Investigation of Industrial Adsorbents by Gas Flow Methods

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2016-05-31

The presentation will begin shortly.
Please be patient while other attendees log in.

Outline

1. **Characterization of Industrial Adsorbents**
2. **Gas Flow Methods**
3. **Examples**
   I. Breakthrough Curves
   CO_2 / N_2 on Activated Carbons
   II. Mixture Isotherms
   CO_2 / N_2 on Activated Carbons
   III. Natural Gas, Biogas Purification
   Separation of CO_2 / CH_4 on Activated Carbons and Zeolites
   IV. Air Separation
   Separation of O_2 / N_2 on Carbon Molecular Sieves
4. **Simulation**
5. **Conclusions**

1. Characterization of Industrial Adsorbents

Number of Samples

Application Progress

Synthesis and First Characterization	Determination of Thermodynamic Data	Basic Process Design, Granulation of Adsorbents	Detailed Process Design, Application

Chemists

- BET
- Pore Volume
- Pore Size Distribution

Chemists, Physicists

- Isotherms
- Heat of Adsorption

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Chemical Engineers

Bench scale, Pilot plants, Industrial Plant

Engineers

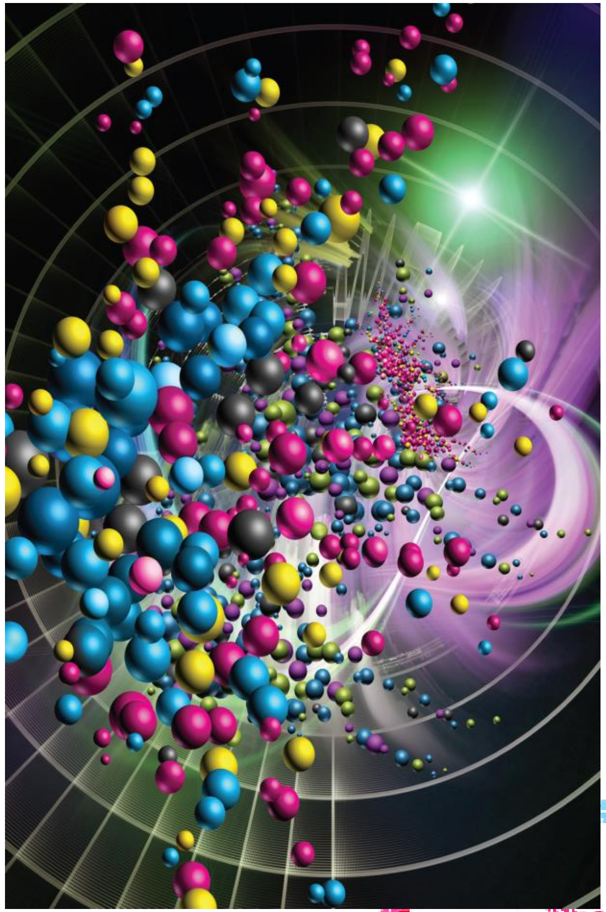
- Process Optimization
- Production

1. Characterization of Industrial Adsorbents

Importance of Gas Flow Methods for Characterization:

- Most **industrial** adsorptive separation processes
  = **dynamic** processes (**Gas Flow**)
- Different **Kinetics** of guest molecules can play a key-role during separation
- In technical separation always **gas mixtures** are present

  →Therefore the **selectivity of adsorbents** is very important
- Better transfer of results into technical processes.
- **Downscaling** of technical processes possible



→ Characterization under **application-related conditions**

2. Gas Flow Methods

Examples of different Gas Flow Methods

- **Rapid Dynamic Flow**
  Gas Flow over sample, measuring during desorption, recording gas **composition**

- **Dynamic Vapor Sorption**
  Gas Flow over sample, recording **weight**

- **Inverse Gas Chromatography**
  Forced-Flow through sample bed, inlet **pulse** functions, recording gas **composition** downstream the sample

- **Breakthrough Experiments**
  Forced-Flow through sample bed, inlet **step** functions, recording gas **composition** downstream the sample

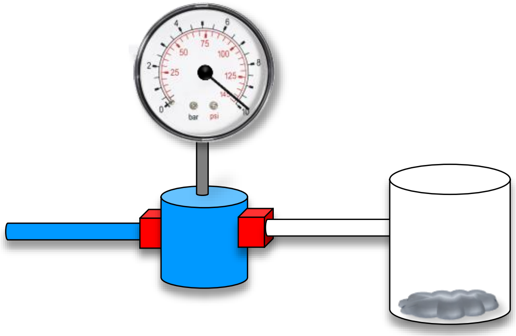
2. Gas Flow Methods

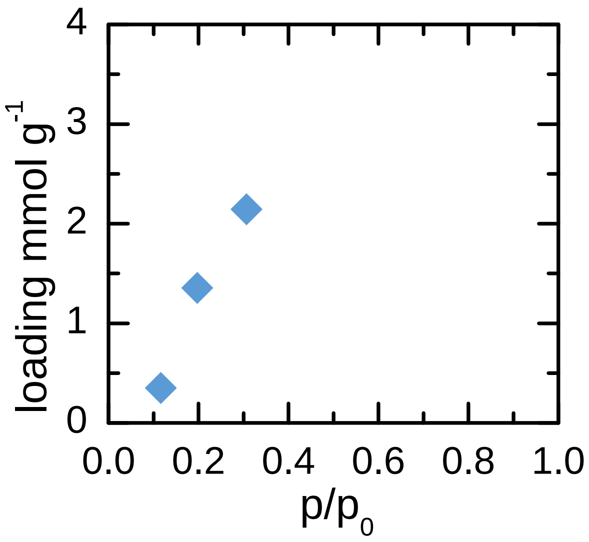
Static Volumetric Measurements

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

Breakthrough Experiment

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



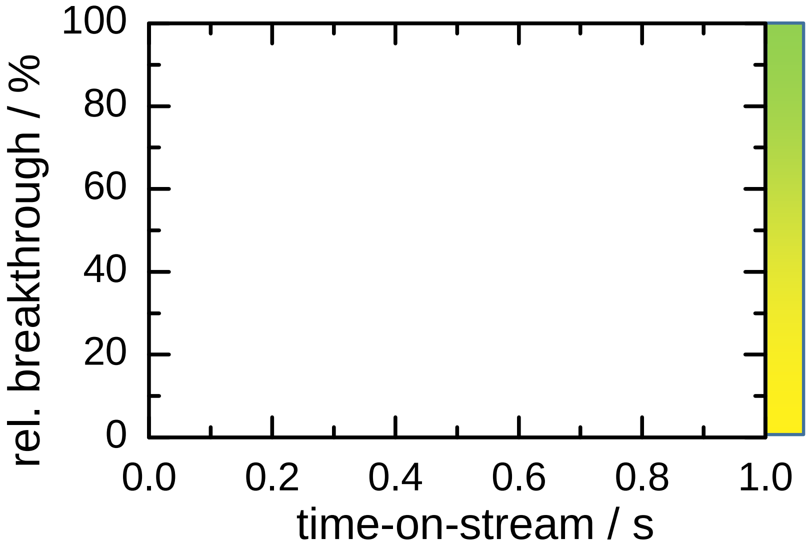


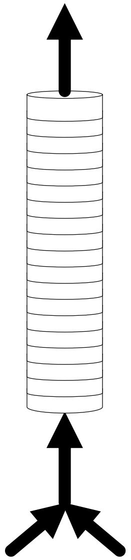
$$n_{\mathrm{ads},i} = n_{\mathrm{dosed},i} - n_{\mathrm{free},i}$$

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

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

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



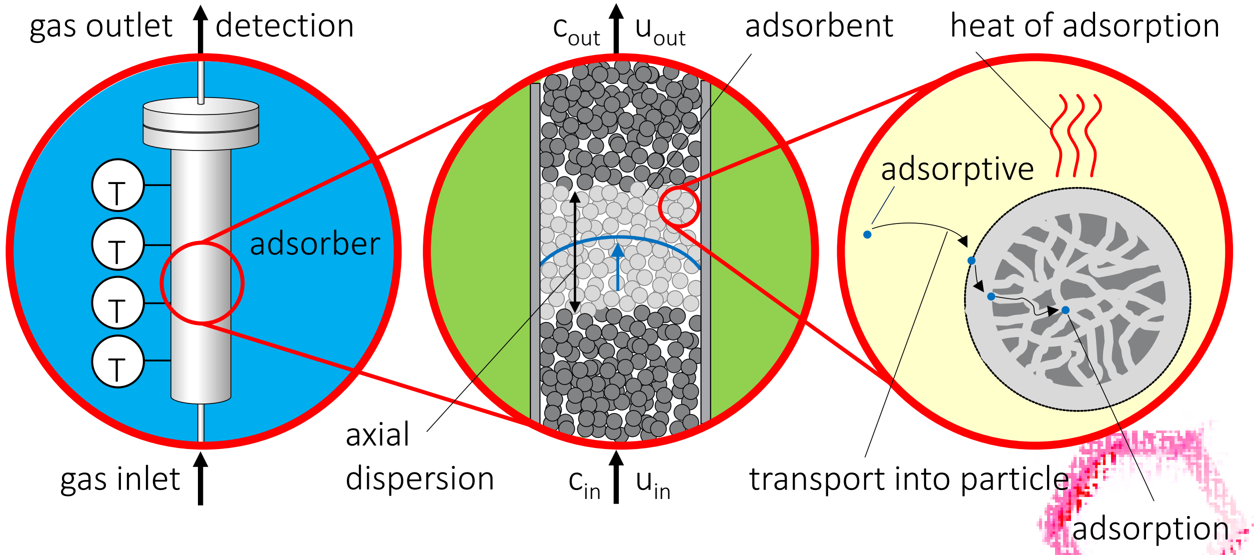


$$n_{\mathrm{adsorbed}} = \int \dot{n}_{\mathrm{in}}(t)\mathrm{d}t - \int \dot{n}_{\mathrm{out}}(t)\mathrm{d}t$$

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

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?

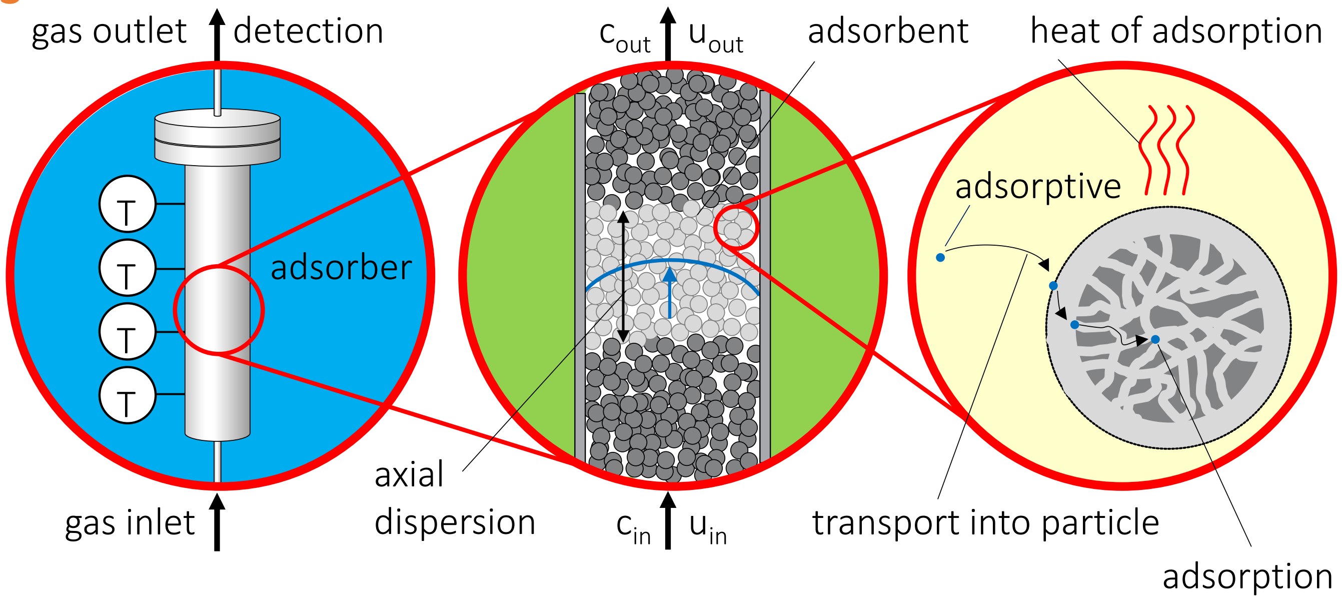
  ✓ **Time** until 5 %, 50 % ,… of breakthrough is the **cycle or production time**

  ✓ **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**

Breakthrough Curves



Macroscopic

- Size of Adsorber
- Shape of Adsorber

Mesoscopic

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

Microscopic

- Textural Properties
- Surface Characteristics
- Accessibility

2. Gas Flow Methods

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- **Fully automated**
- **Gas Mixing**
- Up to 40 L/min Gas Flow, up to **10 bar**
- Up to **4 mass flow controllers (MFCs)**
- Up to 2 **Vapors**
- Monitoring of gas composition by **TCD** at the outlet

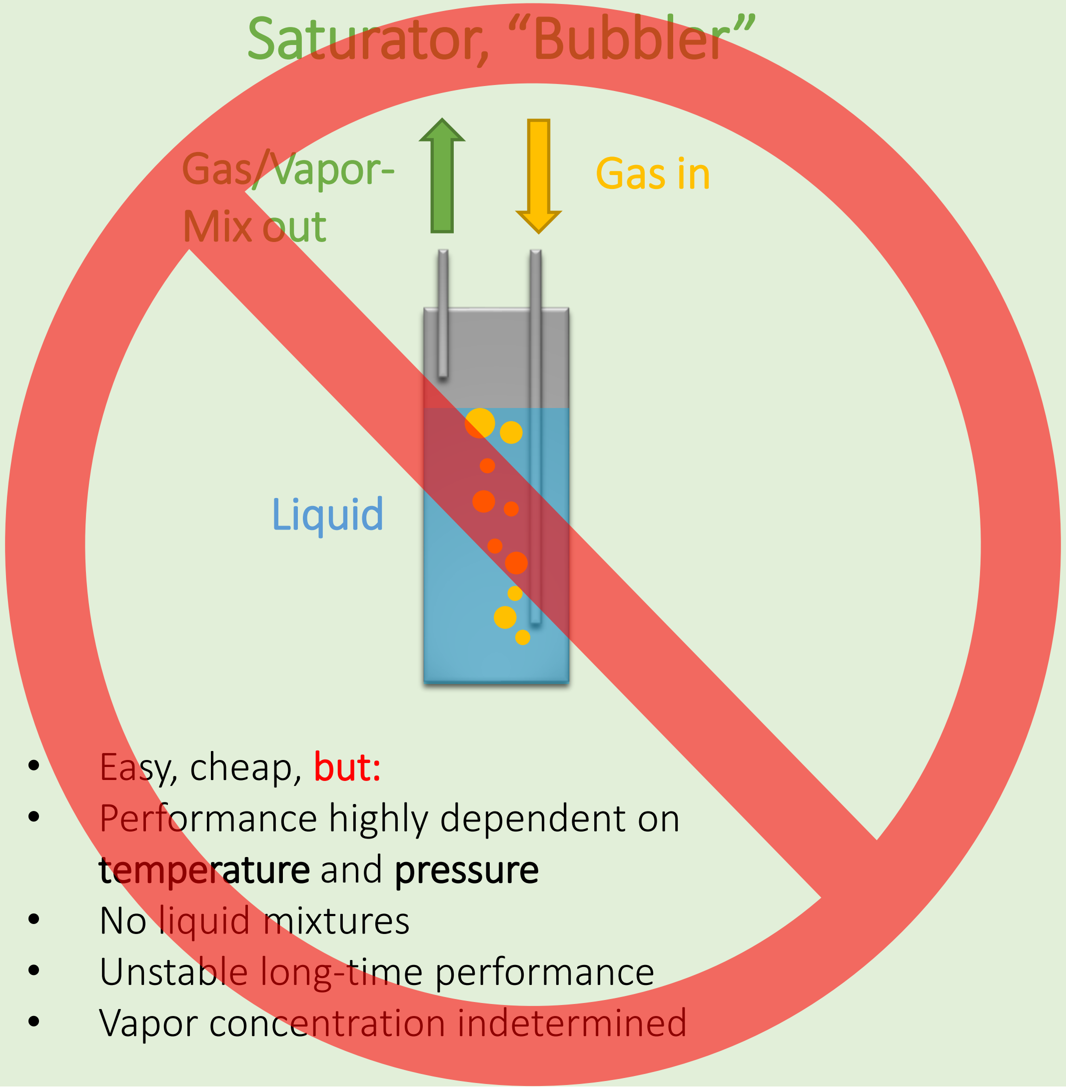
mixSorb L

Dynamic Sorption Analyzer

2. Gas Flow Methods

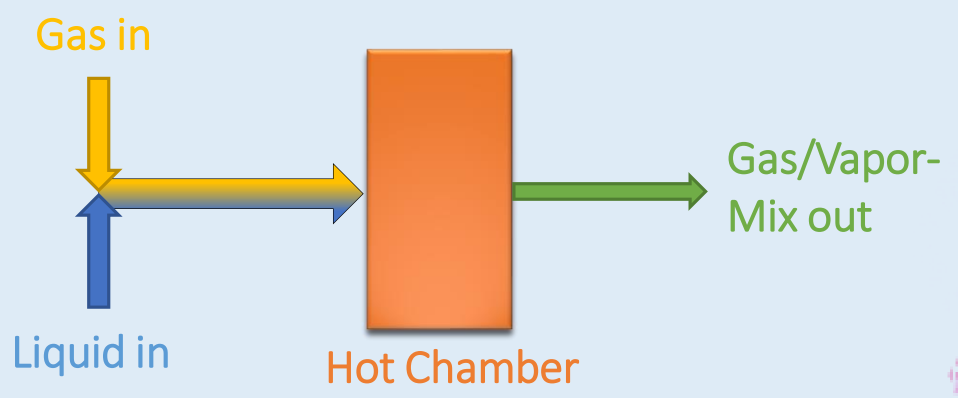
dynaSorb BT Evaporators

Saturator, “Bubbler”



- Easy, cheap, but:
- Performance highly dependent on **temperature** and **pressure**
- No liquid mixtures
- Unstable long-time performance
- Vapor concentration indetermined

Controlled Evaporation

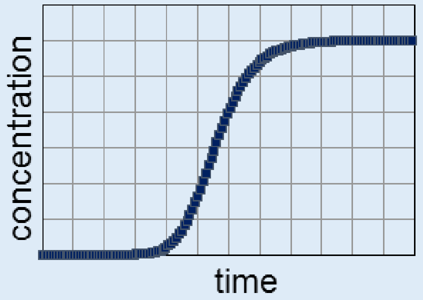


- More complex, but:
- Performance independent on **temperature** and **pressure**
- liquid mixtures possible
- Vapor concentration defined by **liquid flow rate and gas flow rate**
- Gas-Liquid mixing up- or downstream of evaporation process

2. Gas Flow Methods

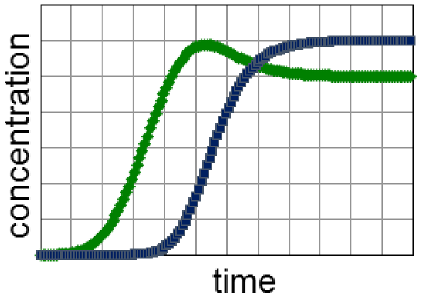
dynaSorb BT

Standard Breakthrough Curves



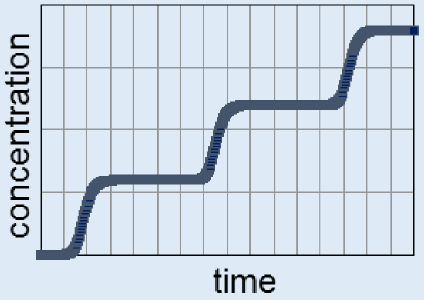
- Breakthrough time
- Mass Transfer
- Technically usable Sorption Capacity
- Modelling

Multicomponent Adsorption



- Competitive Adsorption
- Displacement

Isotherms



- Saturation Capacity
- Isotherms (single or **mixture**)

Cycle stability testing

- Regenerability
- Cycle-Stability

PSA-Emulation

- Emulation of PSA
- Down-Scaling

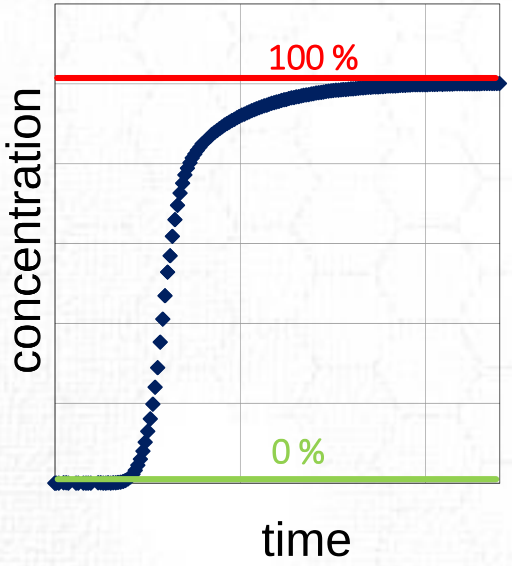
Chromatography

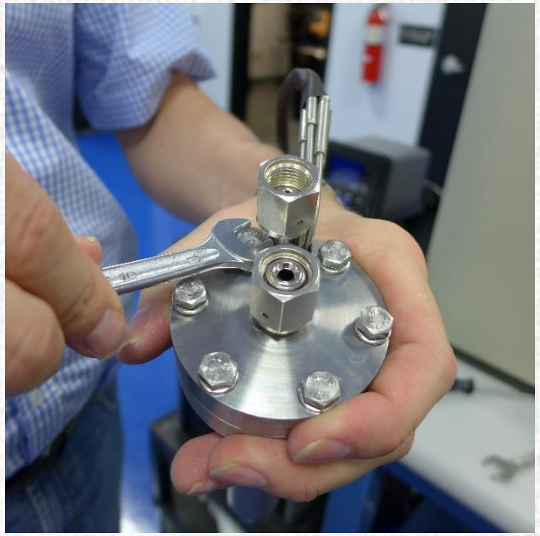
- Chromatographic parameters

3. Examples – I Breakthrough Curve

Procedure

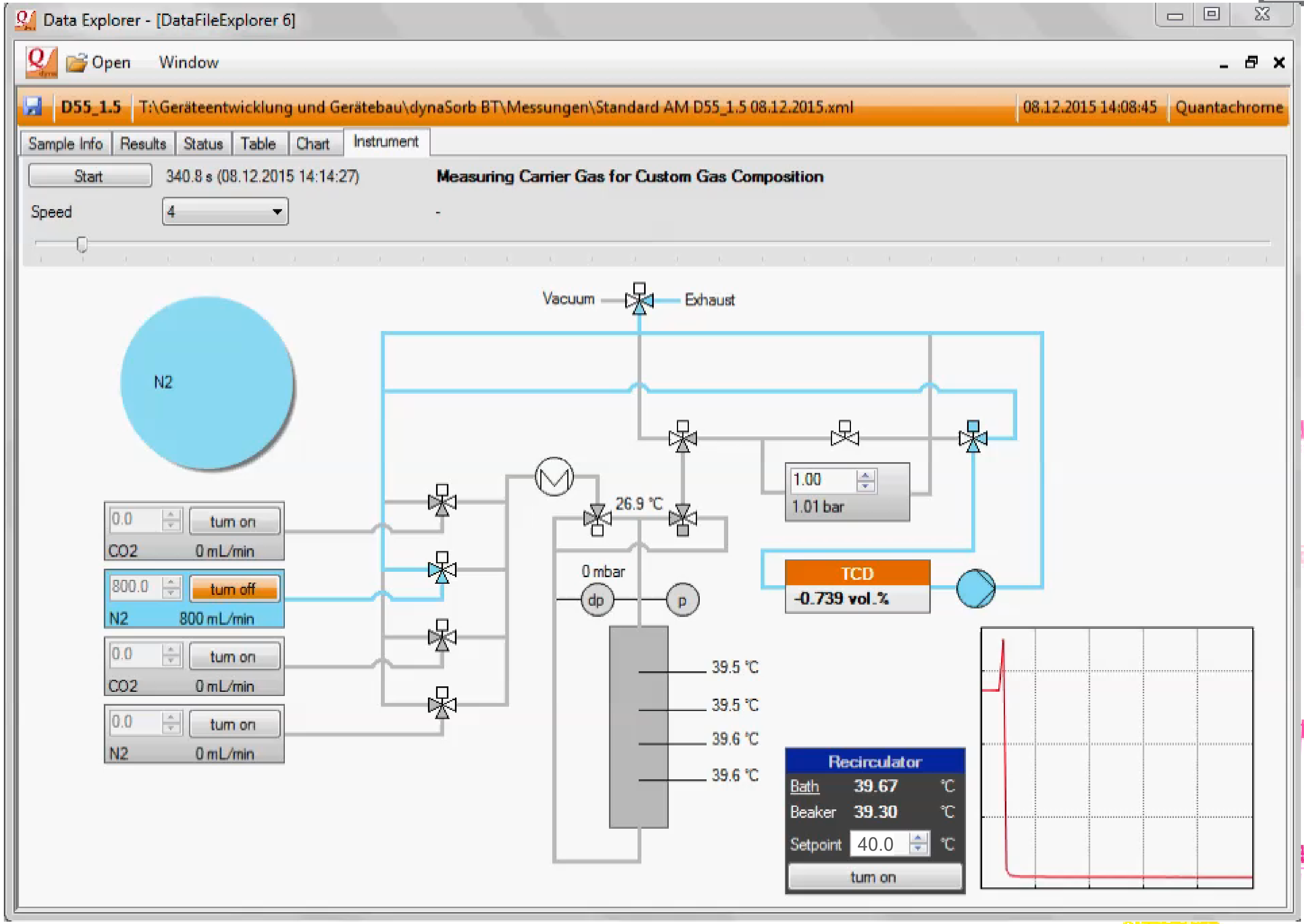
1. Determining **100 %** and **0 %** Breakthrough Signal in **Bypass**
2. Introducing **Carrier Gas** to the Sample Cell (Adsorber)
3. Pressurizing the Adsorber
4. Waiting for **stable** Pressure and Temperatures
5. Introducing additionally **CO_2** to create the **Gas Mixture**
6. Monitoring Adsorber **Temperatures** along the Sample Bed and **Gas Composition** at the Adsorber Outlet
7. Finishing Experiment when Temperatures and TCD Signal are **stable**





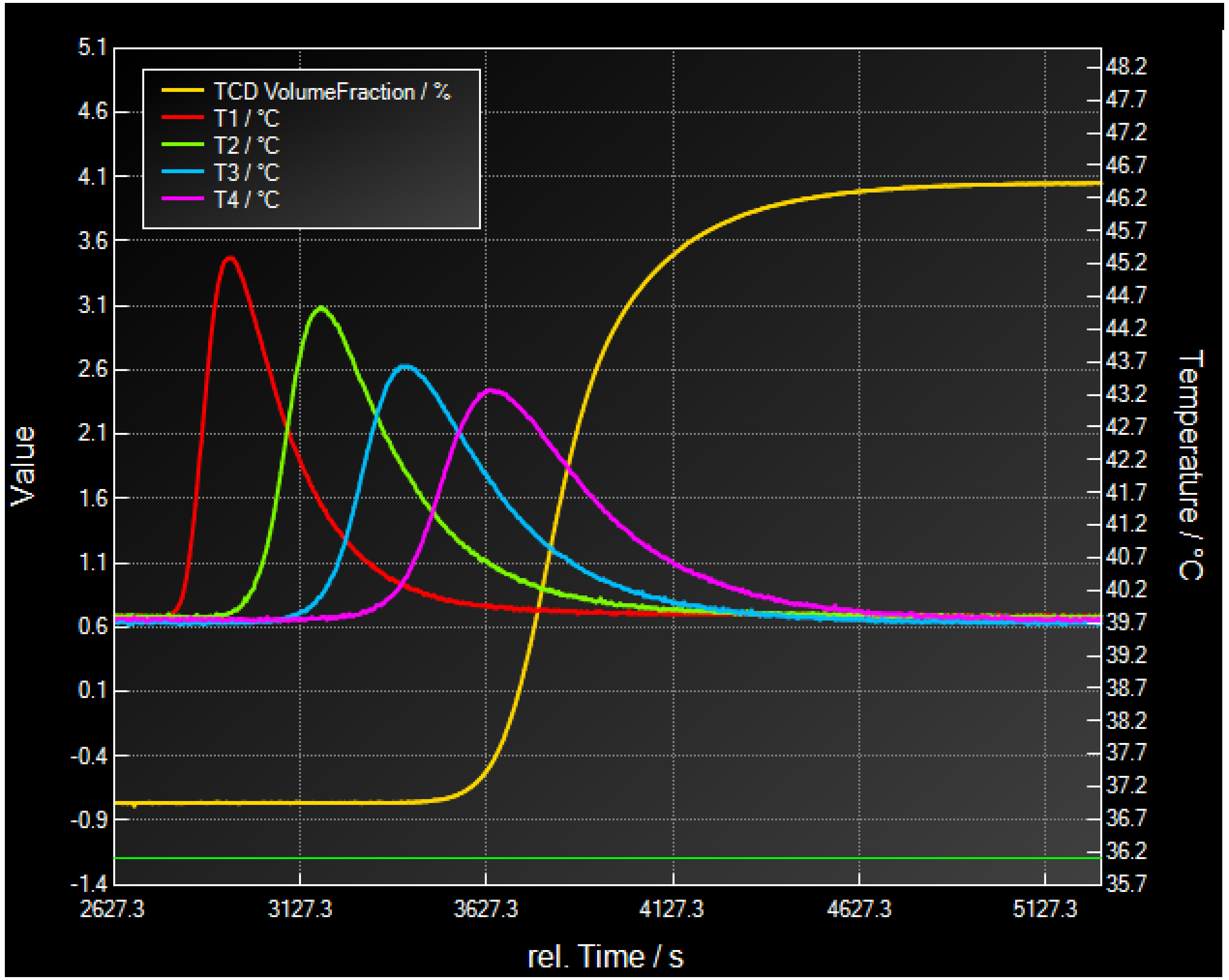
3. Examples – I Breakthrough Curve

Watch a Measurement



3. Examples – I Breakthrough Curve

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

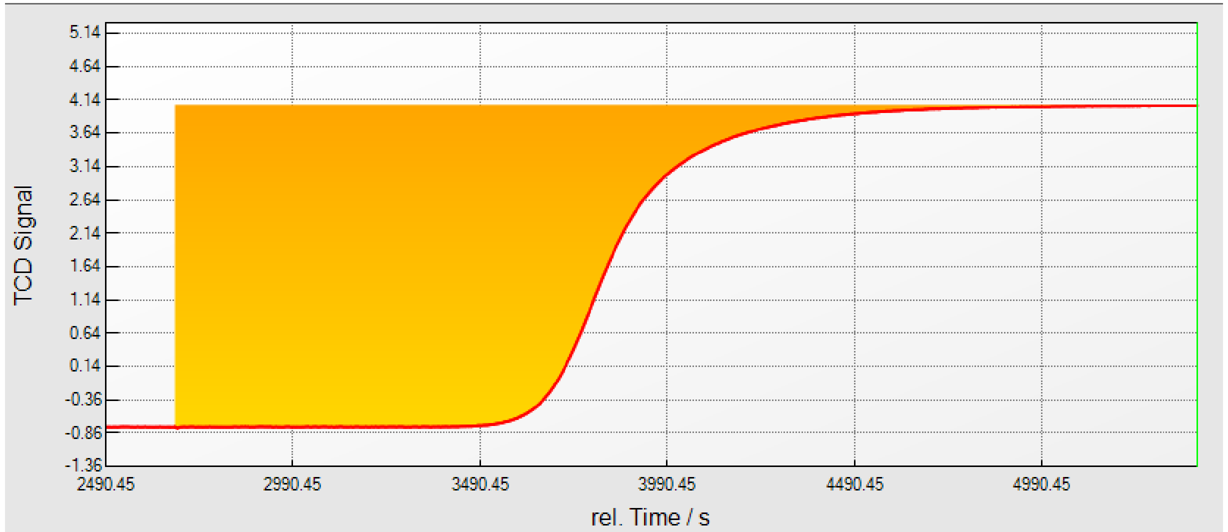
3. Examples – I Breakthrough Curve

Calculating Loadings

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

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

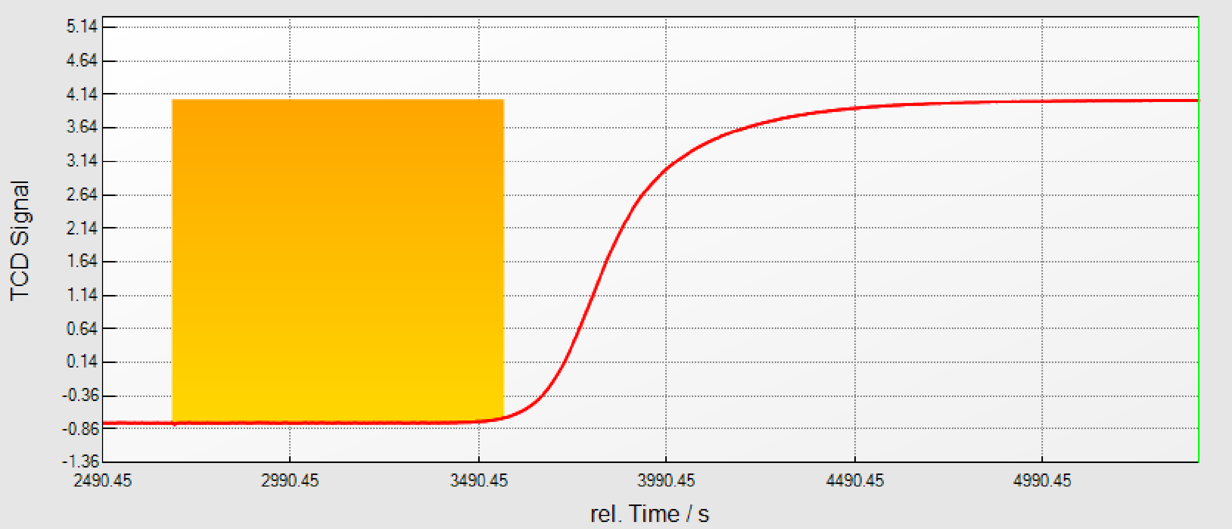
Integrating over the full Curve



Saturation Capacity

dq = 0.611 mmol g^{-1}

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

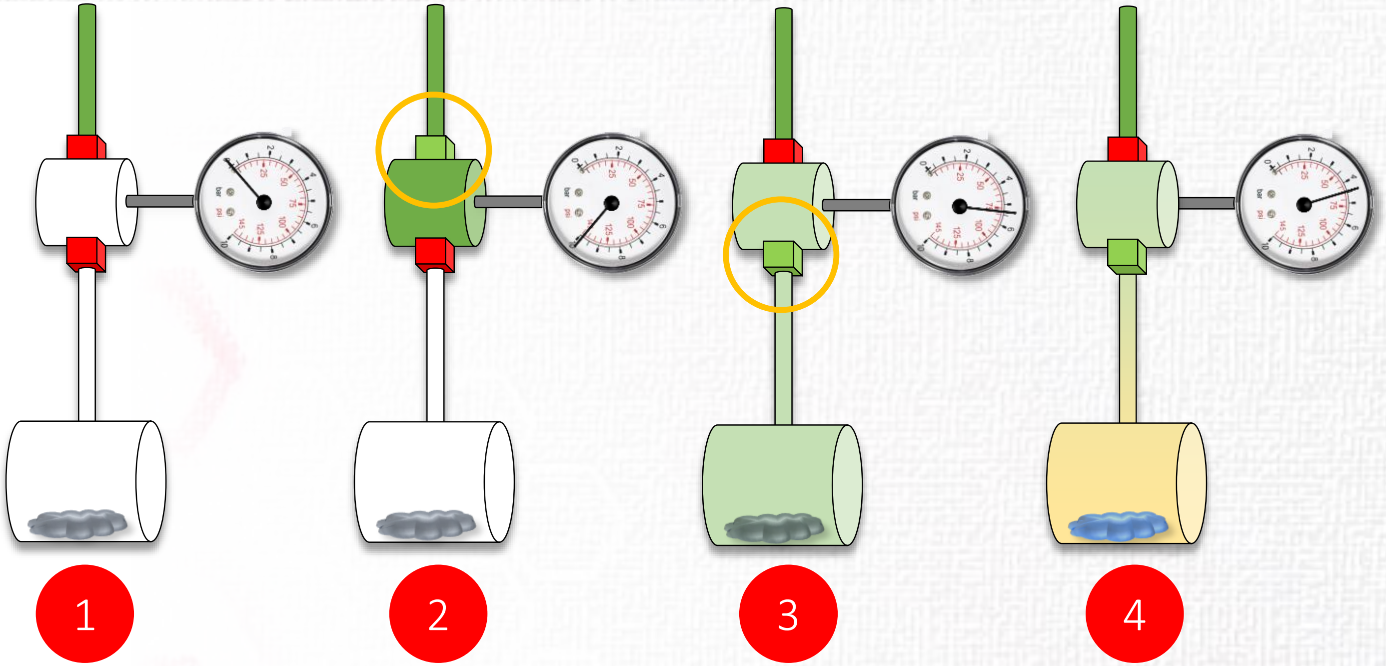


Technically Usable Sorption Capacity

dq = 0.445 mmol g^{-1}

3. Examples – II Mixture Isotherms

General



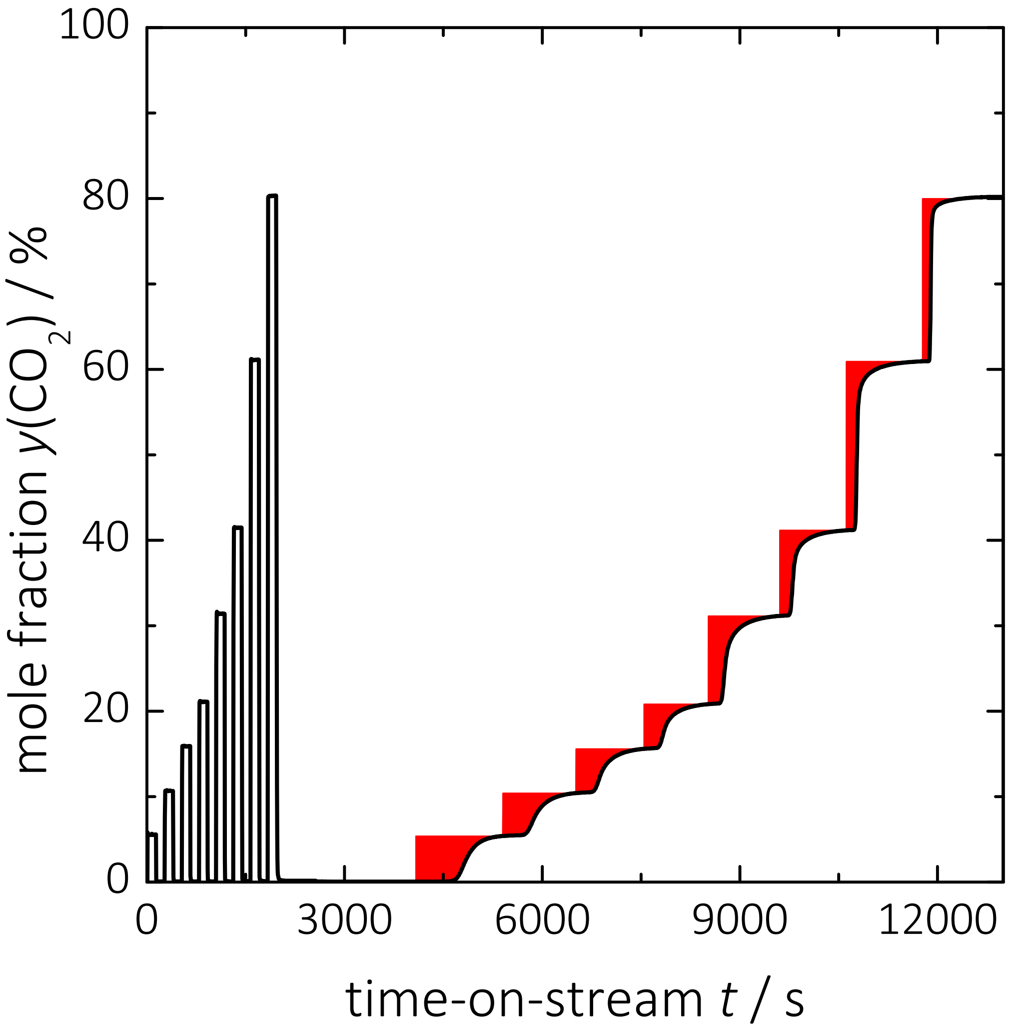
1. Gas Mixture (Green), consisting of Gas 1 (Blue) and Gas 2 (Yellow)
2. Dosing the Gas Mixture (Green) into the Manifold
3. Dosing the Gas Mixture (Green) from the Manifold into the Sample Cell
   → Which Gas is being adsorbed?
   You have to analyze the **Gas Composition**!
4. Assuming that Gas 1 (Blue) is preferentially adsorbed
   → Formation of a **Concentration Gradient** throughout the Sample Cell+Manifold

To measure Mixture Isotherms

- **In Closed System:** Analyze **Gas Composition** and **Pressure** and continuously **mix** the Gas Phase in the Sample Cell+Manifold!
- **In Open System:** Use **Gas Flow Methods** by analyzing **Gas Composition** and continuously **supplying fresh gas**

3. Examples – II Mixture Isotherms

Sequences of Breakthrough Curves



- 20 °C, 2 L min^{-1}
- 10 bar (pressurization with N_2)
- Inlet compositions: From **5 %** CO_2 to **80 %** CO_2 in N_2

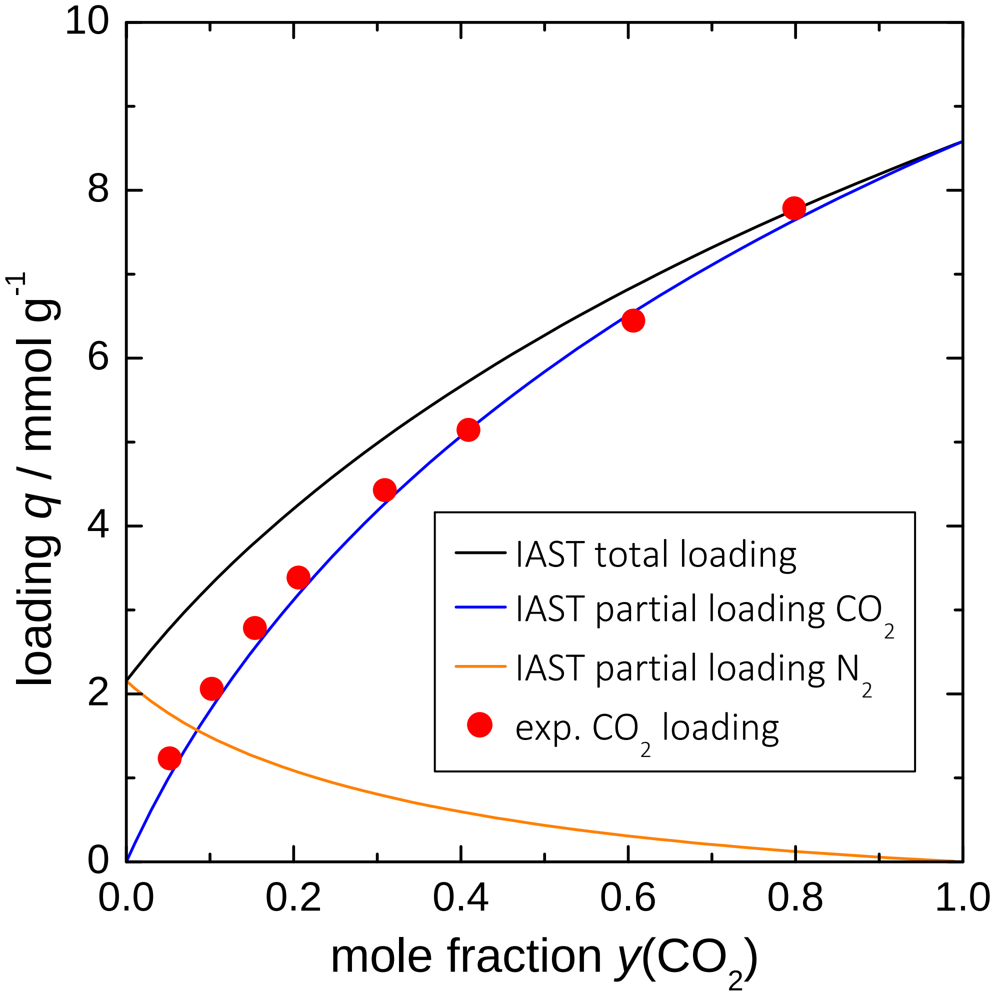
Procedure:

- Starting the next experiment with a higher concentration after breakthrough is steady-state
- **Integration** and **summation** gives the partial loadings of the analyzed component
- Volume Fraction and Total Pressure give the Partial Pressure of CO_2

→ **Mixture Isotherm of CO_2 in N_2**

3. Examples – II Mixture Isotherms

Mixture Isotherm of CO_2 in N_2 @ 10 bar, 20 °C



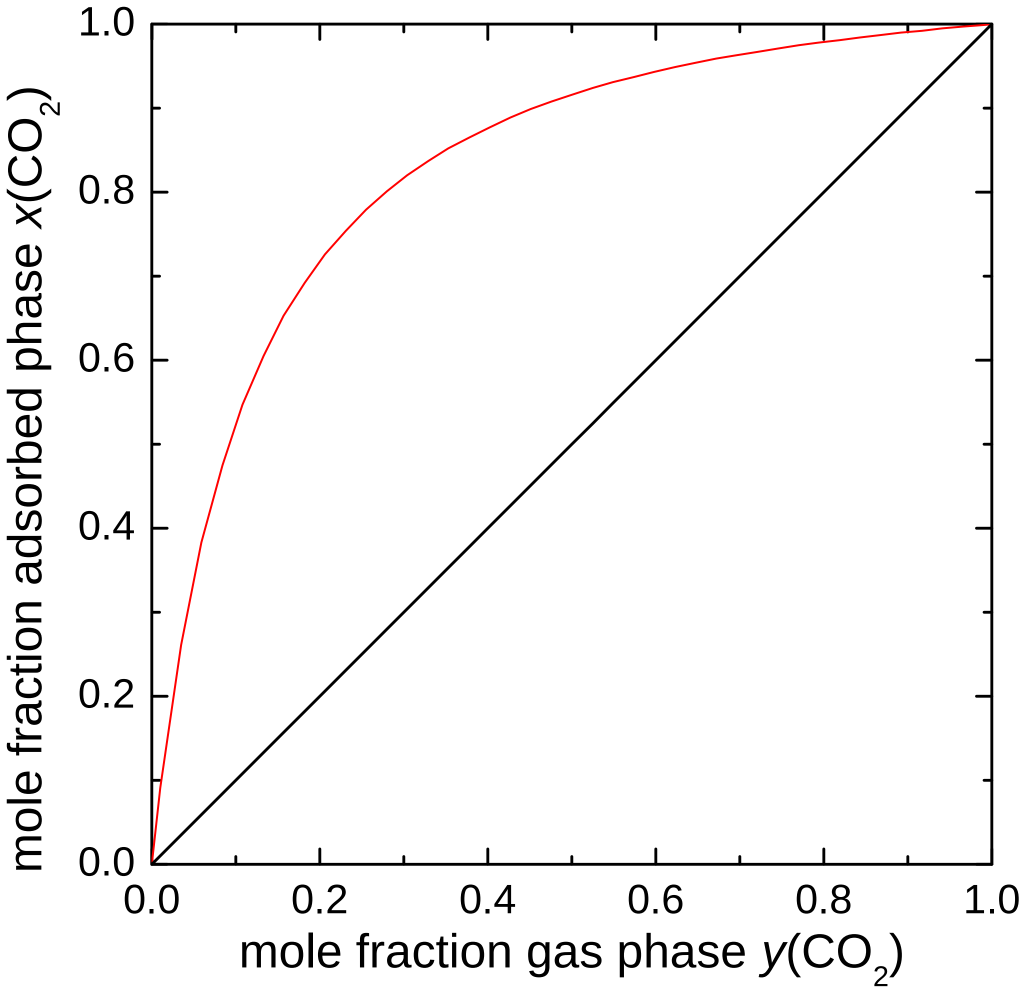
- Measured data (red) compared to **IAST** model (Ideal Adsorbed Solution Theory)
- The model predicts mixture isotherms by using pure component isotherms (CO_2 and N_2)
- Mixture of CO_2 and N_2 shows **ideal** behavior

→ We determined the **partial loading** of CO_2 on an adsorbent in a CO_2/N_2 gas mixture

A. L. Myers, J. M. Prausnitz, AIChe J. 11 (**1965**) 129

3. Examples – II Mixture Isotherms

x/y-Plot @ 10 bar, 20 °C

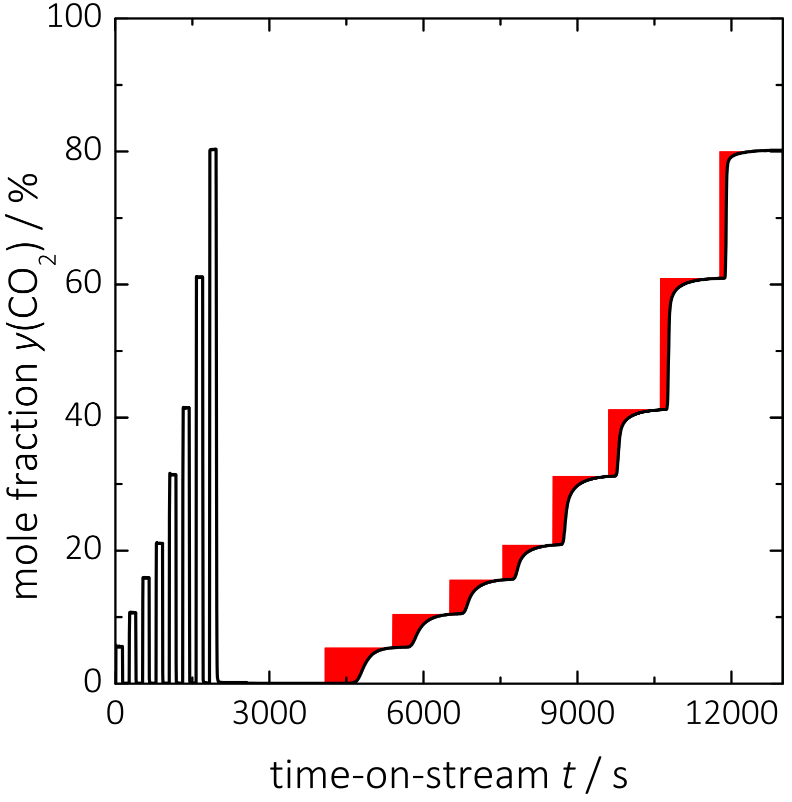


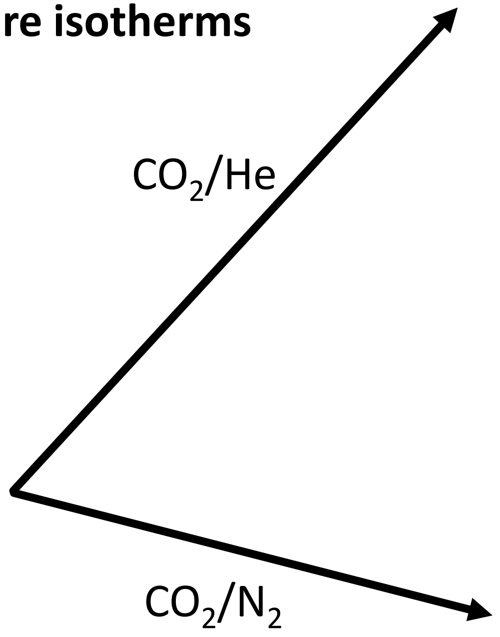
- **IAST** model allows to calculate the **adsorbate** composition at a certain **gas** composition
- x/y-plot
- Visualizes the **enrichment of CO_2** on the surface
- Important information for **separation** processes

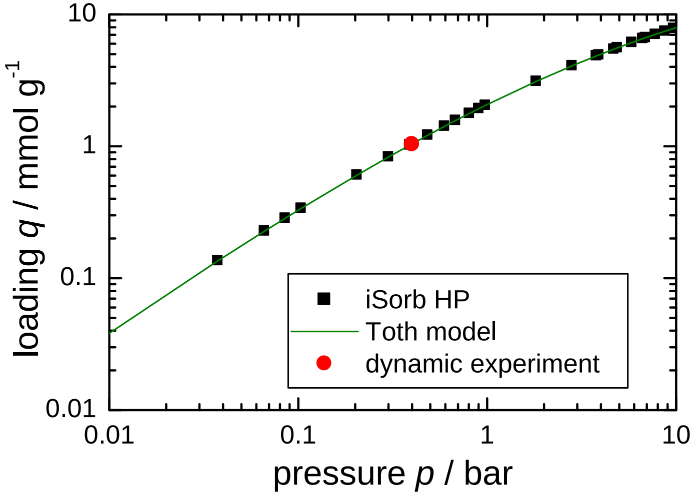
3. Examples – II Mixture Isotherms

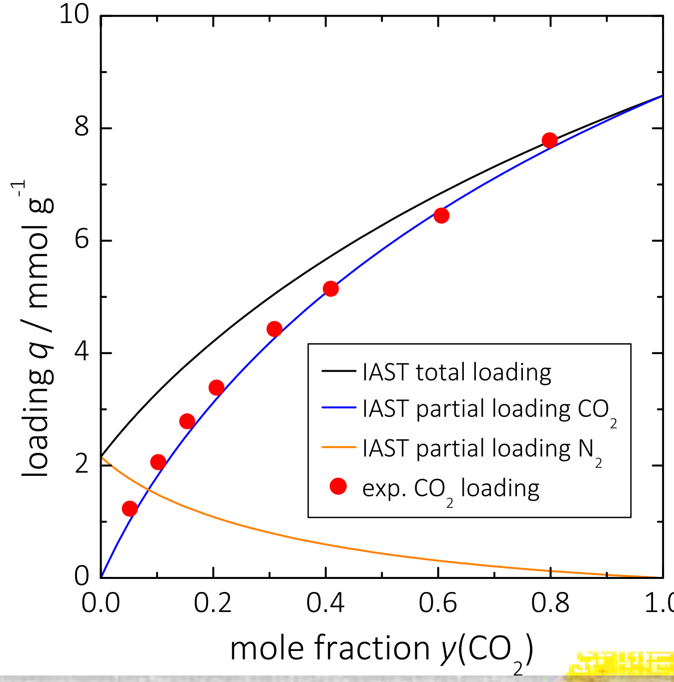
Isotherms

- Using **Helium** as one component and assuming that it is **not adsorbed** allows measurement of **pure component isotherms**
- Using **other gases** than Helium yields in **mixture isotherms**









3. Examples – III Natural Gas, Biogas Purification

General

- Removal of CO_2 from Biogas or Natural Gas to increase **Heating Value**
- Raw Biogas contains up to **50 % CO_2**
- Biogas: Pressure during Adsorption = 2-16 bar.
- Natural Gas: Pressure during Adsorption = 20-80 bar.
- Adsorbents: Zeolites, Carbon Molecular Sieves

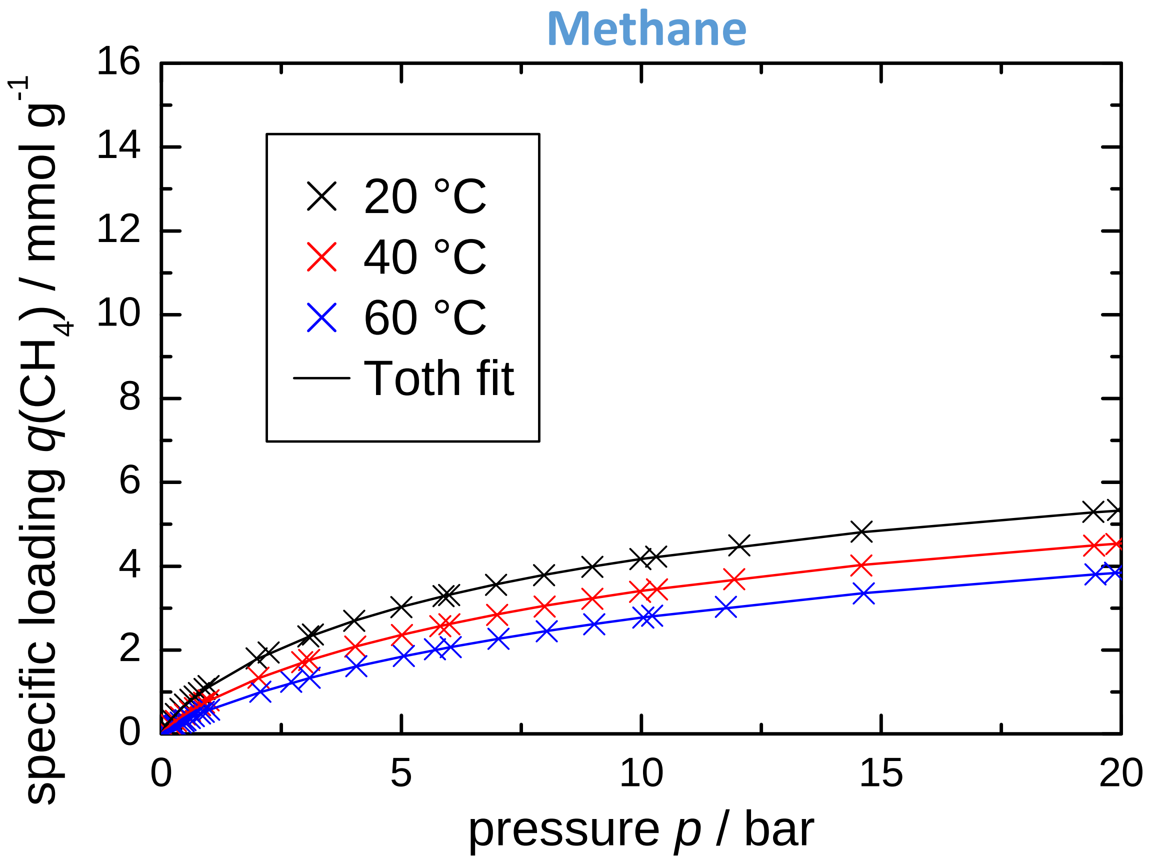
How about Activated Carbons?

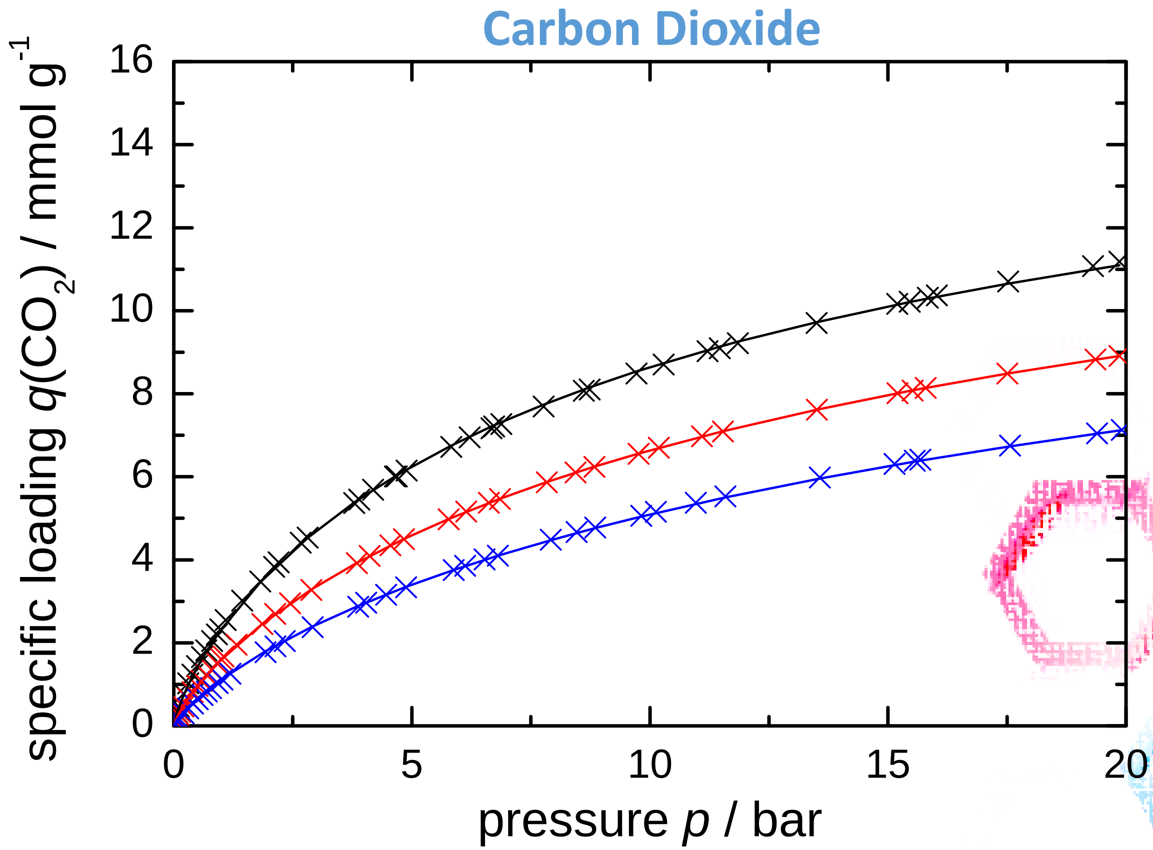
Let's compare an Activated Carbon with a Zeolite!

C. A. Grande, R. Blom, A. Möller, J. Möllmer, *Chemical Engineering Science*, **2013**, *89*, 10
Pictures: www.pixabay.com, www.wikipedia.org

3. Examples – III Natural Gas, Biogas Purification

Activated Carbons: Isotherms



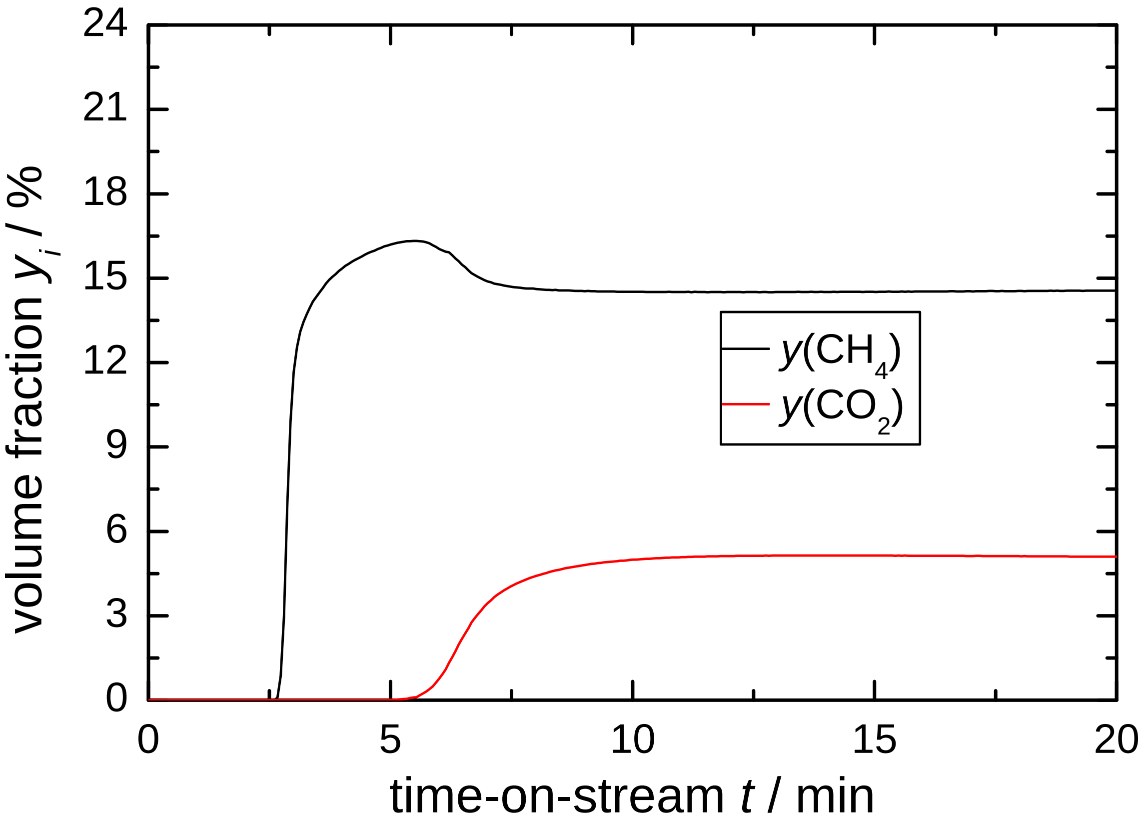


Specific loadings higher for CO_2 than for CH_4 → separation should be possible

C. A. Grande, R. Blom, A. Möller, J. Möllmer, *Chemical Engineering Science*, **2013**, *89*, 10
J. Toth, Adv. Colloid Interface Sci. 55 (**1995**) 1

3. Examples – III Natural Gas, Biogas Purification

Breakthrough Experiment on Activated Carbon

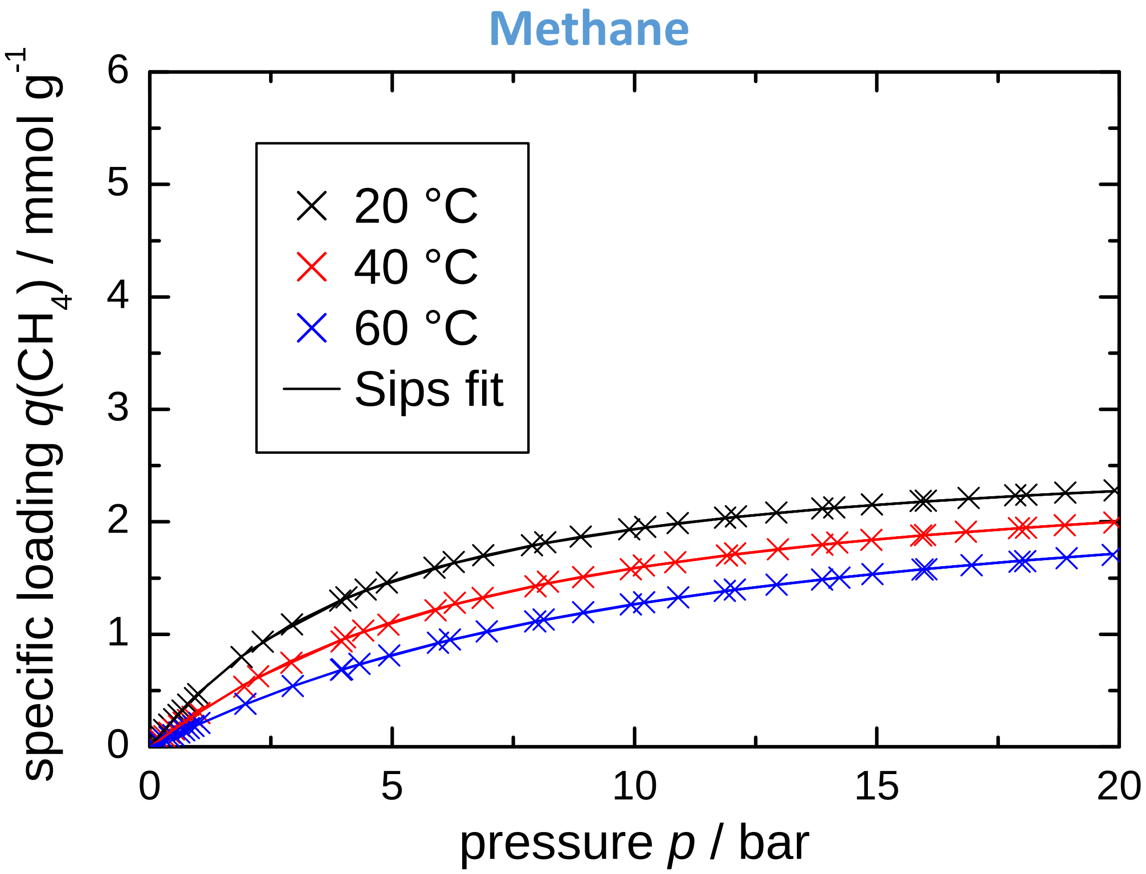


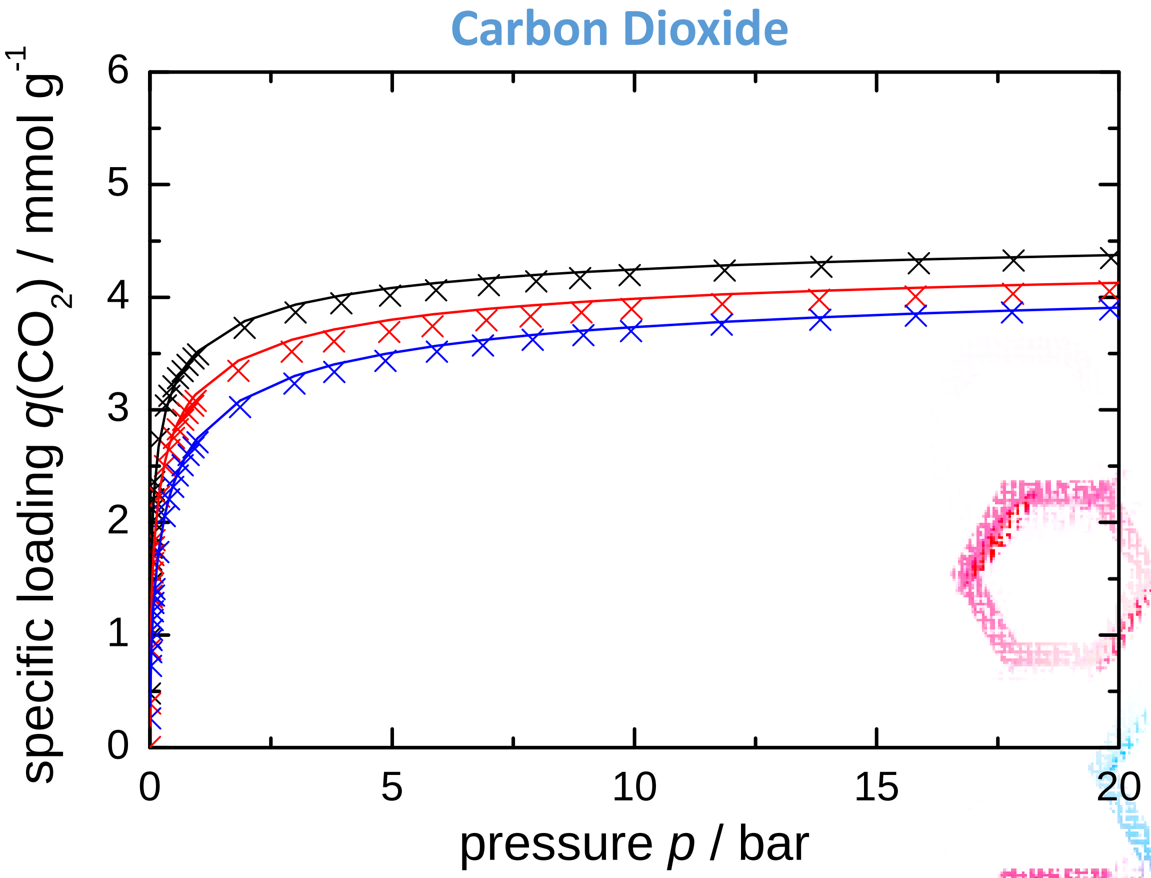
- 25 °C, 2.5 L min^{-1}
- 5 bar (pressurization with He)
- Inlet composition: 15 % CH_4, 5 % CO_2, Balance: He
- Breakthrough of CH_4 and CO_2 according to their **sorption capacities**
  → system is under thermodynamic control

C. A. Grande, R. Blom, A. Möller, J. Möllmer, *Chemical Engineering Science,* **2013**, *89*, 10

3. Examples – III Natural Gas, Biogas Purification

Zeolite 13X: Isotherms





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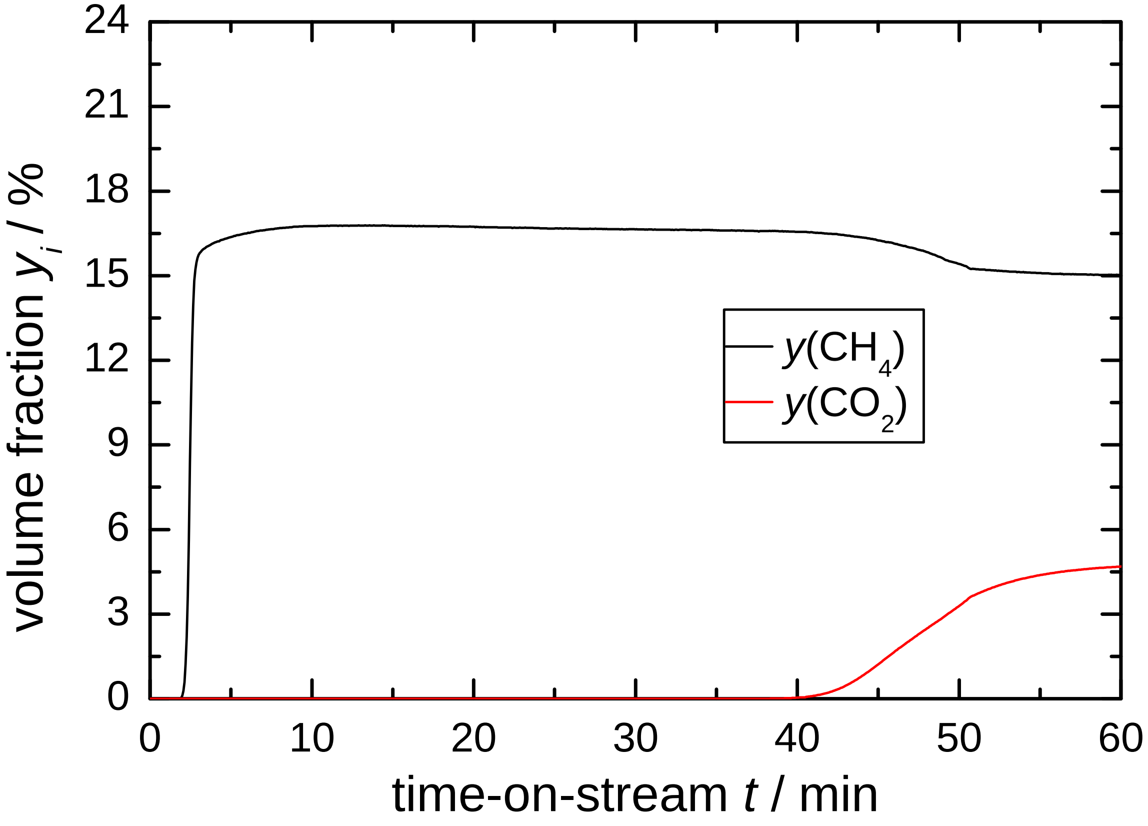
3. Examples – III Natural Gas, Biogas Purification

Breakthrough Experiment on Zeolite 13X

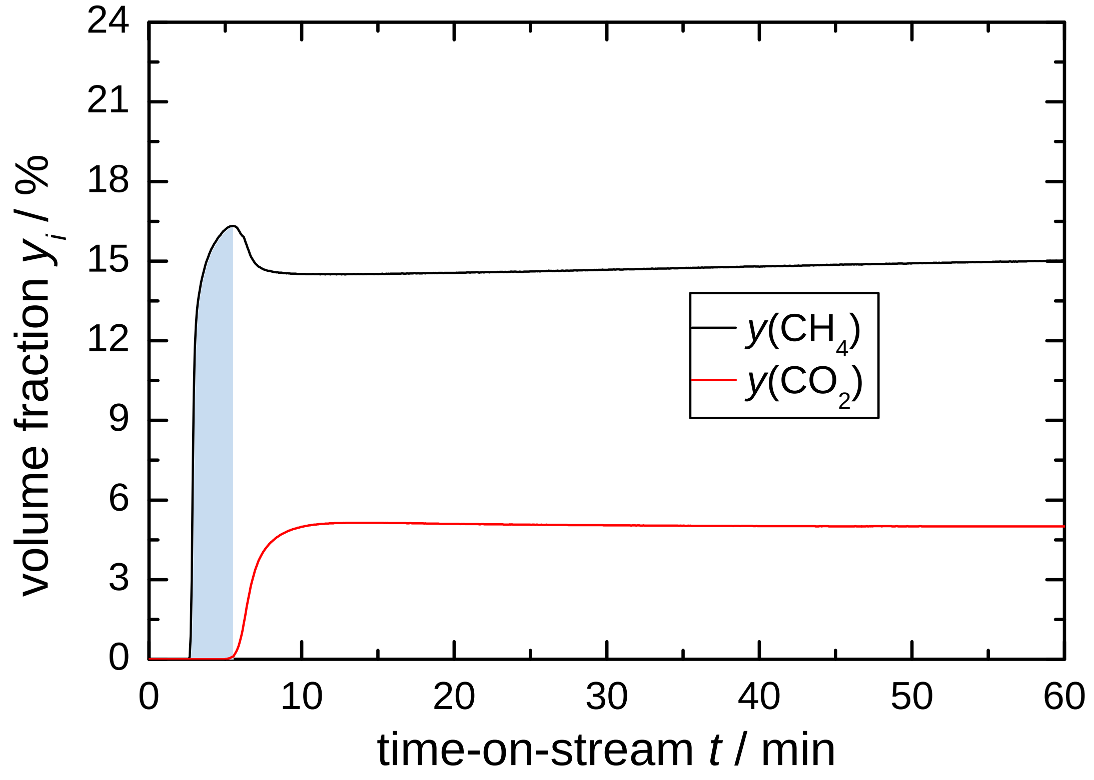


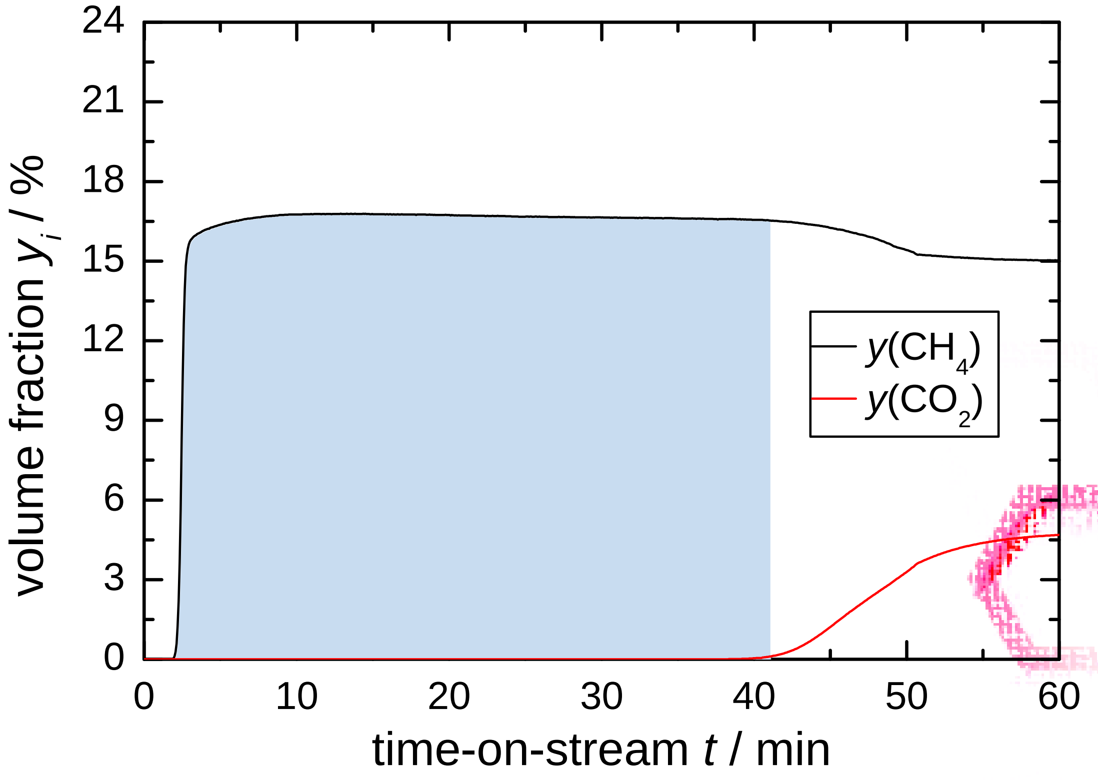
- Breakthrough of CH_4 and CO_2 according to their **sorption capacities**
  → system is under thermodynamic control
- Zeolite 13X show a very high separation performance
- Material should be used only with dry gas flows due to high affinity to water

C. A. Grande, R. Blom, A. Möller, J. Möllmer, *Chemical Engineering Science,* **2013**, *89*, 10

3. Examples – III Natural Gas, Biogas Purification

Activated Carbon – Zeolite 13X: Comparison





Classical Activated Carbons
Selectivity not high enough for economic separation of CH_4 and CO_2!

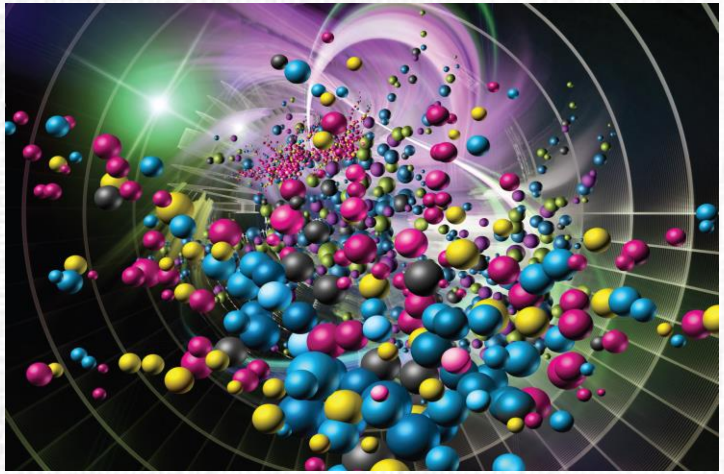
Zeolite 13X:
Very high selectivity enables applications for the separation of CH_4/CO_2 gas mixtures.

C. A. Grande, R. Blom, A. Möller, J. Möllmer, *Chemical Engineering Science,* **2013**, *89*, 10

3. Examples – IV Air Separation

General

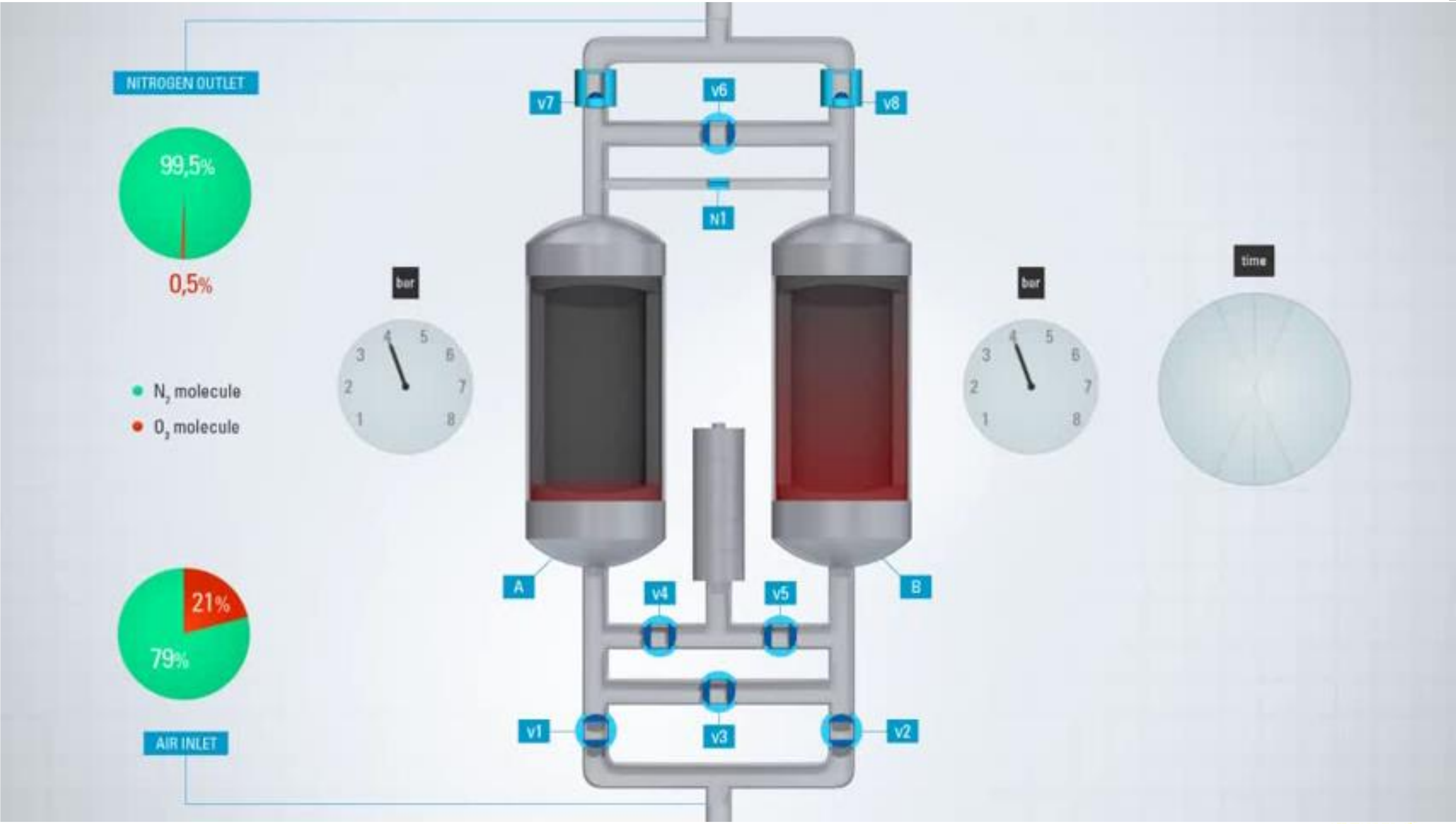
- Air separation for O_2 and N_2 production [production of inert gases, medical applications, steel industry,...]
- Usually done with Pressure Swing Adsorption (PSA)
- Carbon Molecular Sieves (CMS), Zeolites
- Ambient temperatures
- Pressure during Adsorption: 1.1 – 11 bar, typically 8 bar.
- Pressure during Desorption: 0.07 – 1 bar.



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

3. Examples – IV Air Separation

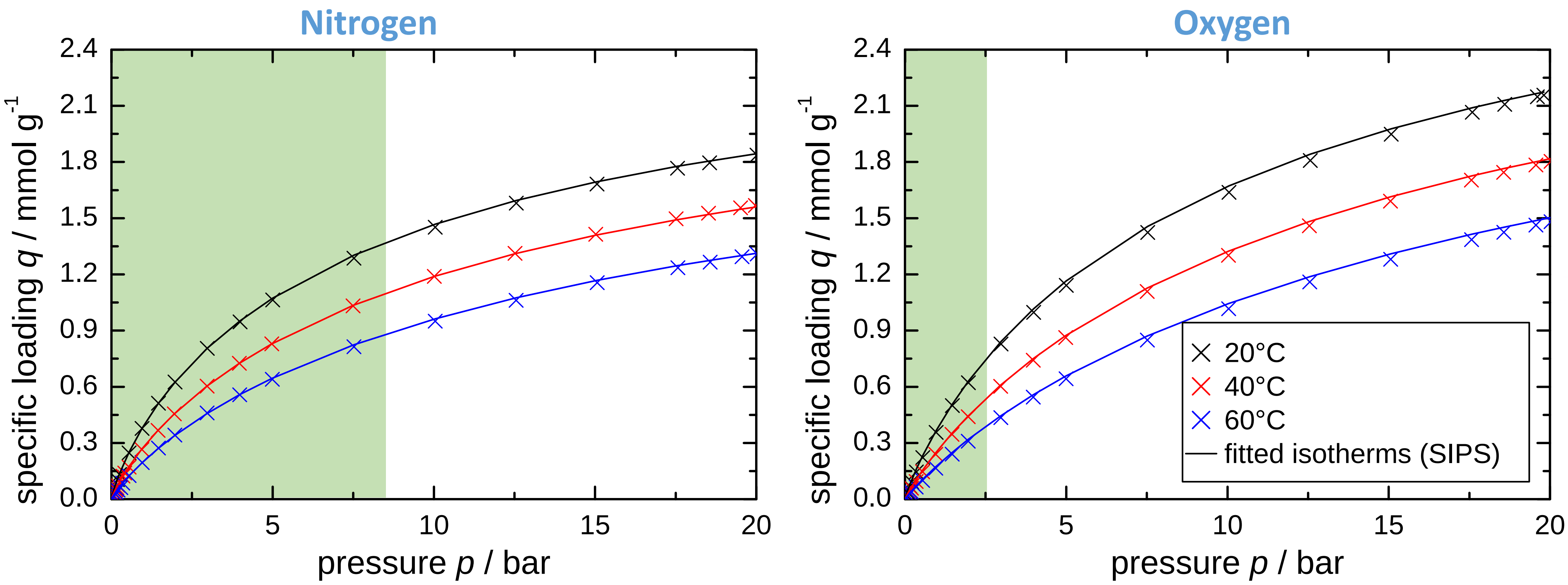
Video



Source: https://www.youtube.com/watch?v=j5mopdfEjq8

3. Examples – IV Air Separation

Isotherms: Carbon Molecular Sieve (CMS)

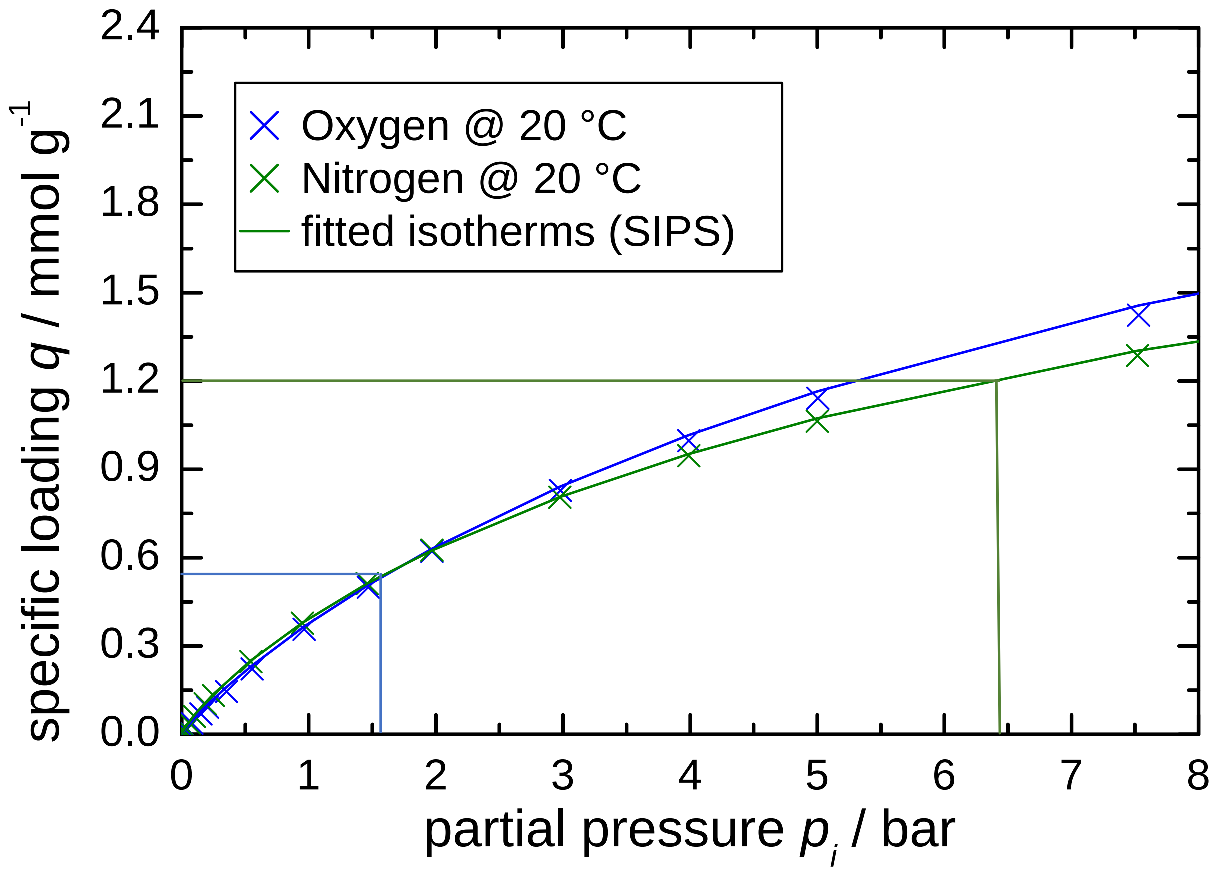


Industrial relevant range

A. Möller, J. Guderian, J. Möllmer, M. Lange, J. Hofmann, R. Gläser, *Chemie Ingenieur Technik* **2013**, *85, 11,* 1680

3. Examples – IV Air Separation

Carbon Molecular Sieve (CMS) - Isotherms:



- Assuming 8 bar Air = $N_2 : O_2 = 4 : 1$

  → partial pressure $p(O_2)$ = 1.6 bar
  partial pressure $p(N_2)$ = 6.4 bar

- According to isotherms, we would **more N_2 than O_2** in adsorbed phase

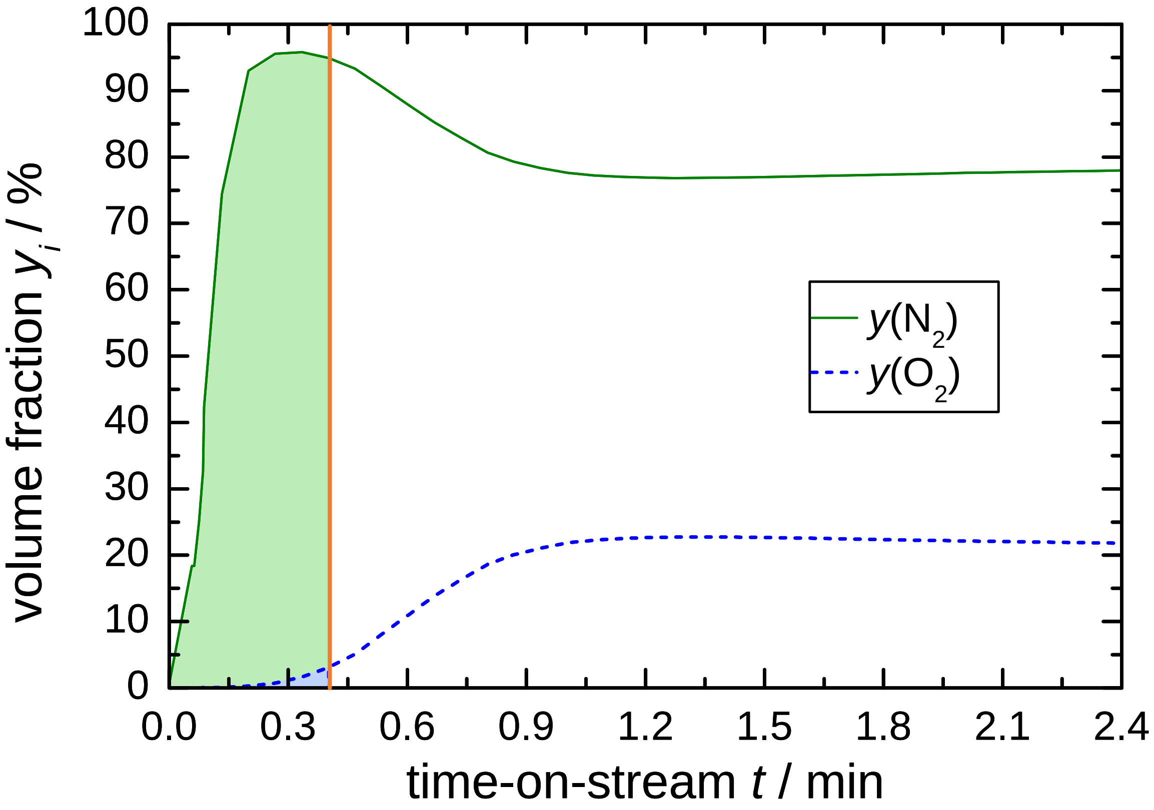
  → 1.2 mmol g^{-1} N_2
  0.5 mmol g^{-1} O_2

But this CMS material is used for the exact opposite case!
→ More O_2 in the adsorbed phase

Adsorption of N_2 is much slower than adsorption of O_2 → Kinetic Separation under Flow Conditions.

3. Examples – IV Air Separation

Carbon Molecular Sieve (CMS) - Breakthrough Curve:



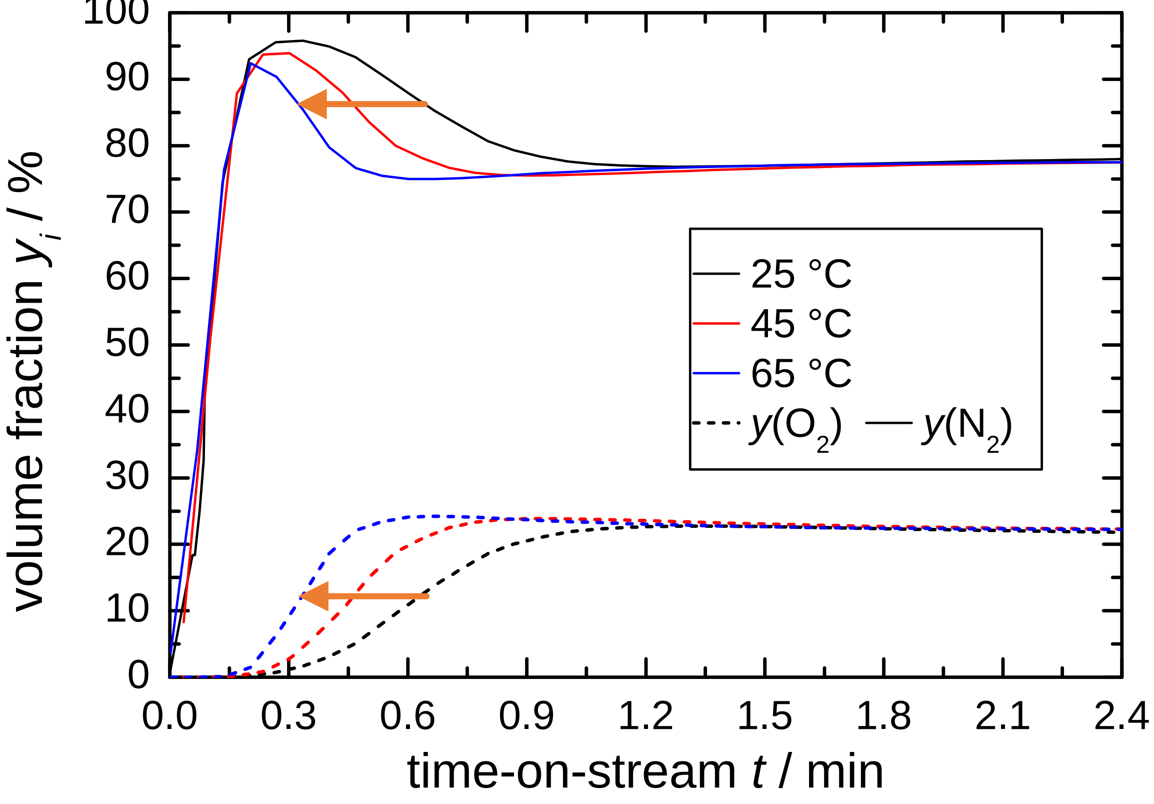
- 25 °C, 5 L min^{-1}
- 8 bar (pressurization with He)
- Inlet composition: 80 % N_2, 20 % O_2

- Spontaneous Breakthrough of N_2
- Adsorption of O_2 is faster
  → O_2 is held back by the adsorber bed
- Production time of pure N_2
- Stopping cycle at a certain breakthrough of O_2

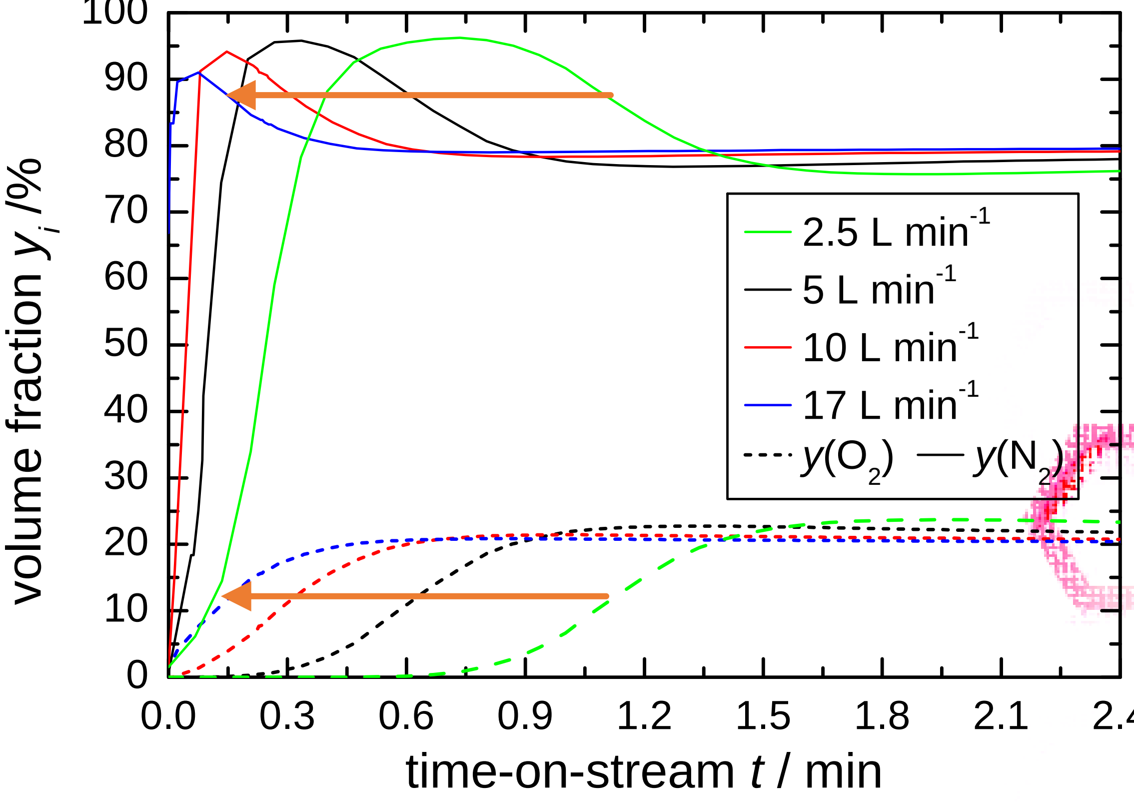
3. Examples – IV Air Separation

Carbon Molecular Sieve (CMS) - Breakthrough Curves:

Temperature Variation at 5 L min^{-1}



Flow Rate Variation @ 25 °C



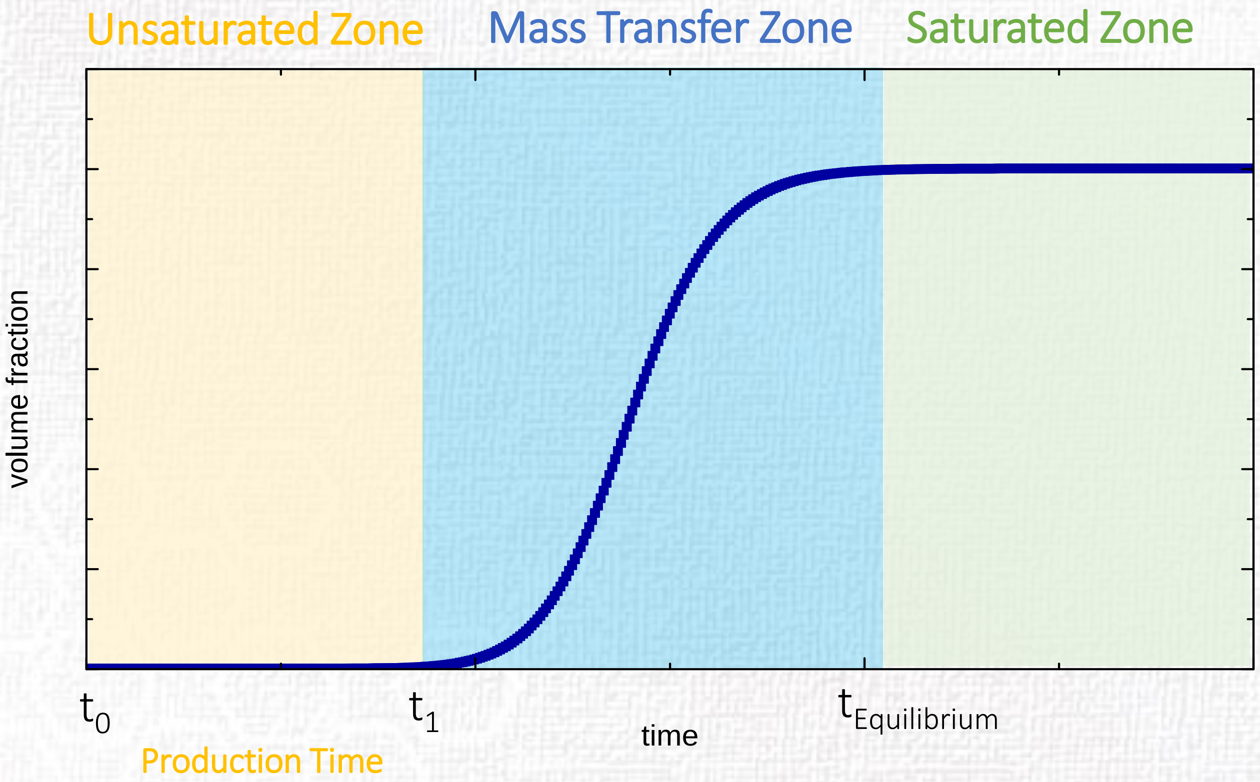
With increasing temperatures
→ Decreasing cycle times

With increasing flow rates
→ No spontaneous breakthrough of O_2

4. Simulation

Parametric Studies & Kinetics

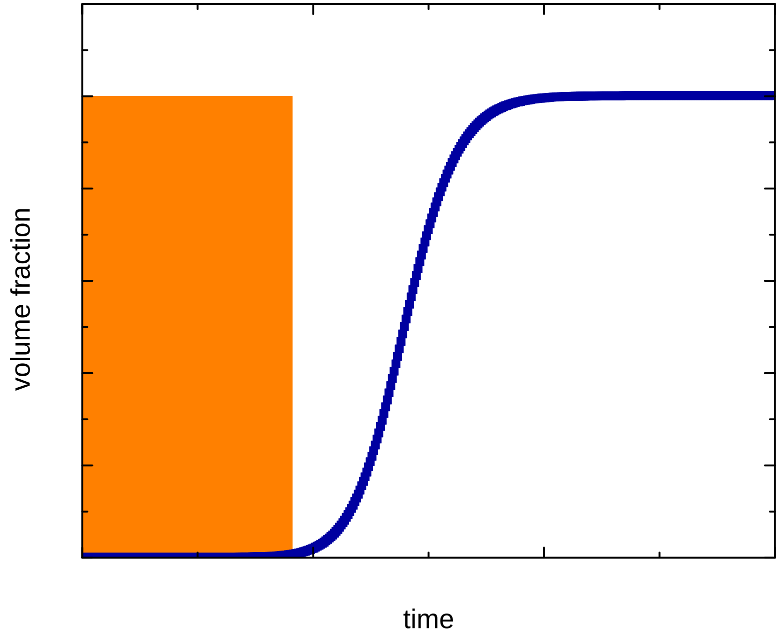
- **Understanding** of Sorption Characteristics on Fixed Bed Adsorbers
- **Experimental time** can be drastically **reduced** and parametric studies can be easily performed
- Calculation of **Equilibrium Data of Mixtures** from Pure Component Isotherms
- Evaluation of Breakthrough Curves based on **Mass- and Energy Balances**



4. Simulation

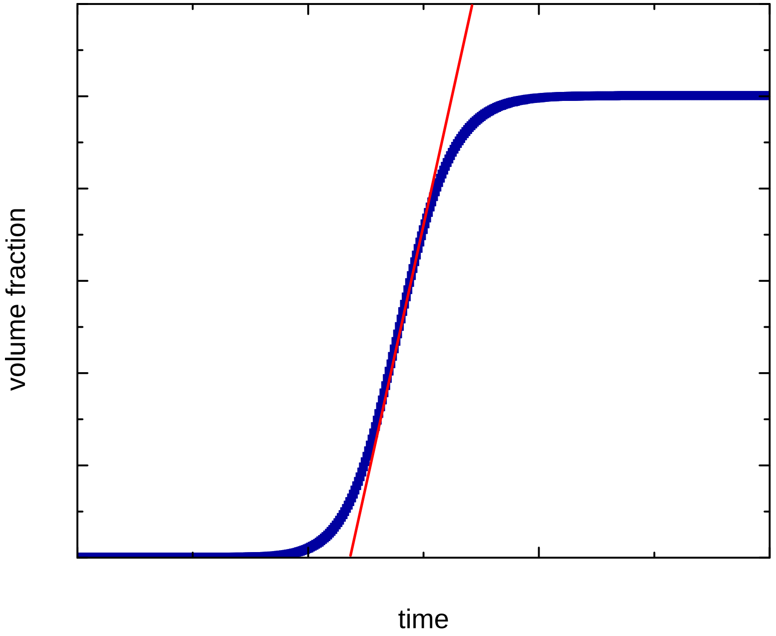
Different Segments

Unsaturated Zone



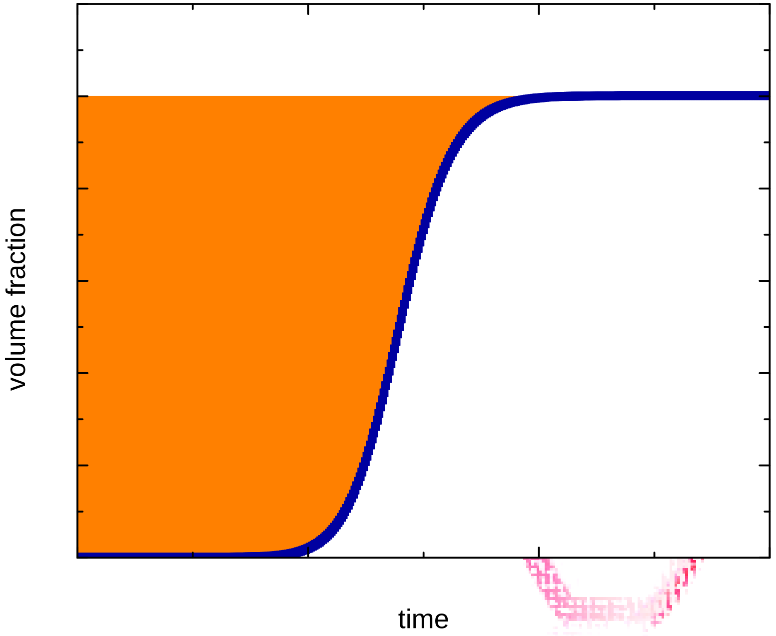
- Determination of **technical usable sorption capacity**
- Can be used as **benchmark** for separation performance of adsorbents

Mass Transfer Zone



- **Mass Transfer** coefficient, axial dispersion, shape of isotherm
- **Heat effects**, heat dissipation
- The time interval of mass transfer zone has to be **minimized**

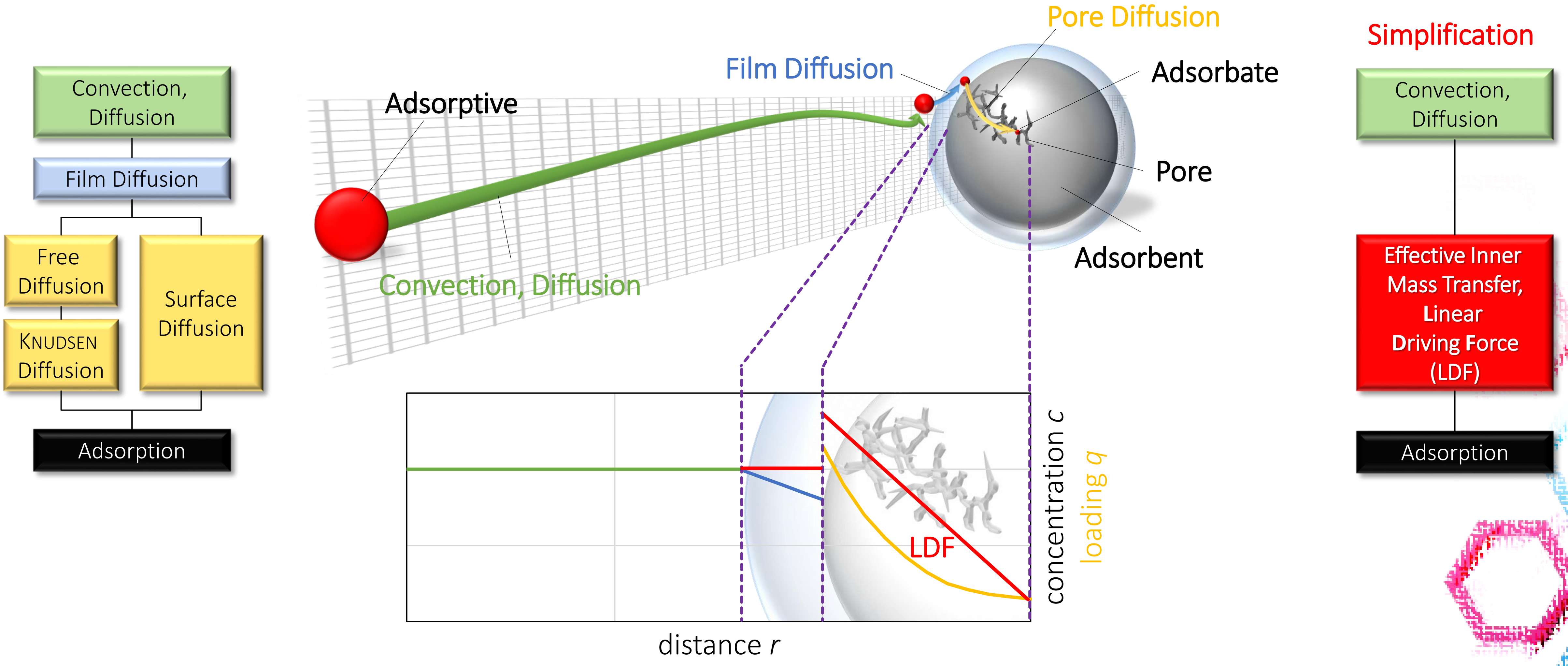
Saturated Zone



- Determination of **saturation capacity**
- By assuming of thermodynamic controlled system → Measurement of **isotherms** possible

4. Simulation

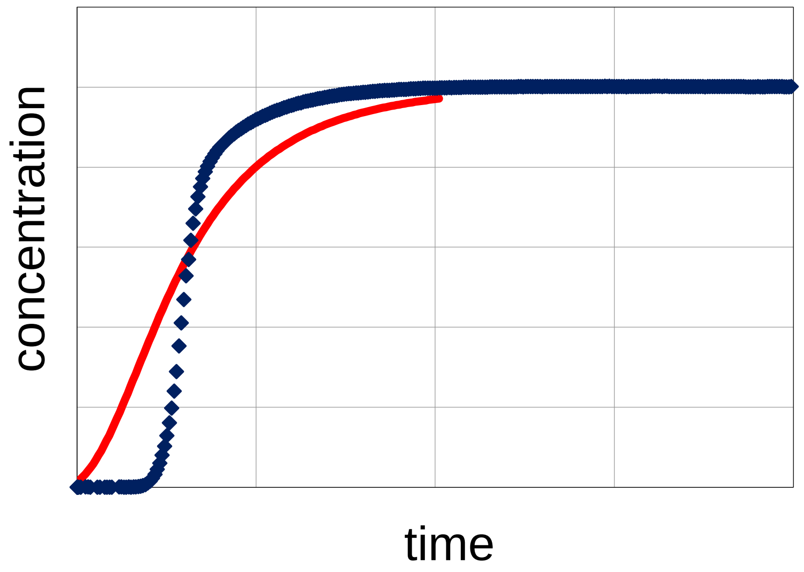
Mass Transfer coefficient k_{LDF}



D. Bathen, M. Breitbach, *Adsorptionstechnik*, 1.Aufl., Springer Verlag, Heidelberg, **2001**.
W. Kast, *Adsorption aus der Gasphase: Ingenieurwissenschaftliche Grundlagen und technische Verfahren*, 1.Aufl., VCH Wiley Verlag, Weinheim, **1988**.

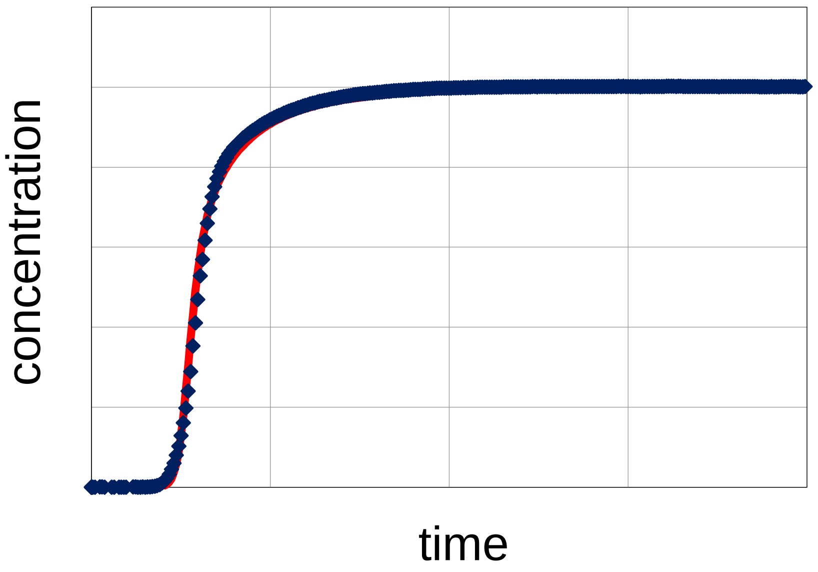
Mass Transfer coefficient k_{LDF}

- Fitting of **simulated** Breakthrough Curves to Experimental Data
- Requirement: Isotherms



Experimental Breakthrough curve (blue) and Simulated data (red) **before** fitting

k_{LDF} **= 1 min^{-1}**



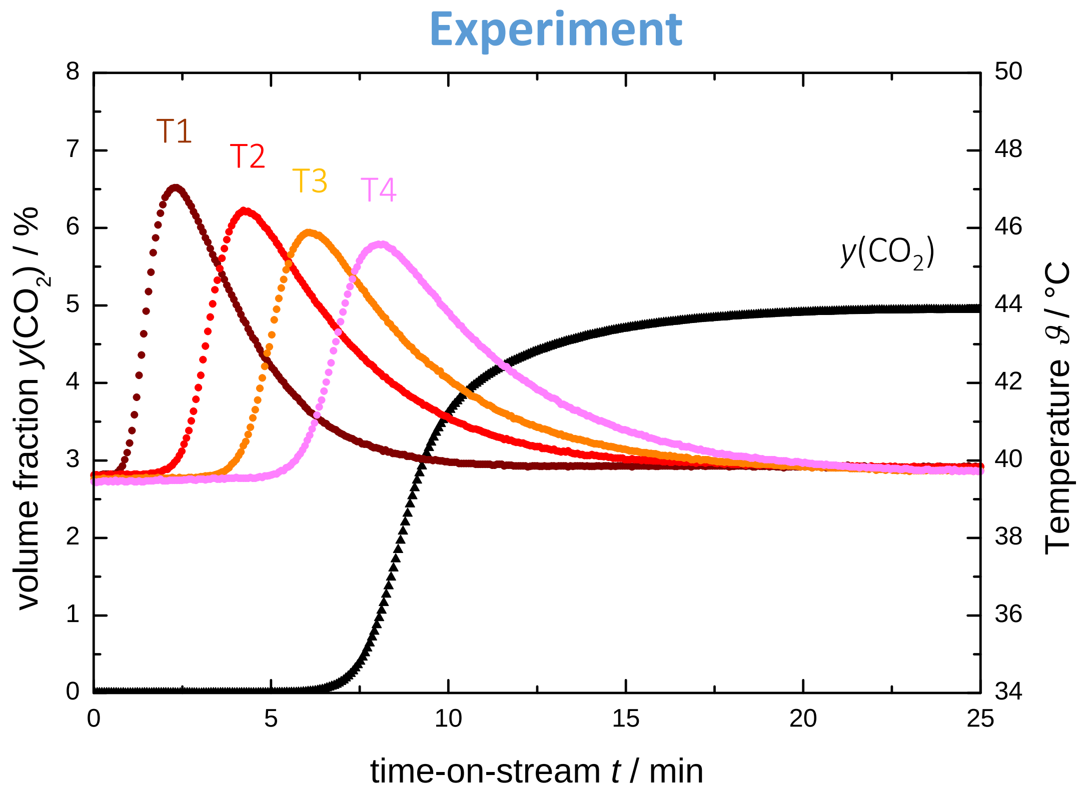
Experimental Breakthrough curve (blue) and Simulated data (red) **after** fitting

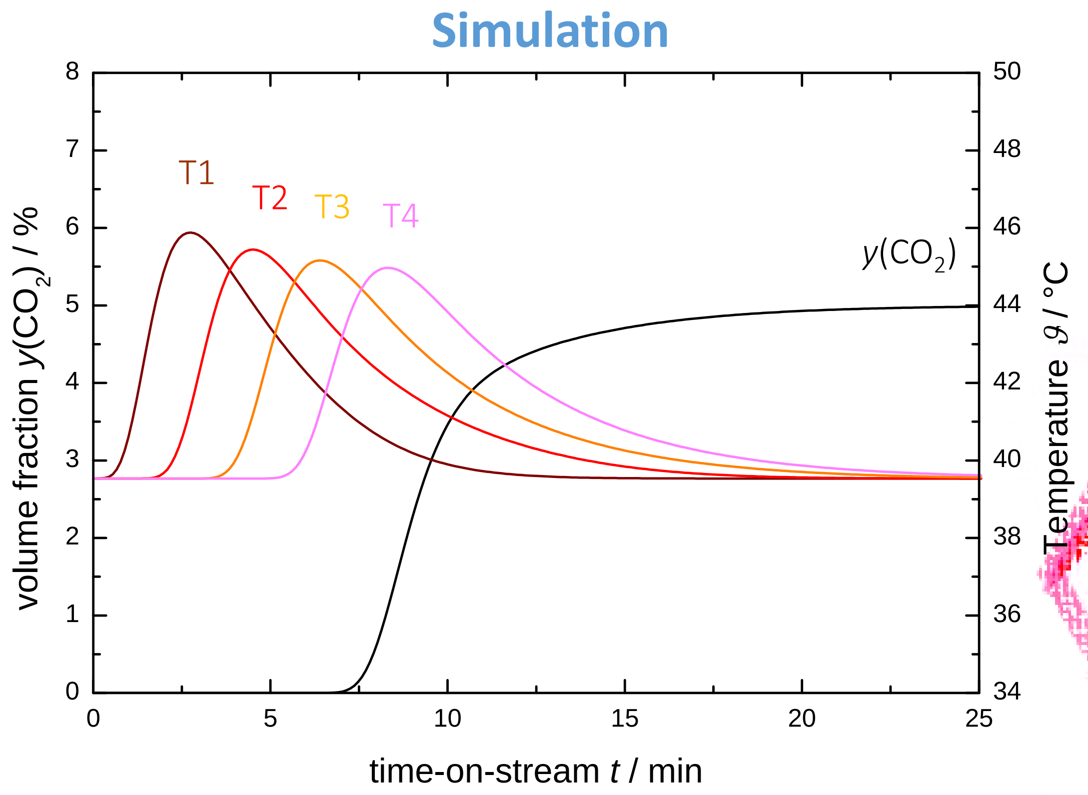
k_{LDF}**=11.7 min^{-1}**

Comparison for different materials under same testing conditions allows statements about the kinetic performance

4. Simulation

Fitting of Breakthrough Curves + Temperatures

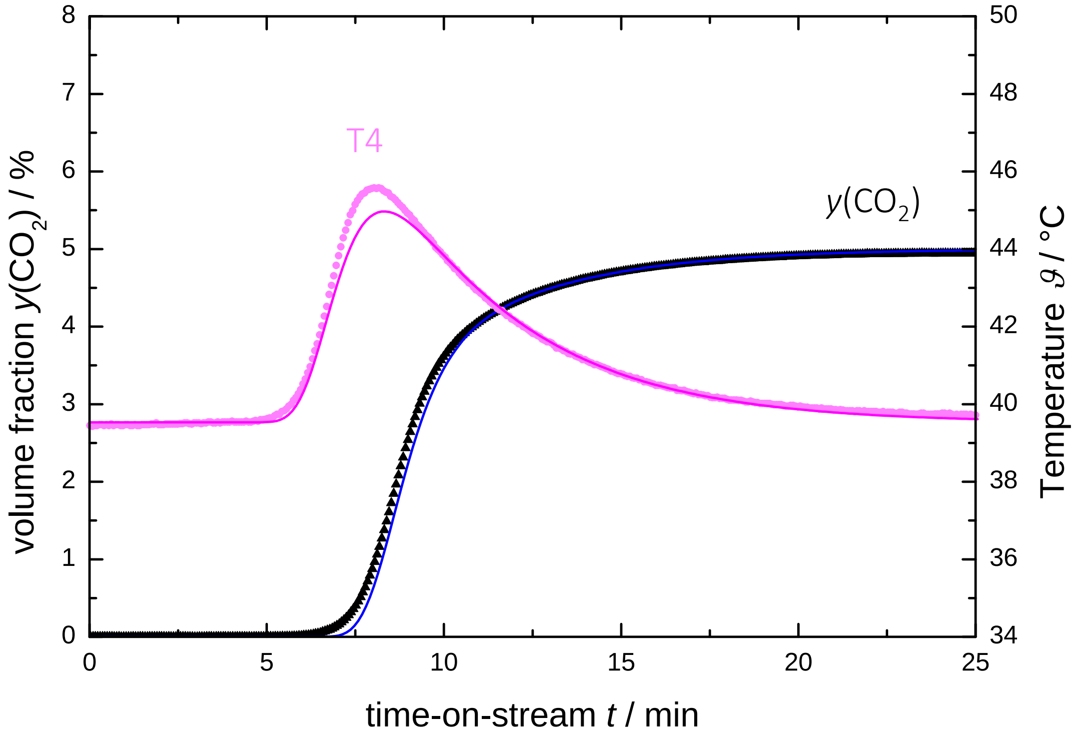




- After fitting the k_{LDF} **Mass Transfer Coefficient** → Good Agreement of Experiment and Simulation in a Standard Breakthrough Example (5% CO_2 in N_2)
- Course of Volume Fraction and Temperatures is depicted correctly

4. Simulation

Fitting of Breakthrough Curves + Temperatures

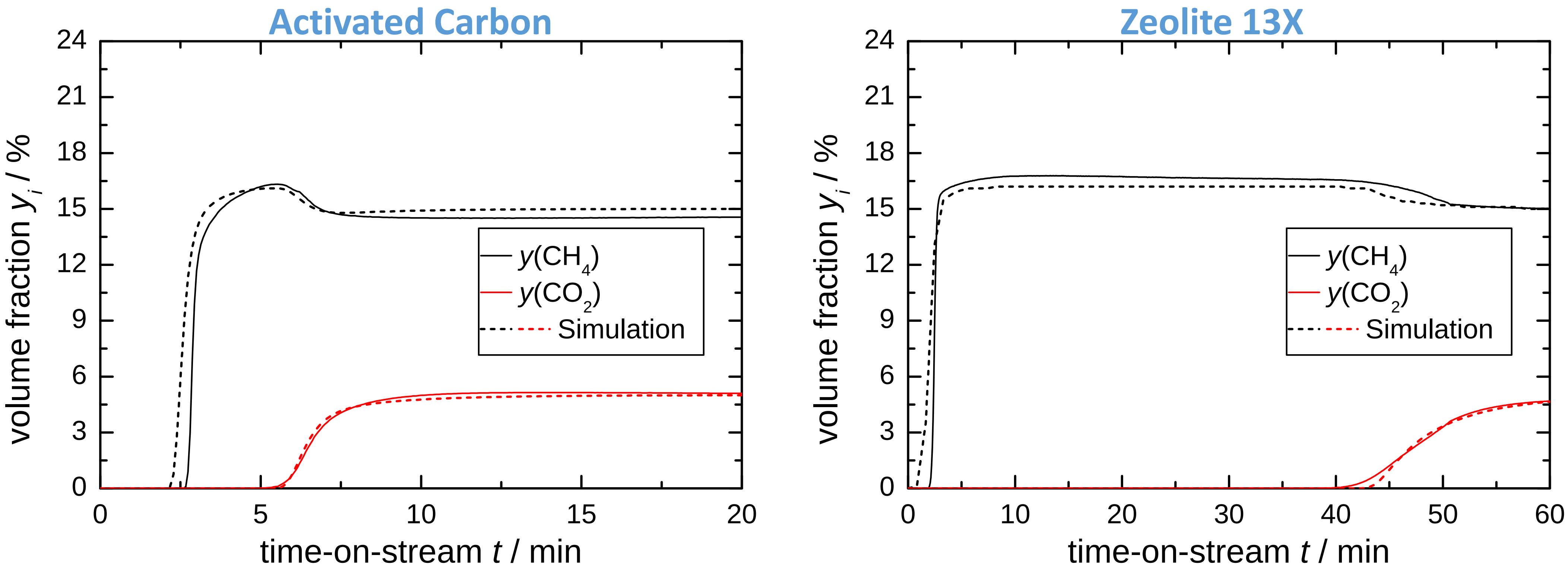


Overlay of Experiment (Points) and Simulation (Line)

- 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

4. Simulation

Fitting of Example III: Activated Carbon – Zeolite 13X Comparison



- Co-Adsorption and Displacement Phenomena can also be simulated

5. Conclusions

- Gas-Flow Methods allow Characterization under **application-related conditions**
- Information that are only accessible by Gas-Flow Methods (*i.g.* Breakthrough Curves):
  - ✓ **Technically usable Sorption Capacity**
  - ✓ Separation performance under application-related conditions
  - ✓ Kinetic Data about Mass Transfer and Energy Transfer
- Measuring **Mixture Data** easily **possible**
- Better transfer of results into **technical processes**
- Simulation and fitting to measured data makes **mass transfer parameters** accessible
- Simulation then **reduces experimental effort** and improves the **understanding** of separation processes

Thank You!

Thank you for your attention!