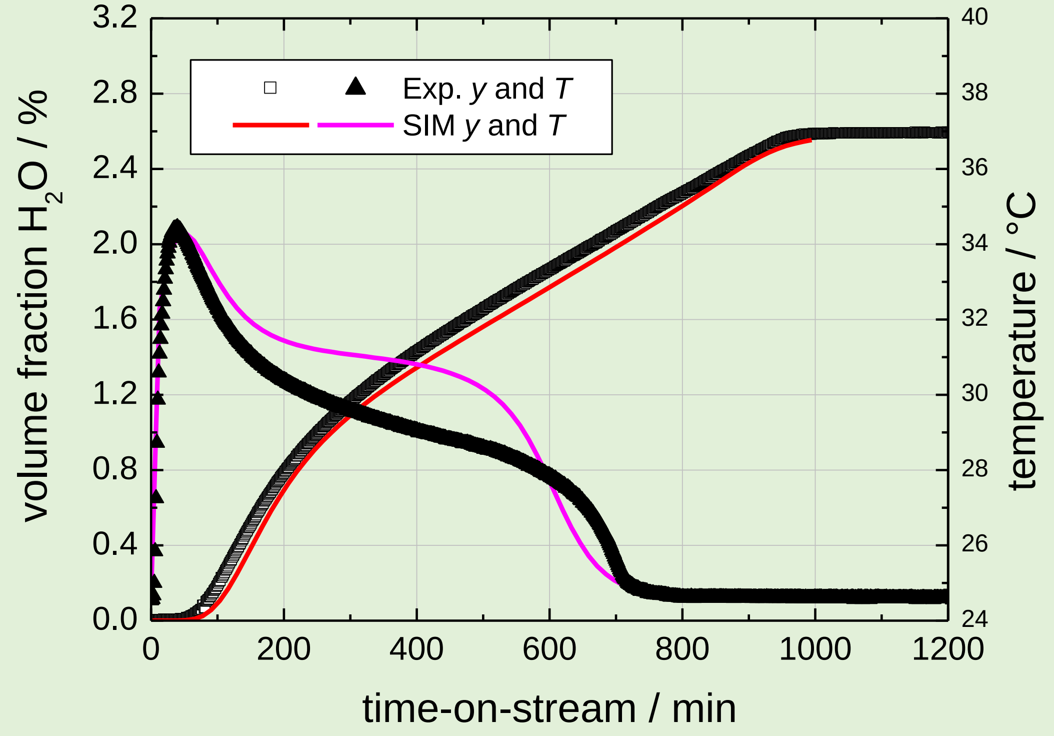
Sample: 13XBFK, conditions: 2.5 % H_2O in N_2, 4 NL min^{-1}, 25 °C (80 % RH)

H_2O on Silica Gel – Modeling with DSLAI-SIPS

Using heats of adsorption Q_1, Q_2, determined by fitting 3 isotherms

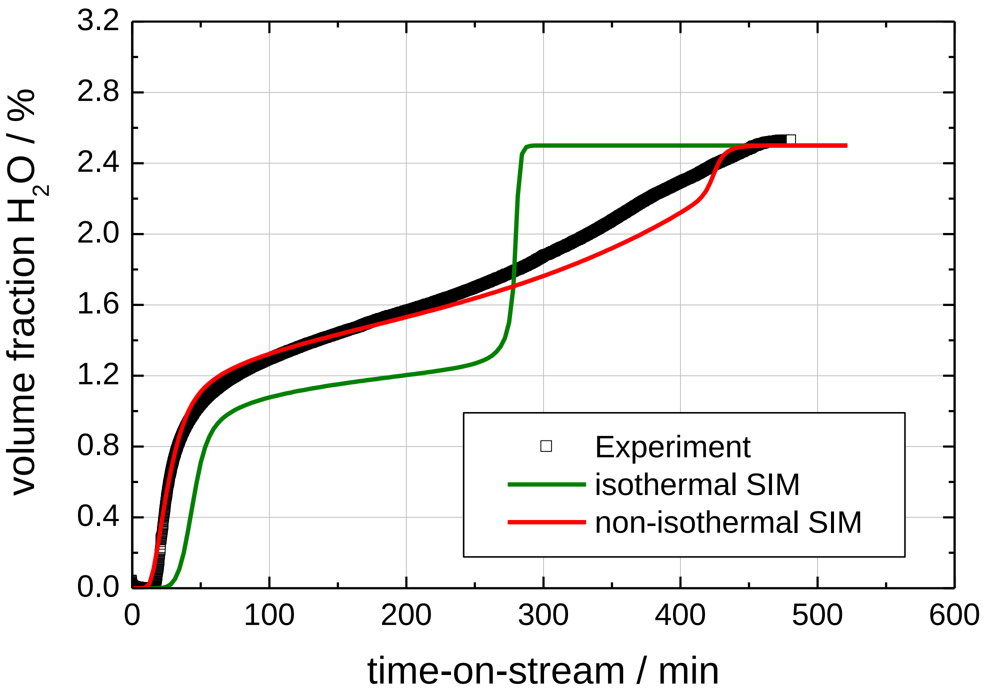


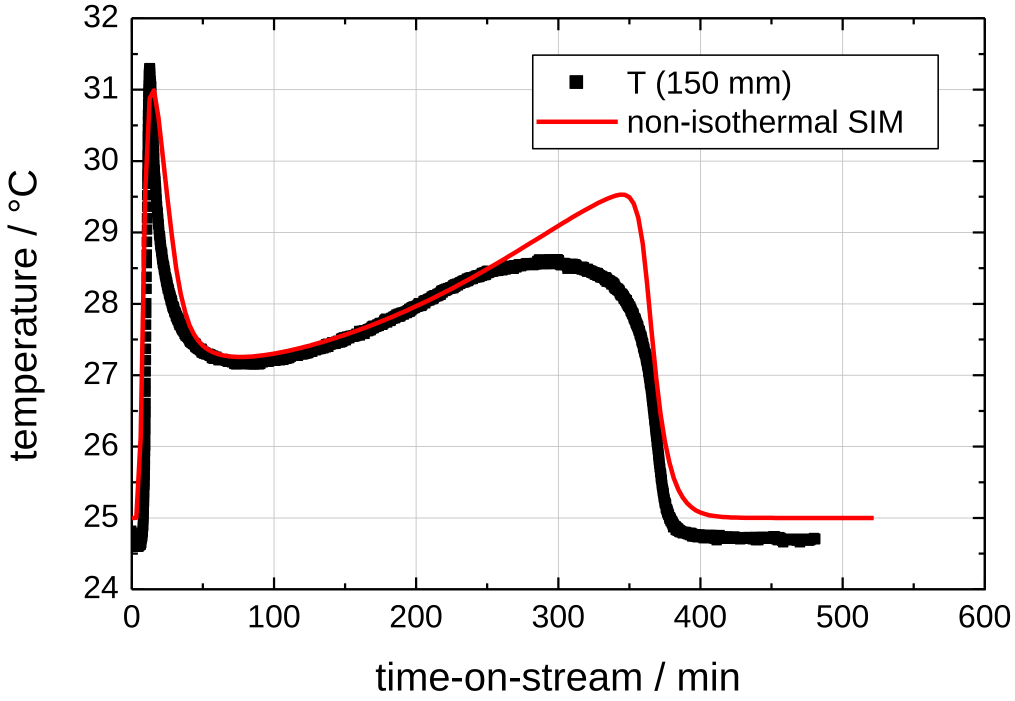
Using heat of adsorption Q_1, determined by fitting 3 isotherms
And **Q_2 = Q_{Evap}**



- **Good correlation** between experiment and simulation
- Better prediction of breakthrough curve with Q_2 = Q_{evap}
- Better description of temperature curves with Q_1, Q_2 = heats of adsorption (1=LANGMUIR, 2=SIPS)

H_2O on Activated Carbon (Type V Isotherm) – Modeling with DSLAI-SIPS



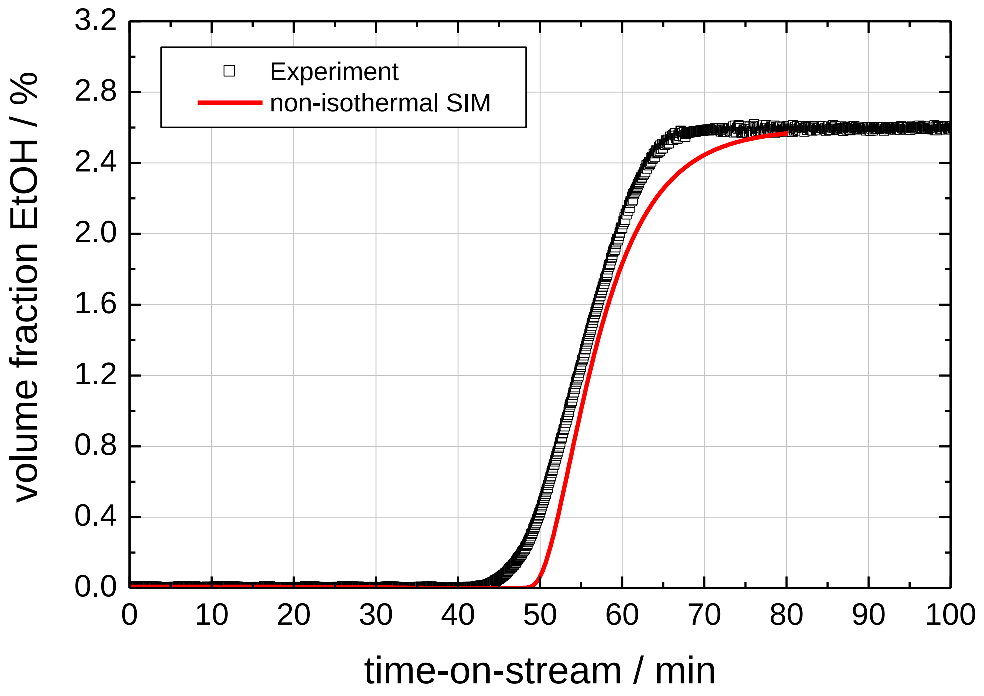


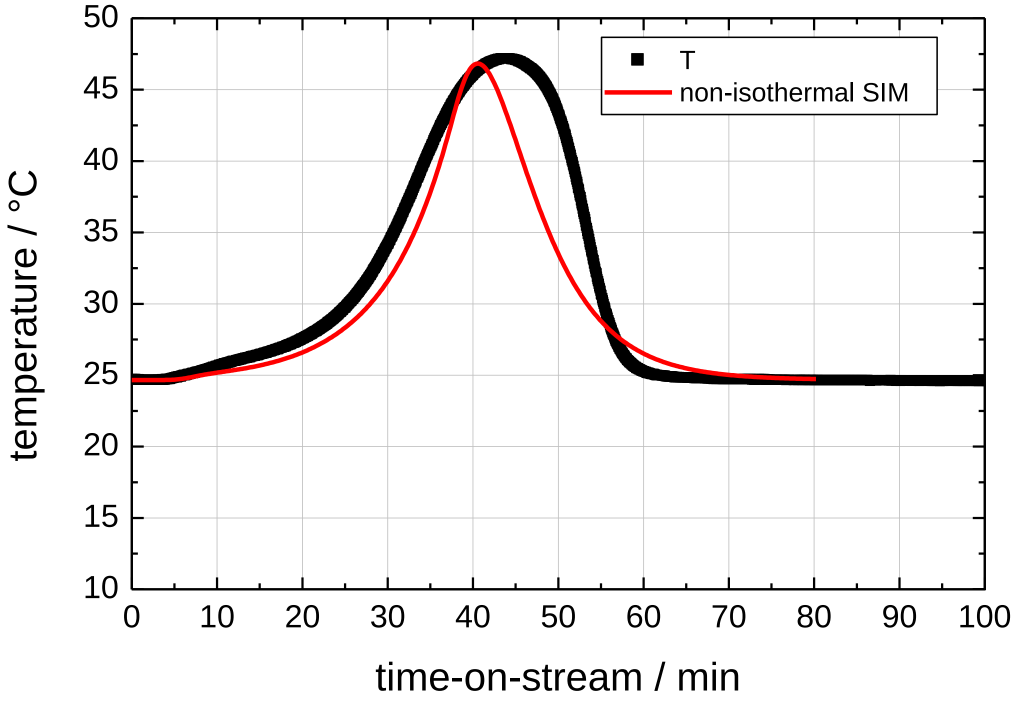
- **Good correlation** between experiment and Simulation for with non-isothermal model
- Poor Correlation for isothermal models

- Improvement of Breakthrough fit by using loading-dependent k_{LDF} → adsorption + pore filling by condensation → **But:** prediction of temperatures gets worse

Sample: Activated Carbon, conditions: 2.5 % H_2O in N_2, 4 NL min^{-1}, 25 °C (80 % RH)
Crank J.; The Mathematics of Diffusion, Oxford University Press, 1975.

EtOH on Activated Carbon – Modeling with DSLAI-SIPS





- **Good correlation** between experiment and simulation
- Future Improvements: → Using 2D, instead of 1D models (radial discretization)
  → Using Isosteric heat instead of heat of adsorption

5. Conclusions

Characterization under application-related conditions!

- **mixSorb L** is very versatile instrument for application-related studies
  - ✓ Vapor Sorption, determine Isotherms, Mixture Isotherms
  - ✓ Breakthrough curves of other Adsorptives in the Presence of Water
  - ✓ Adsorption Studies of Organic Vapors: VOC adsorption
- **3P-SIM** is a powerful simulation tool for Breakthrough Prediction
- Future steps:
  - → Simulation of vapor mixture adsorption
  - → Implementing **2D**, instead of 1D models (radial discretization)
  - → Implementing isosteric heat into non-isothermal models, where possible

Thank You!

Dynamic orption

Thank you for your attention!