

Dieter Bathen, Frederik Berg*

Dynamic Simulation of Gas-Phase Adsorption Processes

Symposium on Dynamic Sorption, Leipzig

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* Prof. Dr.-Ing. Dieter Bathen

Lehrstuhl für Thermische Verfahrenstechnik
Universität Duisburg-Essen



IUTA e.V.
Institut für Energie- und Umwelttechnik, Duisburg



1. Introduction
2. Simulation of Isothermal Adsorption Processes
3. Simulation of Non-Isothermal Adsorption Processes
4. Specific Adsorption Parameters
5. Sophisticated Simulations
6. Summary
7. Recent Selected Publications

1. Introduction



Facts & Data IUTA (2016):

Employees:	ca. 140
Offices:	2.400 m ²
Pilot Plant Area:	5.200 m ²
Industrial Cooperations:	ca. 360
R&D-Cooperations:	ca. 150
Turnover:	8,7 (+ 5,1) Mio €



Facts & Data TVT (2017):

Employees:	15 + 5 + (12)
Offices:	160 m ²
Laboratory:	200 m ²
Third Party Funding:	450 T€

1. Introduction

The Future of Adsorption Technology

Driving Forces for „Classic“ Adsorption Technology

- Worldwide Reduction of Emission Limits
- Growing Market in Energy Production, Storage and Conversion
- Growing Market in Downstream Processing (Biotechnology)
- Growing Demand for Ultra-pure and for Toxic Chemicals

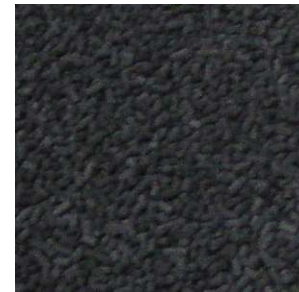
Growing Market for „Hidden“ Adsorption Technology

- New Applications in (High Price) Consumer Sector
- Retarding Pharmaceuticals/Ingredients
- Combination Adsorption + Textiles

High Demand for Research in Adsorption Technology

- Multi-functional and „Cross-over“ Adsorbents
- Efficient Characterisation of Adsorbents
- Adsorption at lowest Concentrations
- Link between Molecular Scale and Process
- Computer-Aided Design of Adsorption Processes (without any Experiments)

1. Introduction



Development of an Adsorption Process

- Choice of Adsorbent
- Adsorption Isotherms (Thermodynamics)
- Breakthrough Curves (Kinetics & Dynamics)
- Desorption Method
- Scale Up



1. Introduction

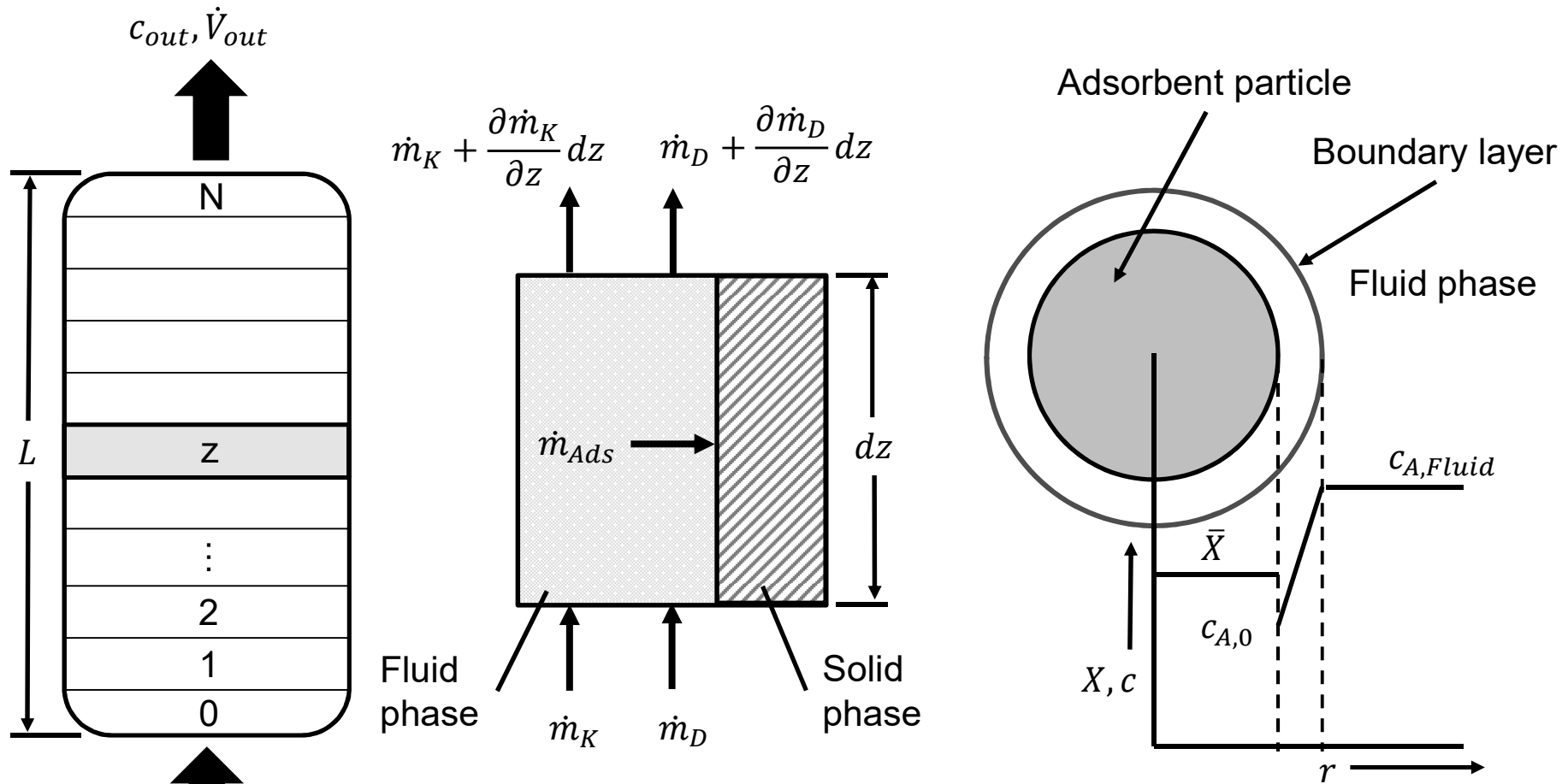
Current research activities (doctorates):

- Coupling of Volumetric and Calorimetric Adsorption Measurements (C. Bläker)
- Characterisation of Adsorbents (J. Treese -> J. Muthmann)
- Adsorptive Purification of Natural Gas (S. Steuten -> V. Chowanietz -> F. Berg)
- Cryogenic Adsorption of Light Hydrocarbons (F. Birkmann -> S. Schmittmann)
- Adsorption of Toxic and Anaesthetising Compounds (R. Ortmann -> D. Bucher)
- Adsorption of Mercury from Batch Processes (M. Ambrosy)
- **Development of Adsorptive (Car) Air Conditioning (Bruckner, Robert Bosch GmbH)**
- **Development of a Rapid TSA-Process (Salazar-Duarte, Linde AG)**
- UV-Spectroscopy of Electrolyte Solutions (C. Cox -> J. Birkmann)
- Raman-Spectrometry in Absorptive Removal of CO₂ from Gases (M. Vogt, IUTA)



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2. Isothermal Adsorption Processes



$$\frac{\partial X}{\partial t} = \frac{k_{eff} \cdot (1 - \epsilon_L) \cdot A_{Sp}}{\epsilon_L} \cdot (X_{eq} - \bar{X})$$

2. Isothermal Adsorption Processes

Often used Assumptions:

- Neglect of radial gradients (T, P, c, X)
- 1D discretization of adsorber column in slices of equal height
- ...
- Geometry of particles is approximated by equal spheres
- Fluid phase obeys Ideal gas law
- Thermal conductivity is independent from concentration
- ...
- Dispersed Plug Flow-Model
- Axial dispersion calculated by approach of Wakao et al.
- ...
- Single component adsorption: no competitive adsorption of carrier gas
- Mass transfer is simplified by the linear driving force (LDF) approach
- External mass transfer resistance taken into account by film diffusion coefficient calculated from Sherwood correlation
- ...

2. Isothermal Adsorption Processes

Set of Partial Differential Equations:

- Mass balance of the solid phase:

$$\frac{\partial X}{\partial t} = \frac{k_{eff} \cdot A_{Sp}}{\rho_s} \cdot (X_{GL} - X)$$

- Mass balance of the fluid phase:

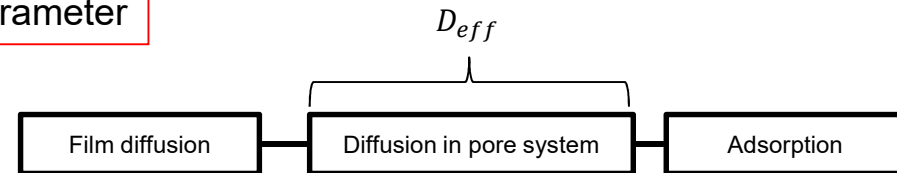
$$\frac{\partial c_A}{\partial t} = D_{ax} \cdot \frac{\partial^2 c_A}{\partial z^2} - \frac{\dot{V}_G}{\epsilon_L \cdot A} \cdot \frac{\partial c_A}{\partial z} - \frac{c_A}{\epsilon_L \cdot A} \cdot \frac{\partial \dot{V}_G}{\partial z} - \frac{k_{eff} \cdot (1 - \epsilon_L) \cdot A_{Sp}}{\epsilon_L} \cdot (X_{GL} - X)$$

Kinetic model

- Homogeneous diffusion model

$$k_{eff} = \frac{15}{R_p^2} * \frac{D_{eff}}{\frac{\rho_p}{\epsilon_P} * \frac{\partial X}{\partial c_{A,g}}} * \frac{1}{1 + \frac{\epsilon_P * 15 * D_{eff}}{R_p^2 * \beta_{Film} * A_{Sp}}}$$

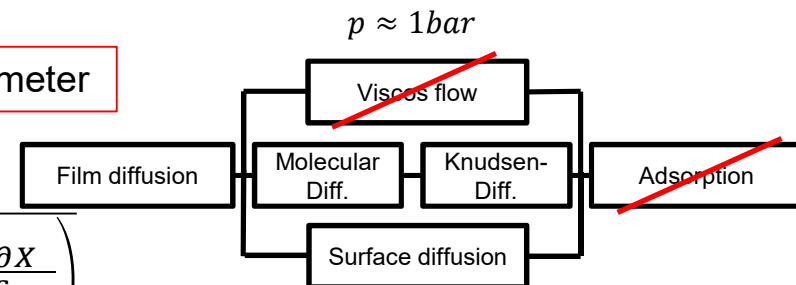
Fit parameter



- Heterogeneous diffusion model

$$k_{eff} = \frac{15}{R_p^2} * \frac{D_{pore} + \frac{D_s \cdot \rho_p}{\mu_s \cdot \epsilon_P} * \frac{\partial X}{\partial c_{A,g}}}{\frac{\rho_p}{\epsilon_P} * \frac{\partial X}{\partial c_{A,g}}} * \frac{1}{1 + \epsilon_P * \frac{15 * \left(D_{pore} + \frac{D_s \cdot \rho_p}{\mu_s \cdot \epsilon_P} * \frac{\partial X}{\partial c_{A,g}} \right)}{R_p^2 * \beta_{Film} * A_{Sp}}}$$

Fit parameter

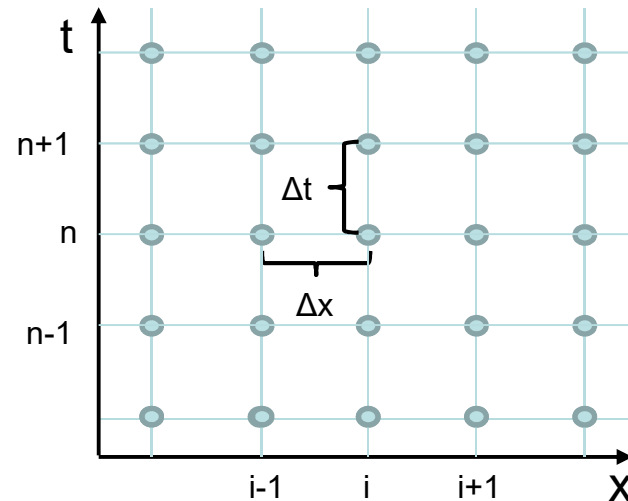


2. Isothermal Adsorption Processes

- Calculation of PDE: Finite differences method
- Transformation of PDE in FDM:

$$\text{PDE} \quad \frac{\partial u(x,t)}{\partial t} + \frac{\partial u(x,t)}{\partial x} = 0$$

$$\text{FDM} \quad \frac{u_i^{n+1} - u_i^n}{\Delta t} + \frac{u_i^n - u_{i-1}^n}{\Delta x} = 0$$



- Discretization method CFD 2 (central differences 2. order)
- Discretization e.g. (laboratory) column in about 200 slices with height of 1 mm
- Ca. 20 % of overhead increments for numerical stability
- Non linear solver: Mixed-Newton with residual convergence criteria (tolerance 1E-05)
- Integration method: implicit Euler, optionally: Runge Kutta 4. order, explicit Euler...

2. Isothermal Adsorption Processes



Initial and boundary conditions

$$X(z, t = 0) = X_0 \quad c_A(z, t = 0) = c_{A,0}$$

$$\dot{V}_G(z = 0, t) = \dot{V}_{G,in} = \text{const};$$

$$c_A(z = 0, t) = c_{A,in} \quad \frac{\partial^2 c_A}{\partial z^2}(z = L, t) = 0$$

- Specific material and fluid parameters calculated by adjoint equations
- Software for simulation PDE-solver:
 - Aspen Custom Modeler® / AdSim®
 - gProms®
 - Speed Up®
 - (Comsol Multiphysics®)
 - AdLin® (Linde Inhouse Software)
 - ...

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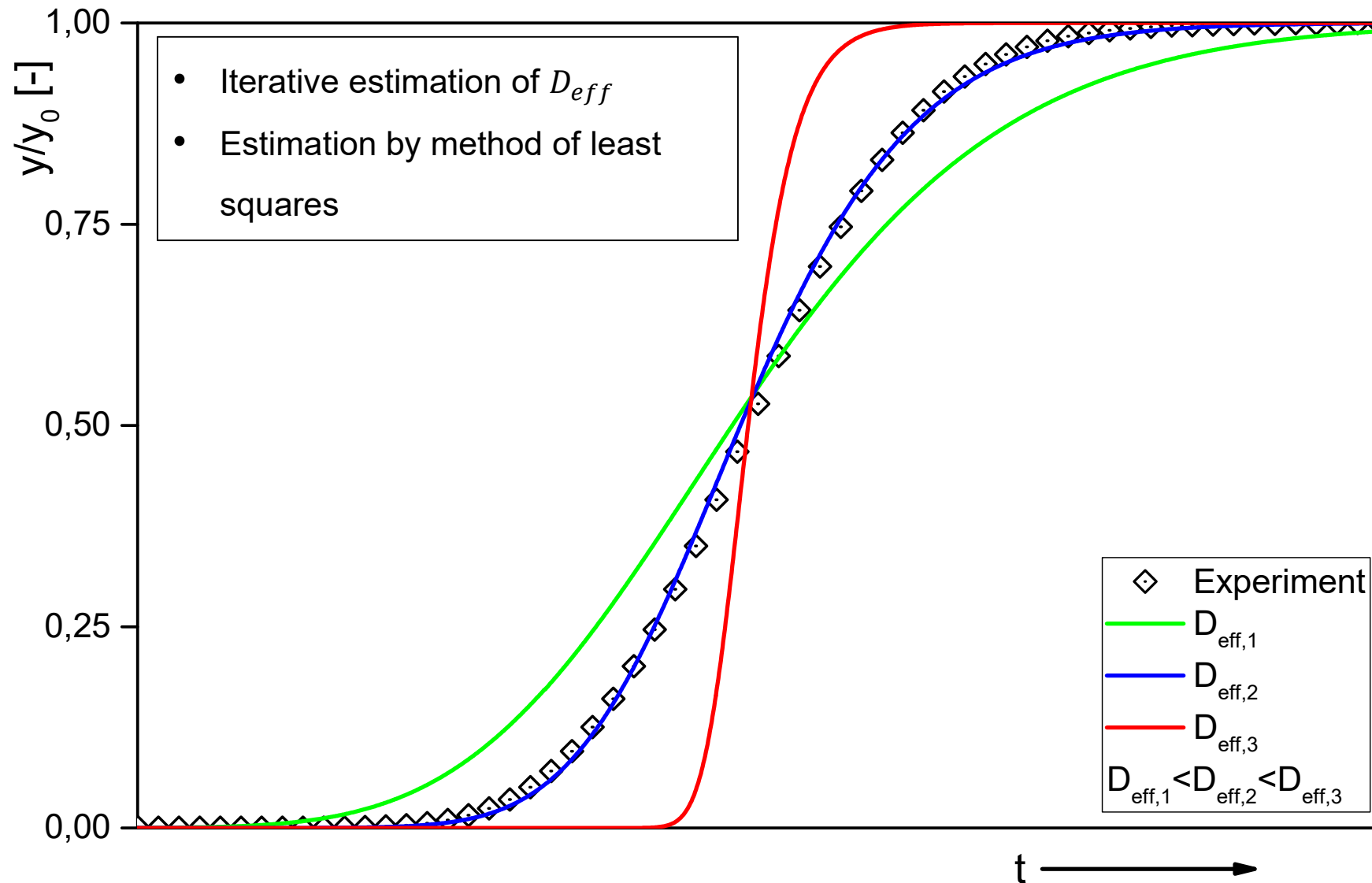
// Simulation: Benzol 1000 ppm - Konstantes Diff - Simulationseinstellung.acmf - Aspen Custom Modeler V8.1 - aspen@DE - (Model - AD)
// File View Search Tools Build Run Windows Help
// Initialization
D_mal = (D0 * D_A_Fluid010^-1) / epsilon; // molekulare Diffusion
+ 0.5 * V_Punkt * d_p / (d_p * epsilon); // Stollung
// Diffusionskoeffizient nach Fuller (Adesorp in Trägerphase)
D_A_Fluid1 = 0.0143 * (T_p)^1.75; // (Dobsonase*(MWBH-01)^-1) + Molbase*(MWBH-01)^-1 + 0.5/p * egr(2) + (DIFF_Mal_02^(1/3) + DIFF_Mal_Adesorp^(1/3))^2;
D_A_Fluid2 = 0.0143 * (T_p)^1.75; // (Dobsonase*(MWBH-01)^-1) + Molbase*(MWBH-01)^-1 + 0.5/p * egr(2) + (DIFF_Mal_02^(1/3) + DIFF_Mal_Adesorp^(1/3))^2;
// Isothermengleichungen
// Freundlich
X_mq1(0,Interior) = X_mq1^1*(0,Interior)/(1-X_mq1)^1*(0,Interior)/(1-X_mq1)^1006(2); //Beladung Bmp.1 (Berechnung aus Reinstoff-Isothermen)
X_mq2(0,Interior) = X_mq2^1*(0,Interior)/(1-X_mq2)^1*(0,Interior)/(1-X_mq2)^1006(2); //Beladung Bmp.2 (Berechnung aus Reinstoff-Isothermen)
// Stoff- & Anlageparameter
Rho_s = Rho_sch / (1-epsilon); // Berechnung der schwebenden Dichte
V_Punkt = V_Punkt0000 * (T_p / 273.15) ^ (1.0122 / p); // Ergänzungsparameter: Umrechnung auf m/s
// ====== Fluid Phase ======
C_1(0,Interior) = D_mal * C_1(0,Interior); d2d2 // Speicherterm = Dispersionsstrom
- (V_Punkt/(d_p * epsilon)) * C_1(0,Interior); ddx // Konvektiver Term
- (k_eff1(0,Interior) * A_mq * ((1-epsilon)/epsilon) * (X_mq1(0,Interior) - X_1(0,Interior))); // Adsorptionsstrom
C_2(0,Interior) = D_mal2 * C_2(0,Interior); d2d2 // Speicherterm = Dispersionsstrom
- (V_Punkt/(d_p * epsilon)) * C_2(0,Interior); ddx // Konvektiver Term
- (k_eff2(0,Interior) * A_mq * ((1-epsilon)/epsilon) * (X_mq2(0,Interior) - X_2(0,Interior))); // Adsorptionsstrom
// ====== feste Phase ======
X_1(0,Interior) = (k_eff1(0,Interior) * A_mq/Rho_s) * (X_mq1(0,Interior) - X_1(0,Interior)); // Speicherterm = Adsorptionsstrom
X_2(0,Interior) = (k_eff2(0,Interior) * A_mq/Rho_s) * (X_mq2(0,Interior) - X_2(0,Interior)); // Speicherterm = Adsorptionsstrom
End
    
```

The screenshot shows the Aspen Custom Modeler interface. On the left, there is a tree view of the simulation model. In the center, a table lists various parameters and their values:

Parameter	Value	Spec
D_mal	0.0143281	m^2/s
D_mal2	0.0143281	m^2/s
D_mal3	0.0143281	m^2/s
D_mal4	0.0143281	m^2/s
D_mal5	0.0143281	m^2/s
D_mal6	0.0143281	m^2/s
D_mal7	0.0143281	m^2/s
D_mal8	0.0143281	m^2/s
D_mal9	0.0143281	m^2/s
D_mal10	0.0143281	m^2/s
D_mal11	0.0143281	m^2/s
D_mal12	0.0143281	m^2/s
D_mal13	0.0143281	m^2/s
D_mal14	0.0143281	m^2/s
D_mal15	0.0143281	m^2/s
D_mal16	0.0143281	m^2/s
D_mal17	0.0143281	m^2/s
D_mal18	0.0143281	m^2/s
D_mal19	0.0143281	m^2/s
D_mal20	0.0143281	m^2/s
D_mal21	0.0143281	m^2/s

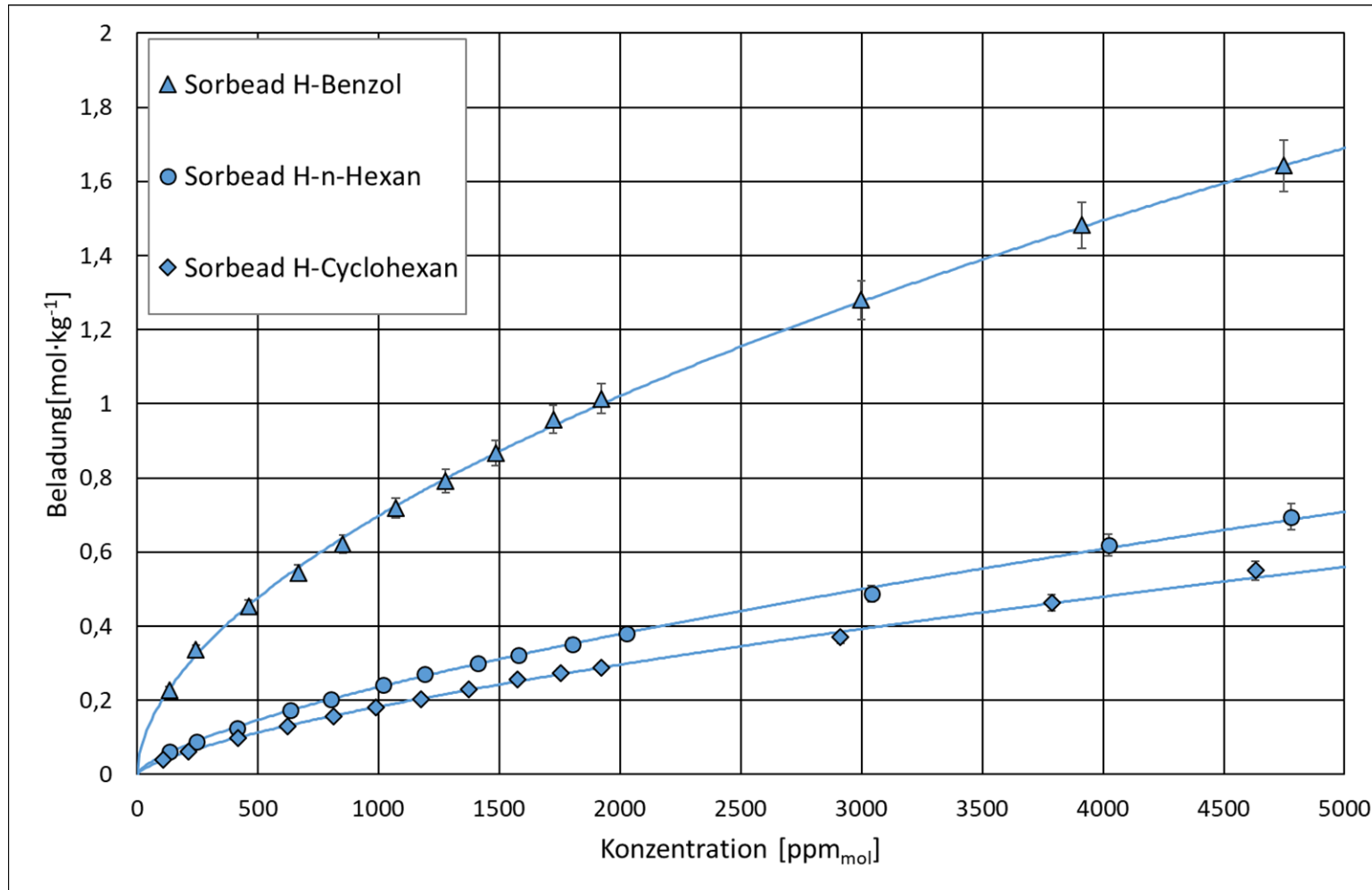
On the right, a 'Run Options' dialog box is open, showing settings for the simulation run, including time units and synchronization options.

2. Isothermal Adsorption Processes

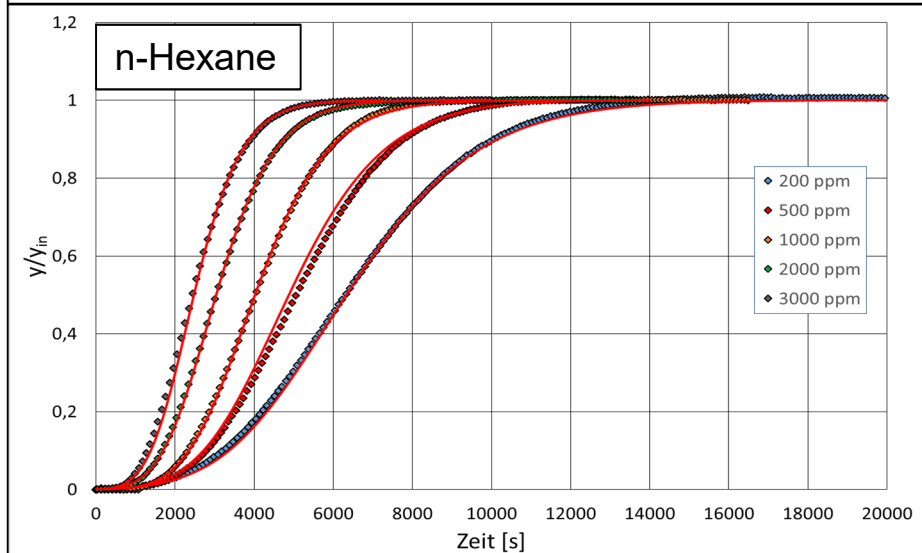
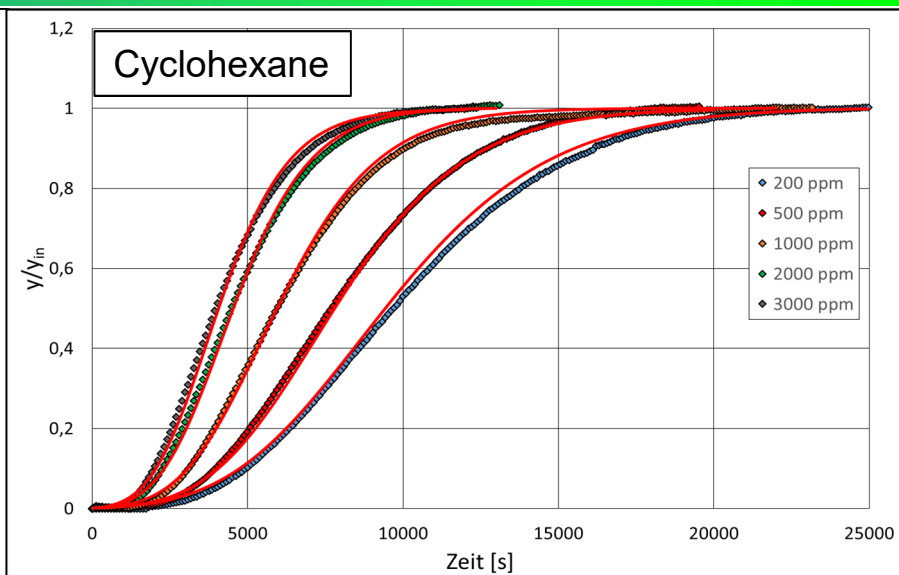
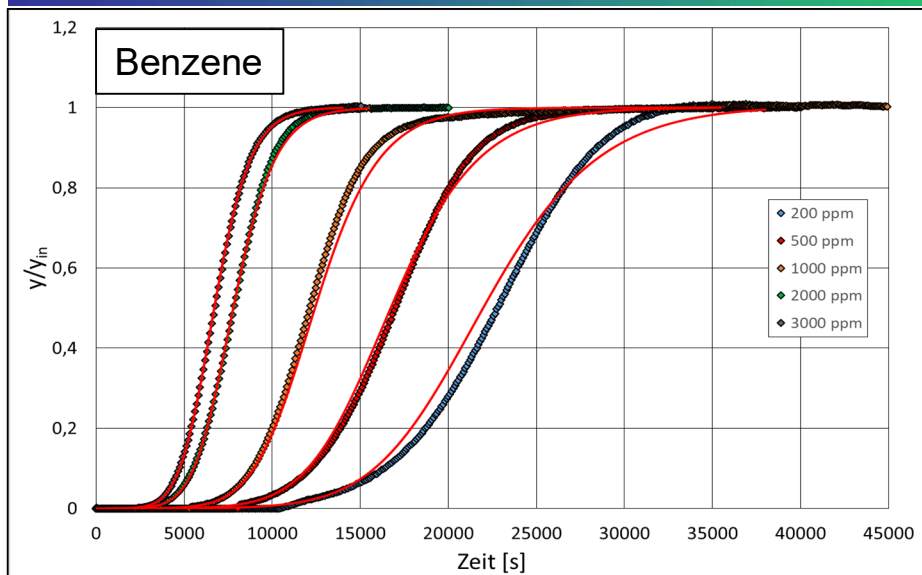


2. Isothermal Adsorption Processes

Isotherms of C₆ hydrocarbons on silica alumina gel at 25°C



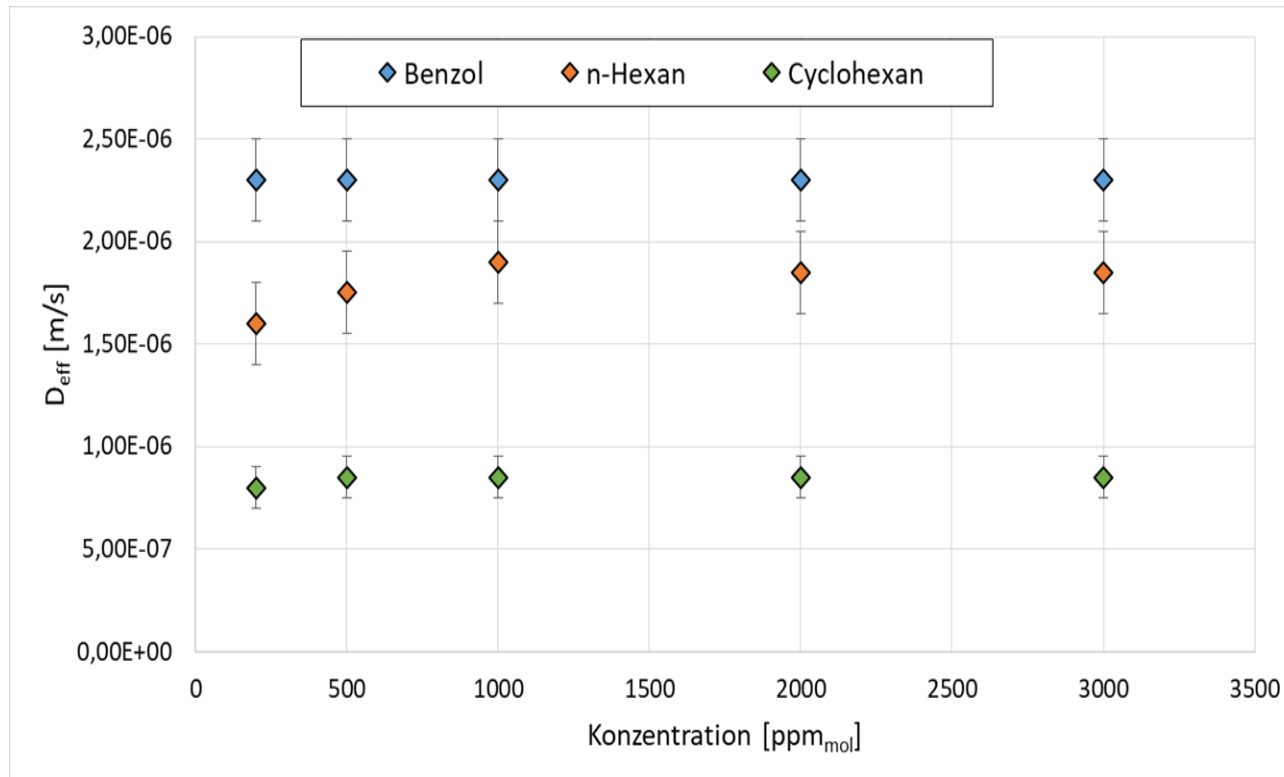
2. Isothermal Adsorption Processes



- C_6 -BTC (homogeneous model)
- Flattening of BTC at low concentrations
- Individual adjustment of $D_{eff}(c_A) \sim 1 * 10^{-6} - 1 * 10^{-7} \frac{m^2}{s}$
- Successful modelling of BTC with constant D_{eff} ($R^2 > 99\%$)

2. Isothermal Adsorption Processes

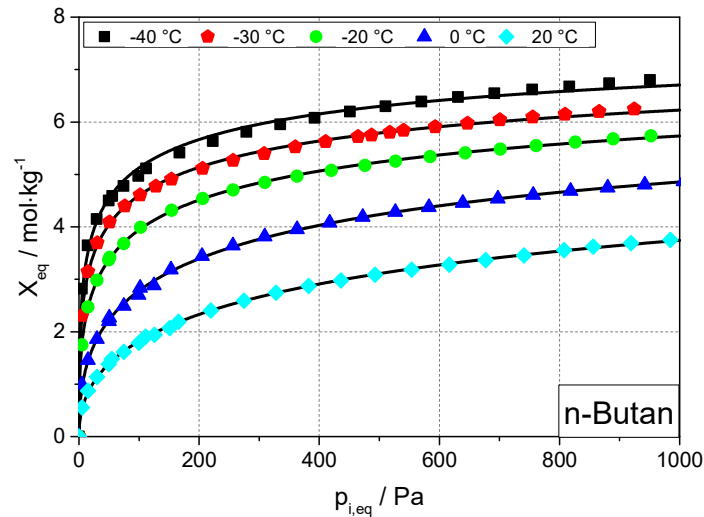
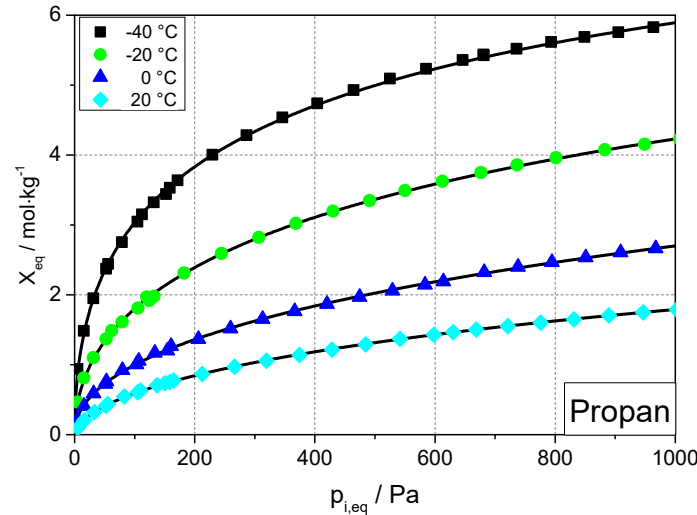
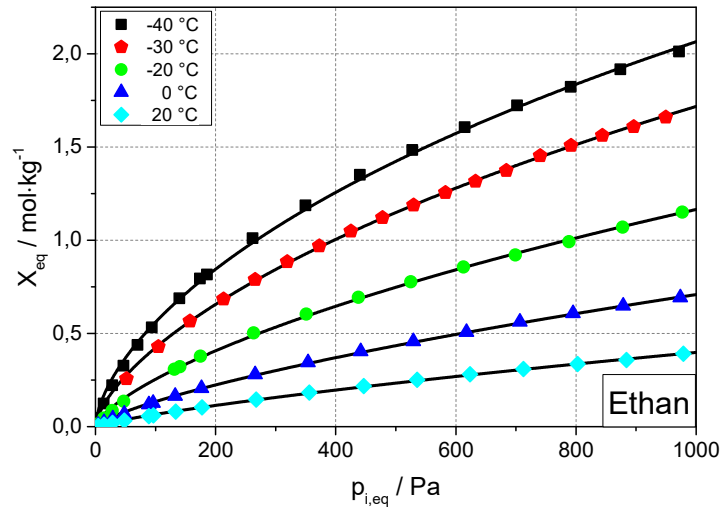
Effective Diffusion coefficients of C₆ hydrocarbons on Silica alumina gel



- Constant D_{eff} over whole concentration range
- Simulation with mean D_{eff} possible

2. Isothermal Adsorption Processes

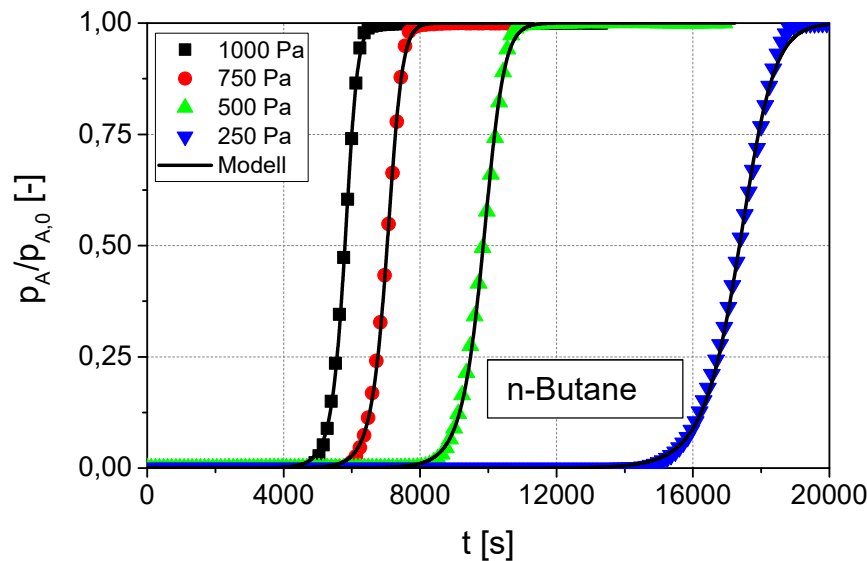
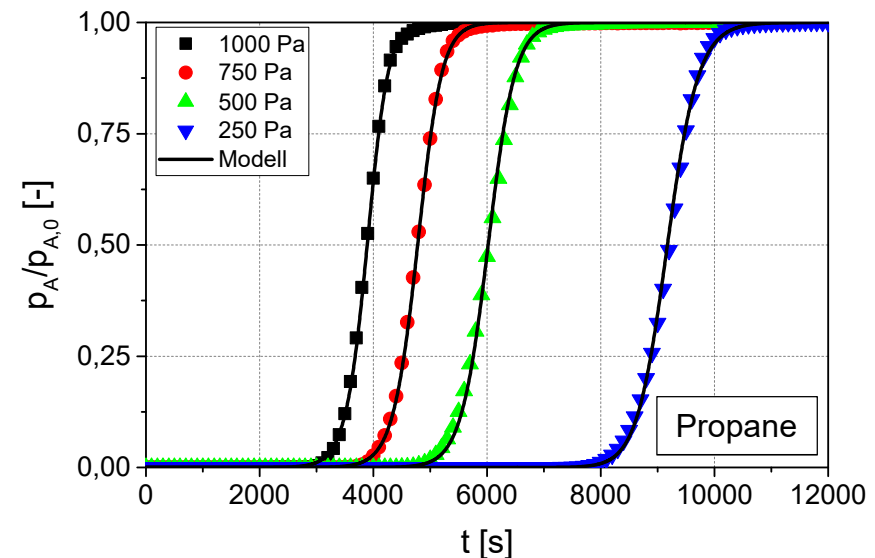
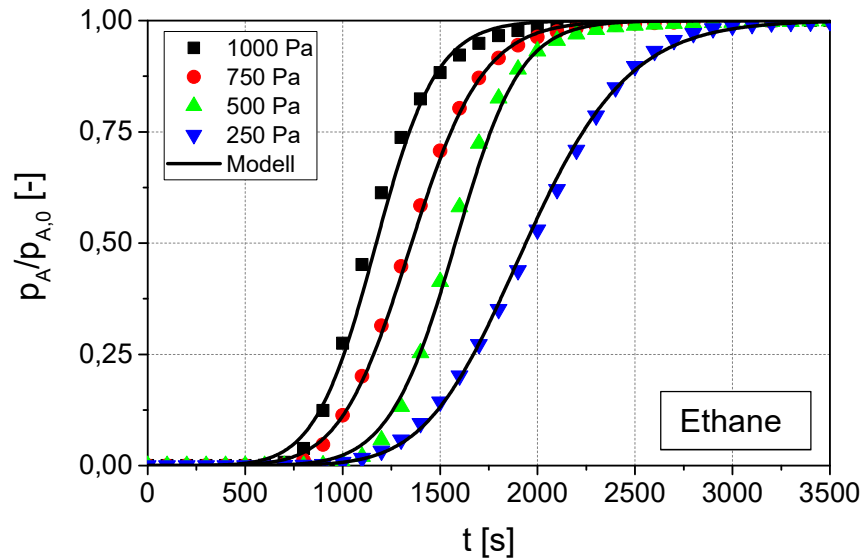
Isotherms of light hydrocarbons on activated carbon



- Isotherms Typ I
- Capacity n-Butane > Propane > Ethane
- Temperature dependency
Ethane > Propane > n-Butane
- Toth-Isotherm ($R^2 > 99,9\%$)

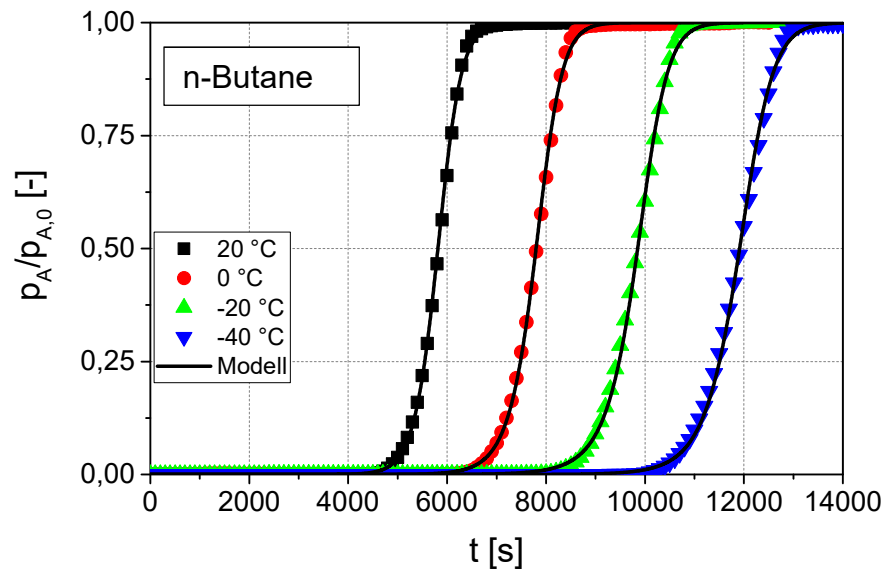
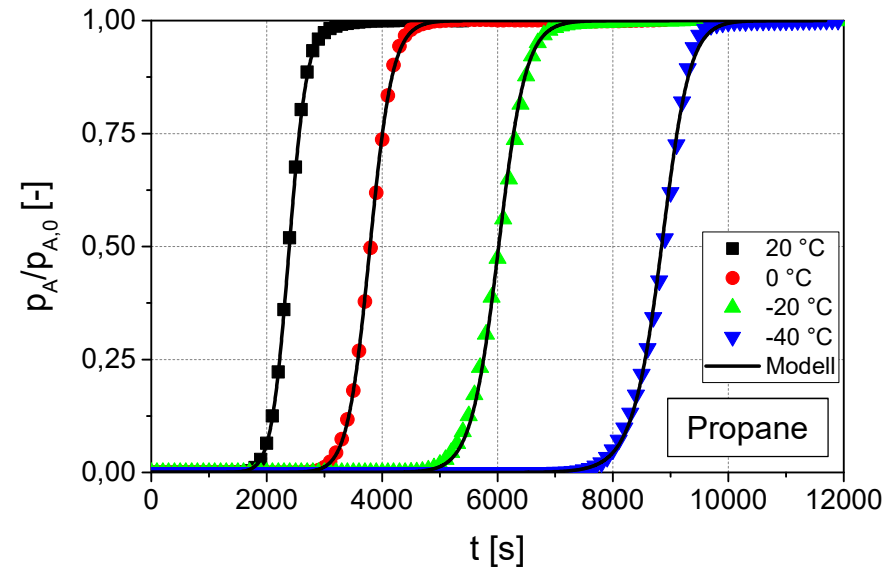
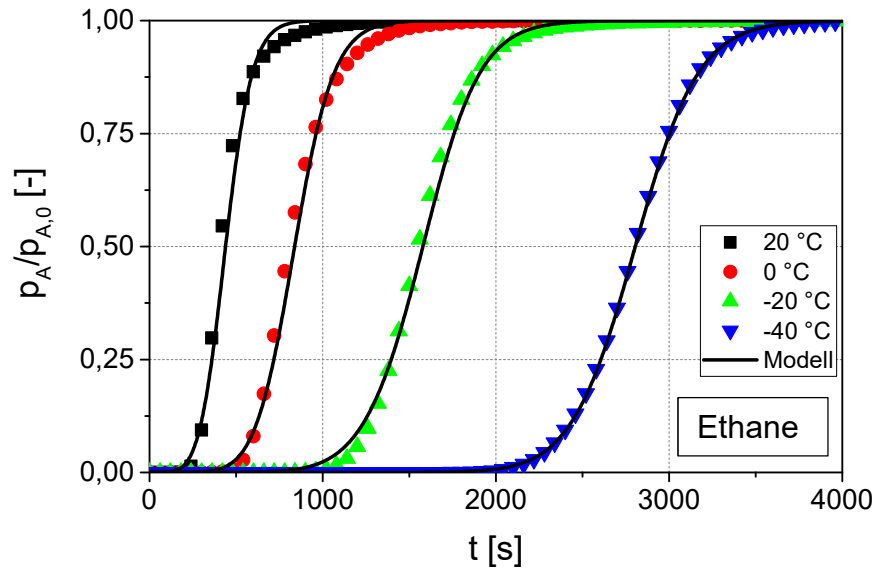
$$X_{eq}(T, p_{i,eq}) = X_{mon}(T) * \frac{b(T) * p_{i,0}}{(1 + (b(T) * p_{i,0})^{n(T)})^{\frac{1}{n(T)}}$$

2. Isothermal Adsorption Processes



- Light hydrocarbon-BTC at - 20°C (homogeneous model)
- Width of MTZ Ethane > Propane > n-Butane
- Flattening of BTC at low concentrations
- Individual adjustment of $D_{eff}(c_A) \sim 1 * 10^{-5} - 1 * 10^{-6} \frac{m^2}{s}$
- Successful modelling of BTC with constant D_{eff} ($R^2 > 99\%$)

2. Isothermal Adsorption Processes

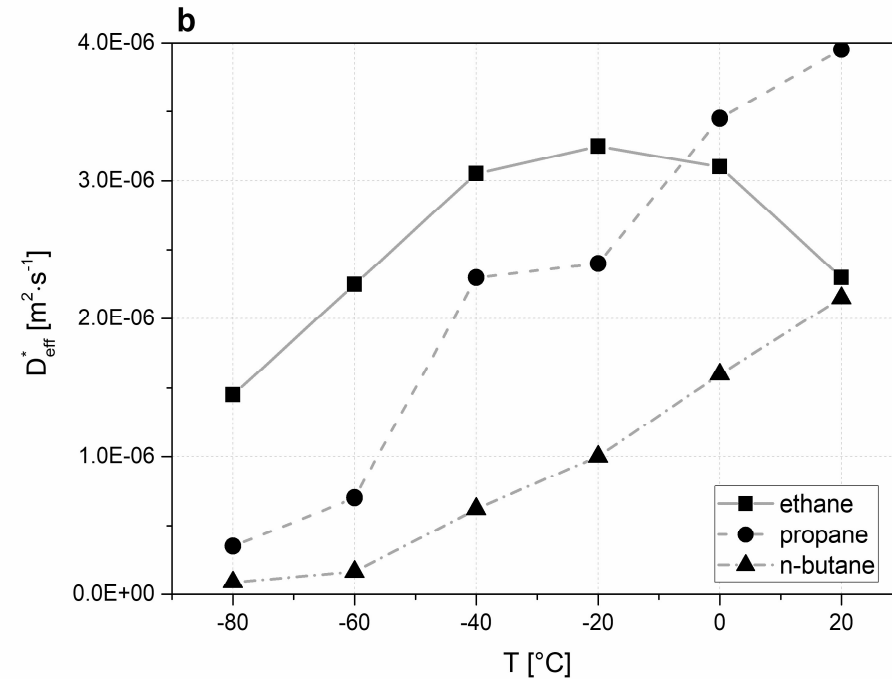
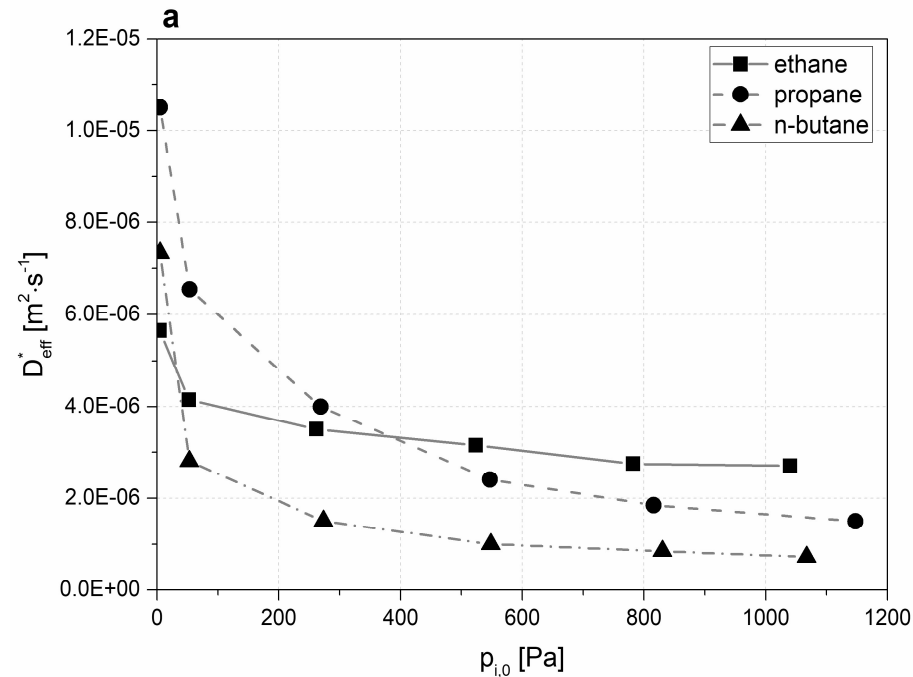


- BTCs at 500 Pa (homogeneous model)
- Flattening of Ethane-BTC by decreasing temperature
- Minor temperature influence on Propane/n-Butane
- Individual adjustment of

$$D_{eff}(c_A) \sim 1 * 10^{-6} - 1 * 10^{-7} \frac{m^2}{s}$$
- Successful modelling of BTC with constant D_{eff} ($R^2 > 99\%$)

2. Isothermal Adsorption Processes

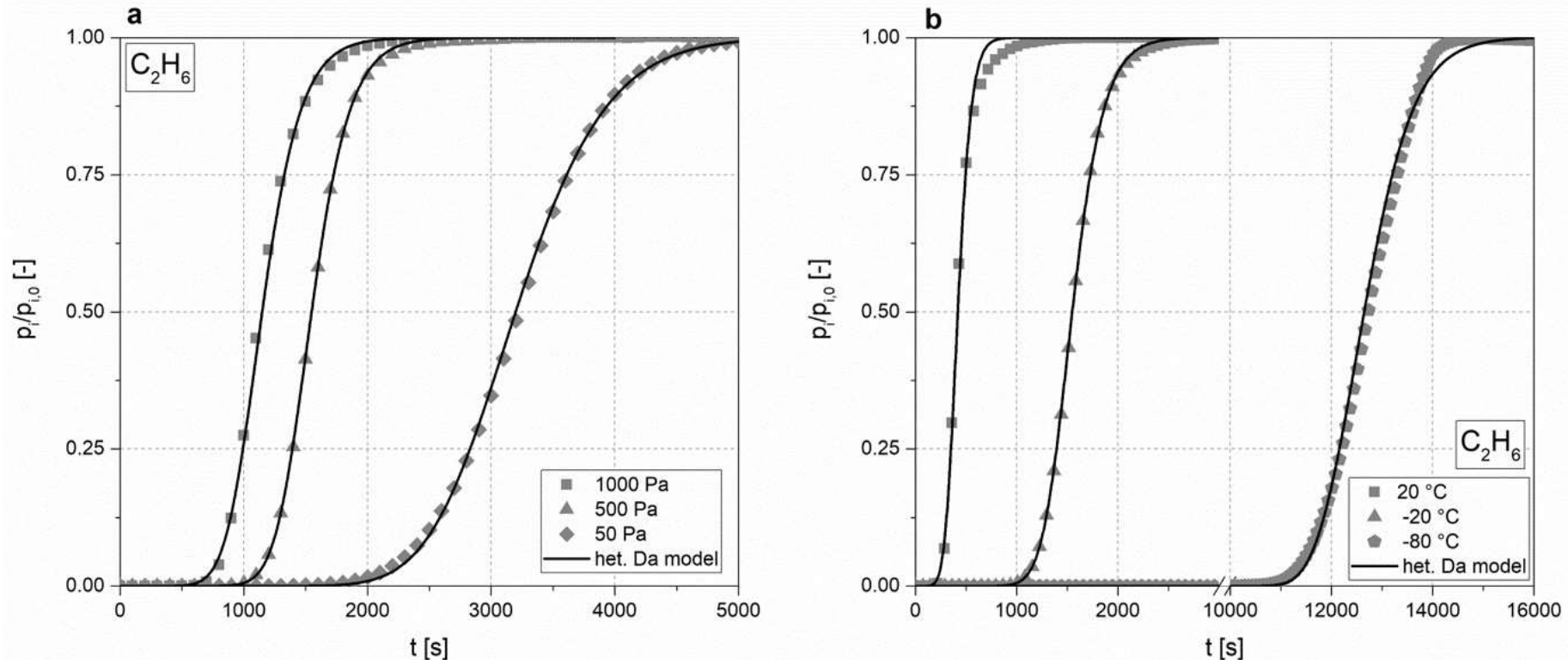
Effective Diffusion coefficients of light hydrocarbons on activated carbon



- Decreasing D_{eff} with increasing concentration
- Mathematic approximation by power function $a \cdot x^{-b}$
- Indication of isotherm shape
- No consistent temperature dependency

2. Isothermal Adsorption Processes

Light hydrocarbon-BTC (heterogeneous model)



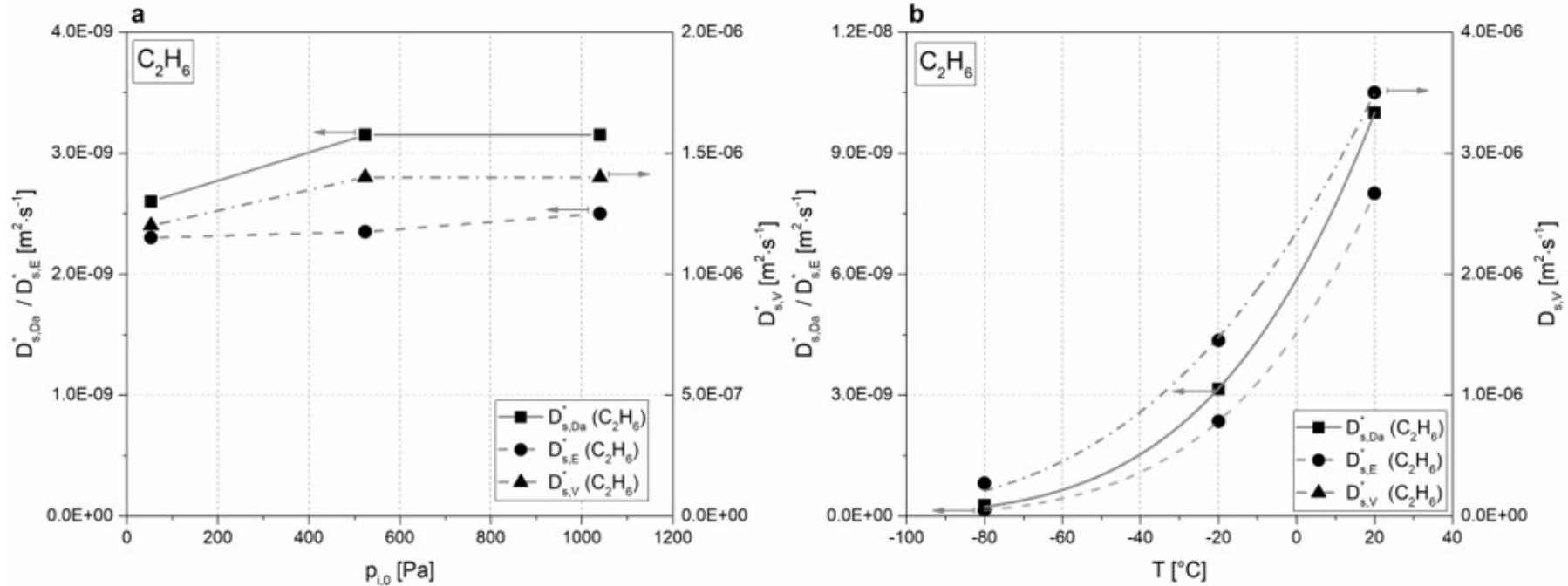
- Surface diffusion by Darken approach:

$$D_{s,Da}(T, X) = D_{s,Da}^*(T) * \frac{\partial \ln c_A}{\partial \ln \bar{X}} = D_{s,Da}^*(T) * \frac{1}{1 - \theta^n}$$

- Successful modelling of BTC with heterogeneous model (surface & pore diffusion) ($R^2 > 99\%$)

2. Isothermal Adsorption Processes

(Limiting) surface diffusion coefficients of light hydrocarbons on activated carbon



- Constant (limiting) surface diffusion coefficient over whole concentration range
- Exponential temperature dependency of (limiting) surface diffusion coefficient

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3. Non-Isothermal Adsorption Processes



Often used Assumptions:

- Neglect of radial gradients (T, P, c, X)
- 1D discretization of adsorber column in slices of equal height
- ...
- Geometry of particles is approximated by equal spheres
- Fluid phase obeys Ideal gas law
- Thermal conductivity is independent from concentration
- ...
- Dispersed Plug Flow-Model
- Axial dispersion calculated by approach of Wakao et al.
- ...
- Single component adsorption: no competitive adsorption of carrier gas
- Mass transfer is simplified by the linear driving force (LDF) approach
- External mass transfer resistance taken into account by film diffusion coefficient calculated from Sherwood correlation
- ...
- Heat capacity of bulk phase inside the pore system neglected
- Properties of the adsorbents are constant (independent from temperature)
- ...

3. Non-Isothermal Adsorption Processes

Partial differential equation system:

- Mass balance of solid phase:

$$\frac{\partial X}{\partial t} = \frac{k_{eff} \cdot A_{Sp}}{\rho_s} \cdot (X_{GL} - X)$$

- Mass balance of fluid phase:

$$\frac{\partial c_A}{\partial t} = D_{ax} \cdot \frac{\partial^2 c_A}{\partial z^2} - \frac{\dot{V}_G}{\epsilon_L \cdot A} \cdot \frac{\partial c_A}{\partial z} - \frac{c_A}{\epsilon_L \cdot A} \cdot \frac{\partial \dot{V}_G}{\partial z} - \frac{k_{eff} \cdot (1 - \epsilon_L) \cdot A_{Sp}}{\epsilon_L} \cdot (X_{GL} - X)$$

- Energy balance of solid phase:

$$\frac{\partial T_F}{\partial t} = \frac{\Delta h_{ads} + c_{p,A} \cdot (T_G - T_F)}{c_{p,S} + X \cdot c_{p,A}} \cdot \frac{\partial X}{\partial t} - \frac{\alpha_P \cdot A_{Sp} \cdot (T_F - T_G)}{\rho_S \cdot (c_{p,S} + X \cdot c_{p,A})}$$

- Energy balance of fluid phase:

$$\frac{\partial T_G}{\partial t} = \frac{\lambda_D}{\rho_G \cdot c_{pG}} \cdot \frac{\partial^2 T_G}{\partial z^2} - \frac{T_G}{A \cdot \epsilon_L} \cdot \frac{\partial \dot{V}_G}{\partial z} - \frac{\dot{V}_G \cdot T_G}{A \cdot \epsilon_L \cdot \rho_G} \cdot \frac{\partial \rho_G}{\partial z} - \frac{\dot{V}_G}{A \cdot \epsilon_L} \cdot \frac{\partial T_G}{\partial z} + \frac{\alpha_P \cdot (1 - \epsilon_L) \cdot A_{Sp}}{\rho_G \cdot c_{pG} \cdot \epsilon_L} \cdot (T_F - T_G) - \frac{4 \cdot \alpha_{W,i}}{D_i \cdot \epsilon \cdot \rho_f \cdot c_{p,f}} \cdot (T_G - T_W)$$

- Energy balance of adsorber wall:

$$\frac{\partial T_W}{\partial t} = \frac{4}{(D_a^2 - D_i^2) \cdot c_{p,W} \cdot \rho_W} \cdot [\alpha_{W,i} \cdot D_i \cdot (T_G - T_W) - \alpha_{W,a} \cdot D_a \cdot (T_W - T_U)]$$

Kinetic model:

- Homogeneous diffusion model

$$k_{eff} = \frac{15}{R_p^2} * \frac{D_{eff}}{\frac{\rho_p}{\epsilon_p} * \frac{\partial X}{\partial c_{A,g}}} * \frac{1}{1 + \frac{\epsilon_p * 15 * D_{eff}}{R_p^2 * \beta_{Film} * A_{Sp}}}$$

3. Non-Isothermal Adsorption Processes



Initial and boundary conditions

$$T_F(z, t = 0) = T_0 \qquad \dot{V}_G(z = 0, t) = \dot{V}_{G,ein}$$

$$T_G(z, t = 0) = T_0 \qquad T_G(z = 0, t) = T_{G,ein}$$

$$X(z, t = 0) = X_0 \qquad \rho_G(z = 0, t) = \rho_{G,ein}$$

$$c_A(z, t = 0) = c_{A,0} \qquad c_A(z = 0, t) = c_{A,ein}$$

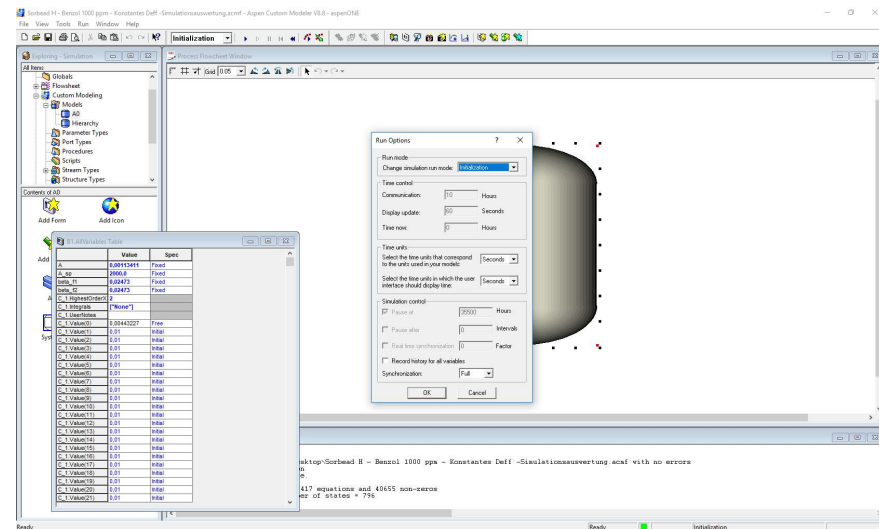
$$\frac{\partial^2 c_A}{\partial z^2}(z = L, t) = 0$$

$$\frac{\partial^2 T_G}{\partial z^2}(z = L, t) = 0$$

- Specific material and fluid parameters calculated by adjoint equations
- Software for simulation PDE-solver:
 - Aspen Custom Modeler® / AdSim®
 - gProms®
 - Speed Up®
 - (Comsol Multiphysics®)
 - AdLin® (Linde Inhouse Software)
 - ...

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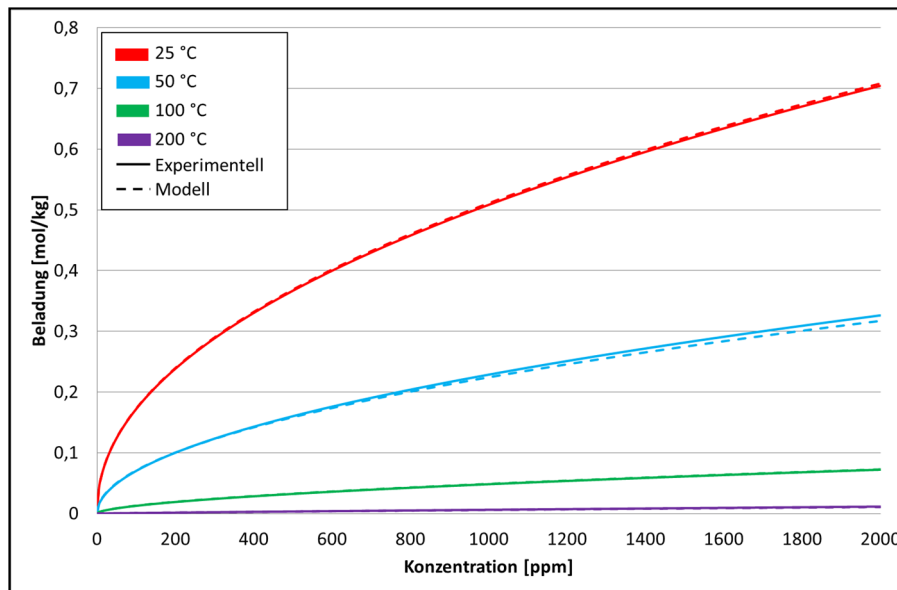
Simulation: Benzol 1000 ppm - Konstantes Diff - Simulationserstellung.acmf - Aspen Custom Modeler V8.3 - aspen@DE - (Model - Ad)
...
// molekulare Diffusion
D_mol = (D0 * T^1.75) / (epsilon * rho_solid * rho_gas) // Stoßweg
// Diffusionskoeffizient nach Fuller (Adsorpt in Trägerphase)
D_A_Fluid = 0.00143 * (T^1.75) * (rho_solid * rho_gas)^0.5 * (1 + rho_solid * (M_Benzol - 1)^-1) * 0.5 / (p * epsilon^2) * (DIFT_mol_D2^1/3) + DIFT_mol_AdsorptV^1/3)^2/3
D_B_Fluid = 0.00143 * (T^1.75) * (rho_solid * rho_gas)^0.5 * (1 + rho_solid * (M_H2 - 1)^-1) * 0.5 / (p * epsilon^2) * (DIFT_mol_D2^1/3) + DIFT_mol_AdsorptV^1/3)^2/3
// Isothermengleichungen
// Freundlich
X_mq1(B.Interior) = X_max1 * C_1(B.Interior)^(1/(1-n_1)) * V_1(C_1(B.Interior)^(1/(1-n_1))) * 1006 (2) //Beladung Bmp.1 (Berechnung aus Heintzsch-Isothermen)
X_mq2(B.Interior) = X_max2 * C_2(B.Interior)^(1/(1-n_2)) * V_2(C_2(B.Interior)^(1/(1-n_2))) * 1006 (2) //Beladung Bmp.2 (Berechnung aus Heintzsch-Isothermen)
// Stoff- & Anlageparameter
rho_s = rho_solid / (1-epsilon) // Berechnung der schwebenden Dichte
V_mol = V_mol * 1000 * (T_0 / T) * (1.01325 / p) // Ausgangsvolumen: Umrechnung auf mb/s
// Massenbilanz flüssige Phase
C_1(B.Interior) = D_mol * C_1(B.Interior) * d2d2 // Speicherterm = Dispersionsstrom
- (V_Punkt / (A * epsilon)) * C_1(B.Interior) * dx // Konvektiver Term
- (k_eff(B.Interior) * A_m * (1-epsilon) / epsilon) * (X_mq1(B.Interior) - X_1(B.Interior)) // Adsorptionsstrom
C_2(B.Interior) = D_mol * C_2(B.Interior) * d2d2 // Speicherterm = Dispersionsstrom
- (V_Punkt / (A * epsilon)) * C_2(B.Interior) * dx // Konvektiver Term
- (k_eff2(B.Interior) * A_m * (1-epsilon) / epsilon) * (X_mq2(B.Interior) - X_2(B.Interior)) // Adsorptionsstrom
// Massenbilanz feste Phase
X_1(B.Interior) = (k_eff1(B.Interior) * A_m * rho_s) * (X_mq1(B.Interior) - X_1(B.Interior)) // Speicherterm = Adsorptionsstrom
X_2(B.Interior) = (k_eff2(B.Interior) * A_m * rho_s) * (X_mq2(B.Interior) - X_2(B.Interior)) // Speicherterm = Adsorptionsstrom
End
    
```



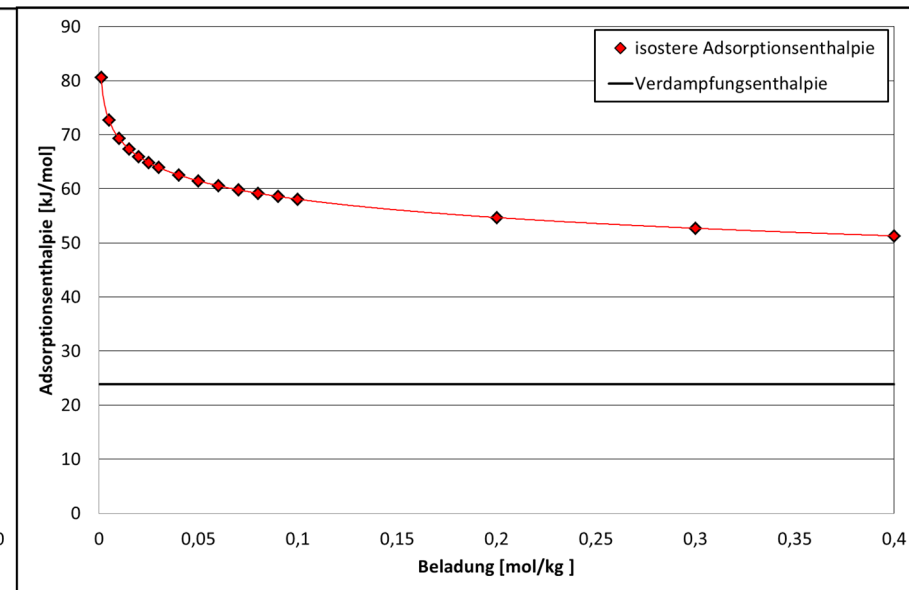
3. Non-Isothermal Adsorption Processes

Necessary data for non-isothermal simulation:

- $X_{eq} = f(T, c)$
- $\Delta h_{ads} = f(X)$
- (have to be determined experimentally)



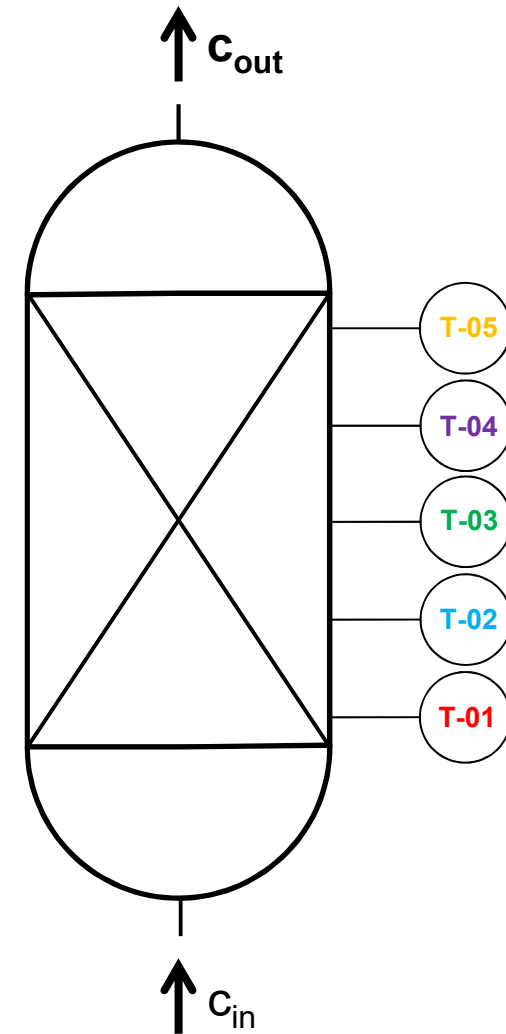
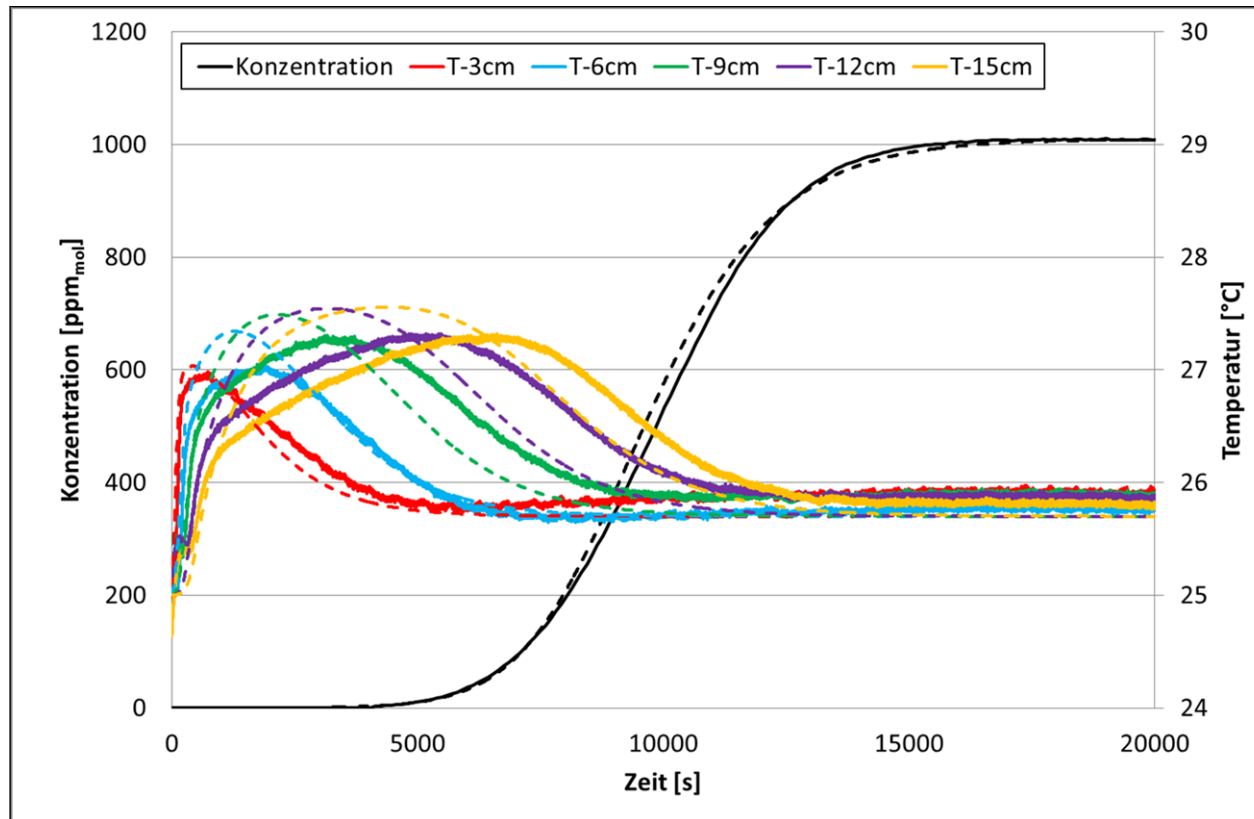
Experimental and calculated field of isotherms of C_2H_5SH on Sorbead H



Isosteric heat of adsorption of C_2H_5SH on Sorbead H

3. Non-Isothermal Adsorption Processes

Adsorption Profiles of C₂H₅SH on Sorbead H

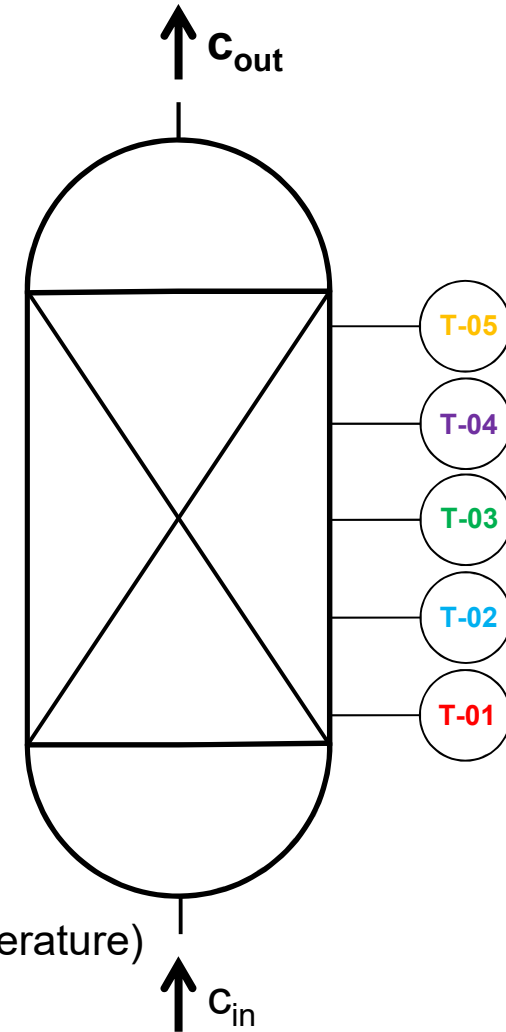
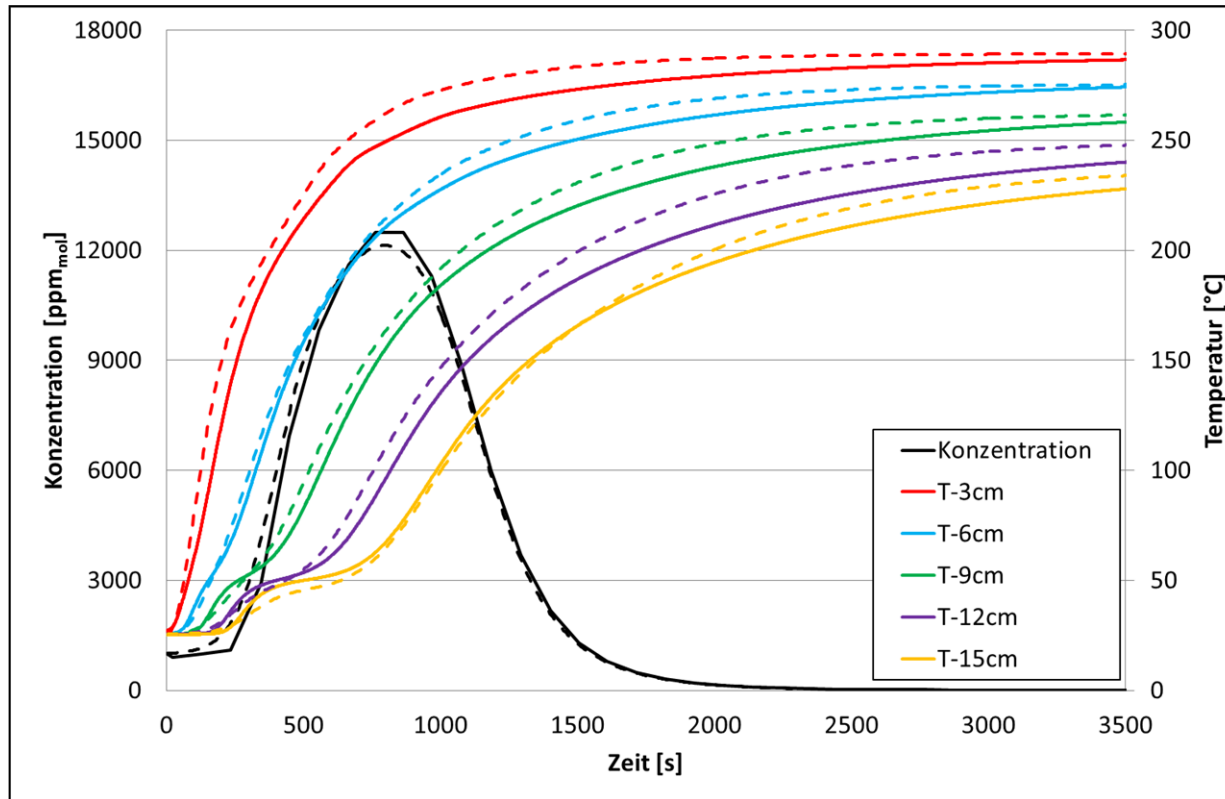


High accuracy of dynamic simulation (concentration and temperature profile)

- Deviation of temperature peak < 0,3 °C
- Slightly faster cooling of fixed bed in the simulated case

3. Non-Isothermal Adsorption Processes

Desorption profiles of C₂H₅SH on Sorbead H



- Simulation with same set of parameters
- High accuracy of dynamic simulation (concentration and temperature)
- Characteristic temperature plateaus with deviation 2 - 5 °C

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2. Simulation of Isothermal Adsorption Processes
3. Simulation of Non-Isothermal Adsorption Processes
4. Specific Adsorption Parameters
5. Sophisticated Simulations
6. Summary
7. Recent Selected Publications

4. Specific Adsorption Parameters

Dynamic Simulation of Adsorption Processes

⇒ 1. Differential Equation (Mass Balance Fixed Phase):

$$\frac{\partial X}{\partial t} = \frac{k_{eff} \cdot A_{spec}}{\rho_S} \cdot (X_{Gl} - X)$$

Adsorption Kinetics

⇒ 2. Differential Equation (Mass Balance Fluid Phase):

$$\frac{\partial c_A}{\partial t} = D_{ax} \frac{\partial^2 c_A}{\partial z^2} - \frac{V_G}{A \cdot \epsilon_L} \frac{\partial c_A}{\partial z} - \frac{c_A}{A \cdot \epsilon_L} \frac{\partial V_G}{\partial z} - \frac{k_{eff} \cdot A_{spec} \cdot (1 - \epsilon_L)}{\epsilon_L} (X_{Gl} - X)$$

MISSING DATA!

Adsorption Thermodynamics

⇒ 3. Differential Equation (Energy Balance Fixed Phase):

$$\frac{\partial T_F}{\partial t} - \frac{\Delta h_{Ads}}{M_A \cdot \left(c_{pS} + X c_{pA} + \frac{m_{Wand} \cdot c_{pWand}}{\rho_S A L (1 - \epsilon_L)} \right)} \frac{\partial X}{\partial t} = \frac{\alpha_P \cdot A_{Sp}}{\rho_S \cdot (1 - \epsilon_L) \left(c_{pS} + X c_{pA} + \frac{m_{Wand} \cdot c_{pWand}}{\rho_S A L (1 - \epsilon_L)} \right)} (T_F - T_G)$$

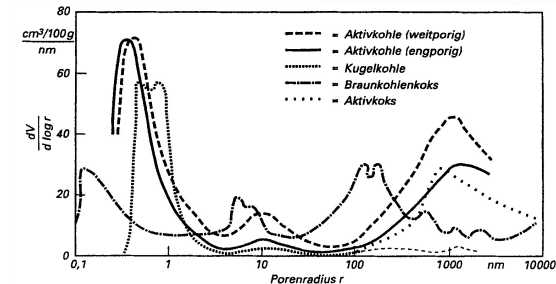
...

4. Specific Adsorption Parameters

Characterisation Methods

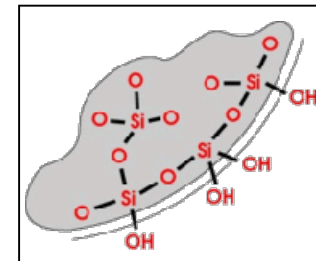
Structural properties:

- ⇒ Nitrogen Adsorption (BET)
- ⇒ **Probe Molecule Method (Size Exclusion)**
- ⇒ Hg-Porosimetry
- ⇒ Methylene Blue / Iodine Number



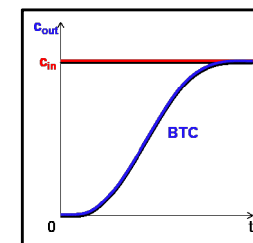
Chemical properties:

- ⇒ Elemental Analysis
- ⇒ IR-Spectroscopy
- ⇒ **Boehm Titration**
- ⇒ EDX, SAXS, ...



Adsorption properties:

- ⇒ **Excess Isotherms**
- ⇒ **Adsorption Enthalpies**
- ⇒ Breakthrough Experiments in small Columns
- ⇒ Methylene Blue / Iodine Number



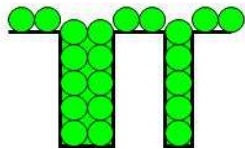
4. Specific Adsorption Parameters

Molecular Probe Method

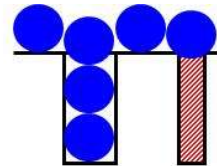


#	Adsorptive	T _{Ads} [K]	p ₀ [kPa]	MIN-1	MIN-2
1	Nitrogen	77	101,35	3,6 Å	
2	n-Hexan	298	20,13	4,2 Å	4,6 Å
3	Cyclohexan	298	13,04	5,1 Å	6,8 Å
4	2,2-Dimethylbutan	298	42,54	5,9 Å	6,0 Å
5	2,2,4-Trimethylpentan	298	6,59	6,2 Å	6,7 Å

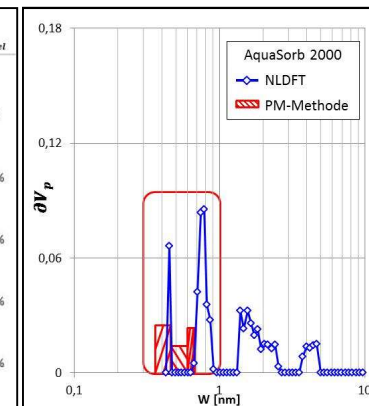
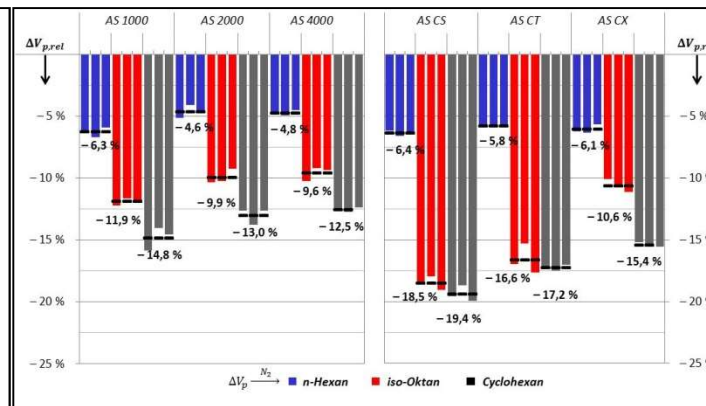
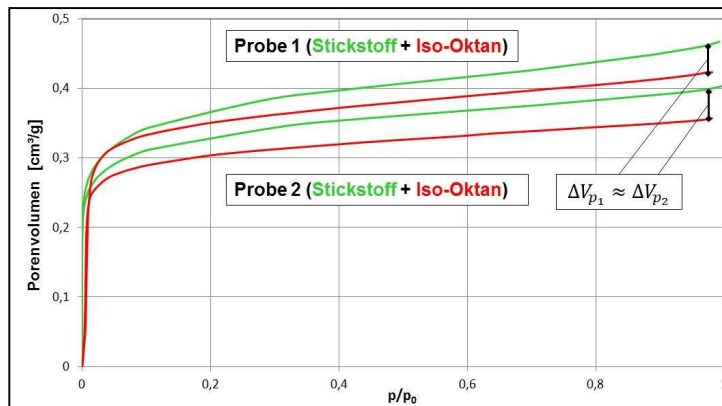
Molecule A:



Molecule B:



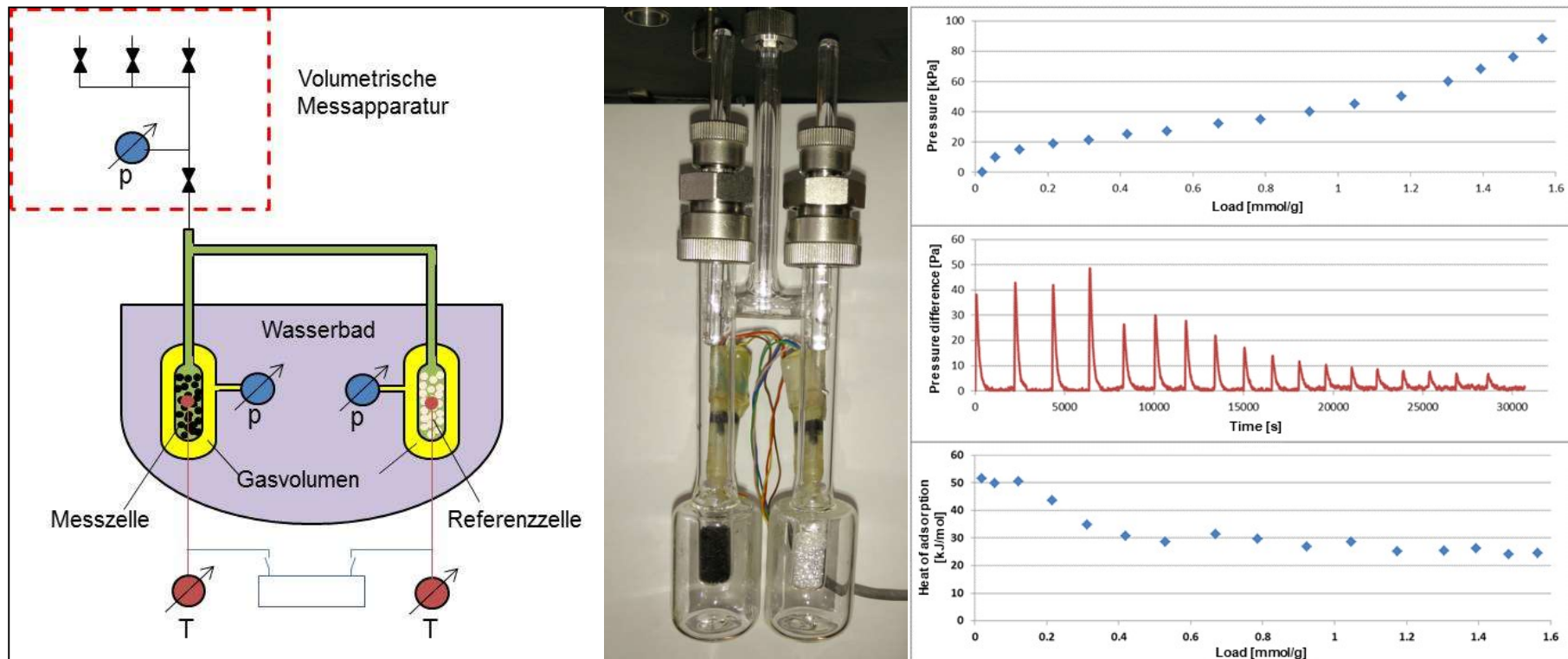
$$\Delta V_p = V_{p_A} - V_{p_B}$$



4. Specific Adsorption Parameters

Coupling of Volumetric and Calorimetric Adsorption Measurements

- Extension of Existing Measurement Device (N₂-BET)
- Volumetric Measurement of Adsorption Isotherms
- Simultaneous Measurement of Adsorption Enthalpy by Analysis of Pressure Rise and Decline in Surrounding Gas Volume



4. Specific Adsorption Parameters

Excess Adsorption Isotherms (in Liquid Phase)

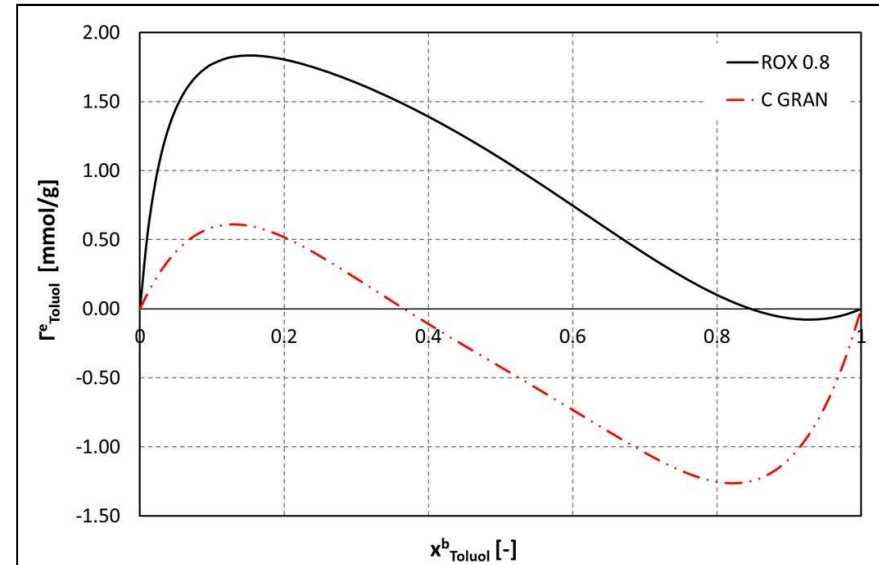
- Interaction Adsorbent \leftrightarrow Adsorptive \leftrightarrow Solvent
- Group Contribution Model



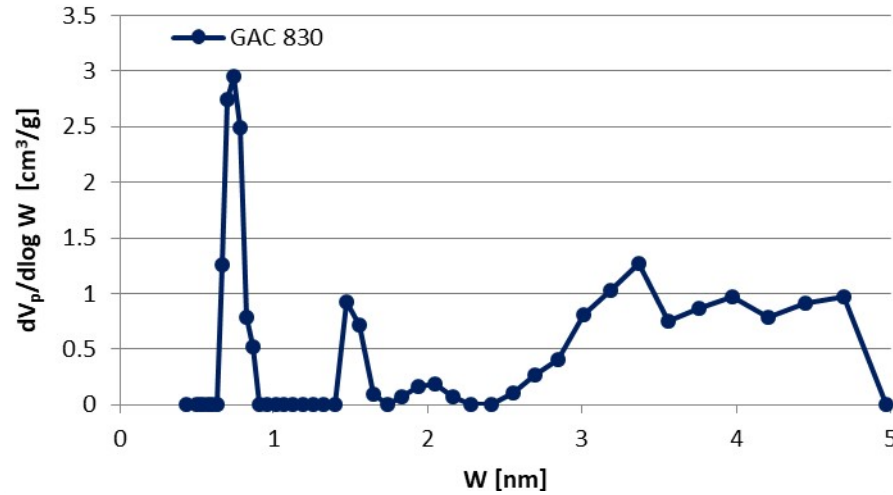
- Characterisation of Activated Carbon by Analysis of Binary Adsorption Isotherms
- Adsorptives:
 - Methyl-Cyclohexane (non-polar)
 - Toluene (aromatic)
 - Acetone (polar)
- Calculation of Adsorptive Sites' Distribution with Layer-Models



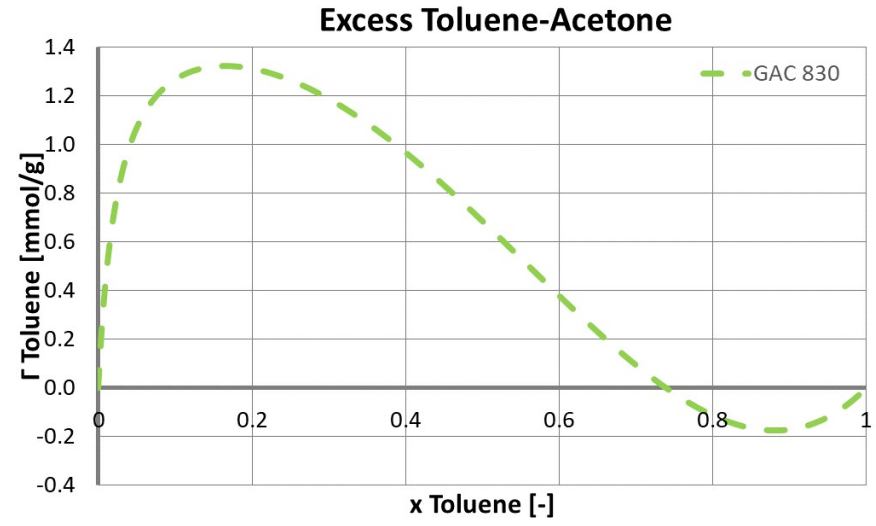
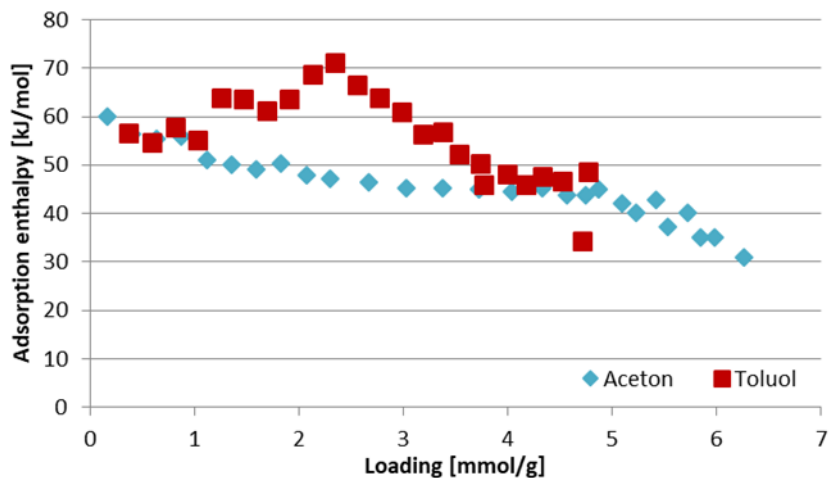
- Calculation of Adsorption Isotherms using the Adsorbate-Solid-Solution-Theory (Ulbig, TU Dortmund)



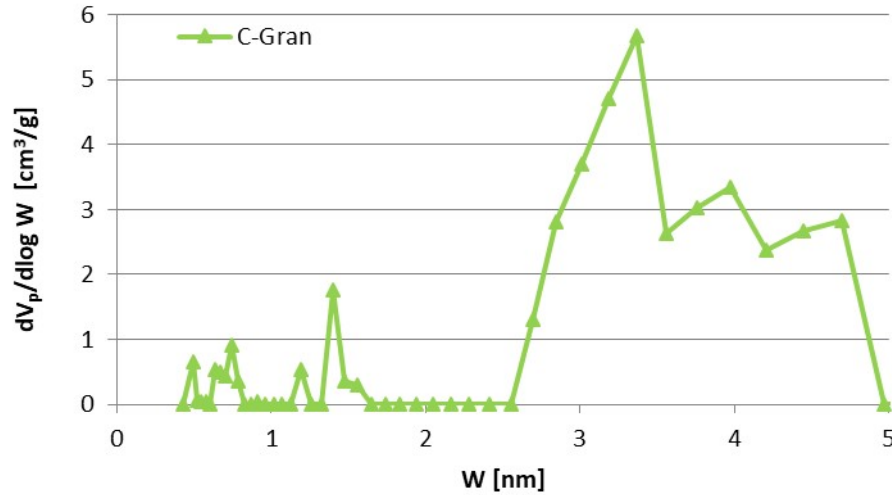
4. Specific Adsorption Parameters



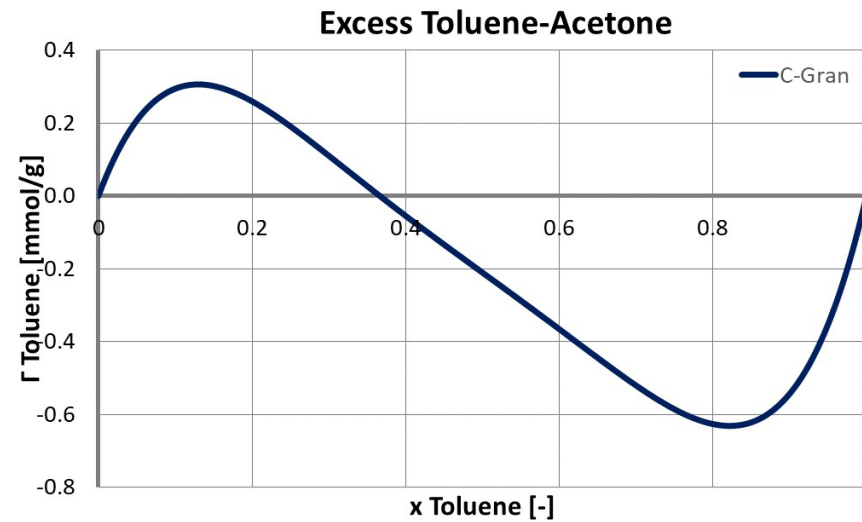
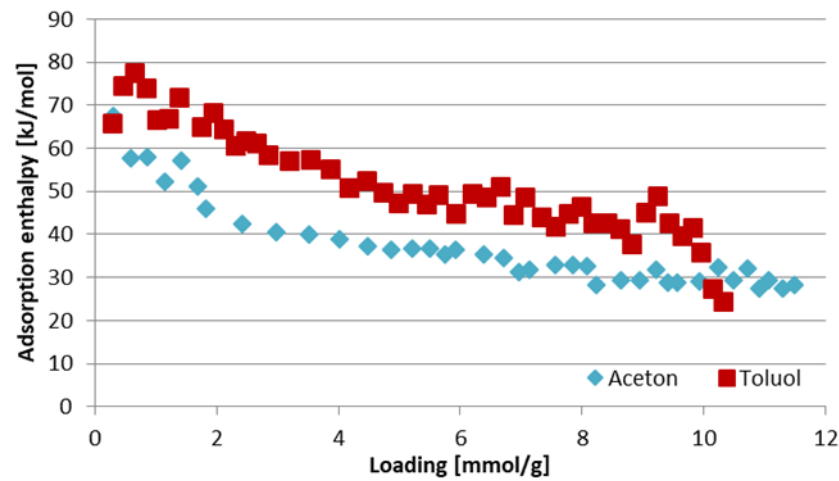
Activated Carbon	A_{BET}	V_p	C	H	O
	$\left[\frac{m^2}{g}\right]$	$\left[\frac{cm^3}{g}\right]$	[wt-%]	[wt-%]	[wt-%]
GAC 830	960	0.57	89.50	0.25	4.32



4. Specific Adsorption Parameters



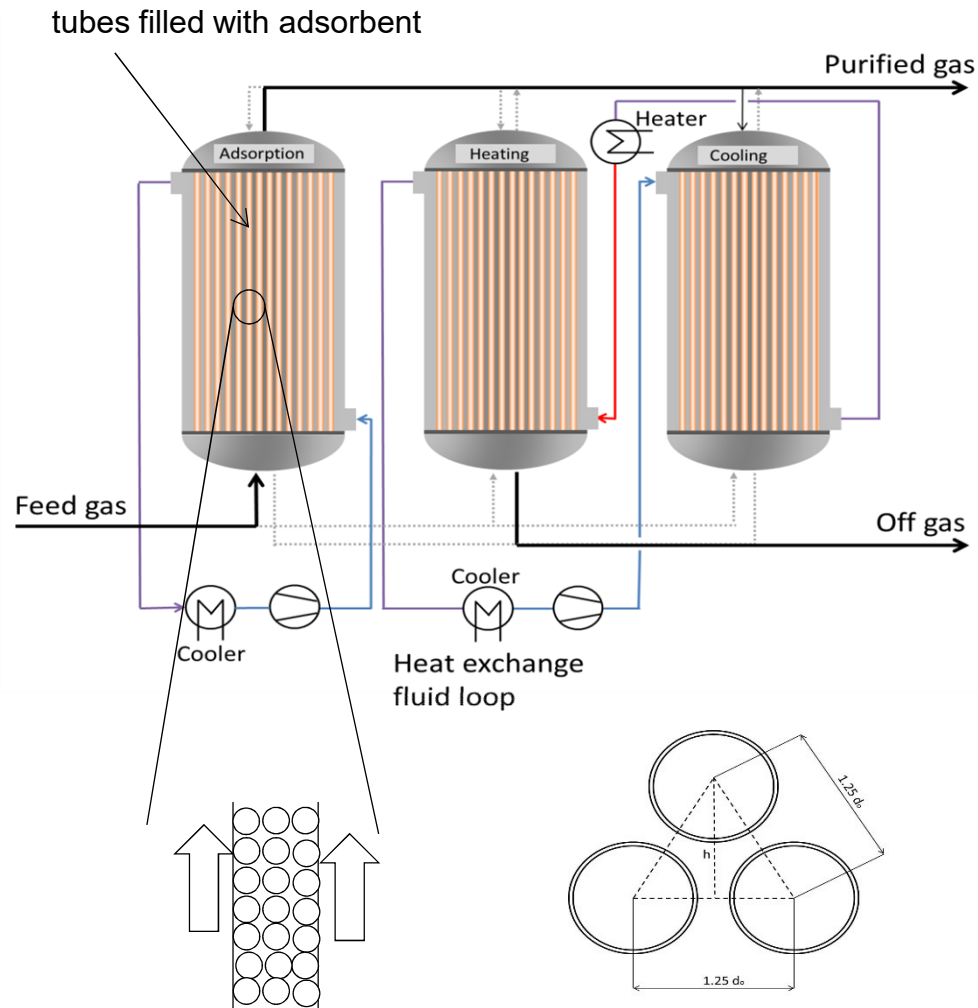
Activated Carbon	A_{BET}	V_p	C	H	O
	$\left[\frac{m^2}{g}\right]$	$\left[\frac{cm^3}{g}\right]$	[wt-%]	[wt-%]	[wt-%]
C Gran	1162	1.02	73.4	1.9	22.0



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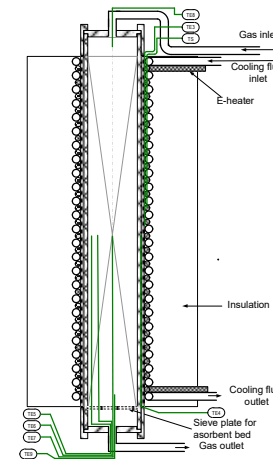
5. Sophisticated Simulations

Rapid TSA-Process (Linde AG)



Concept:

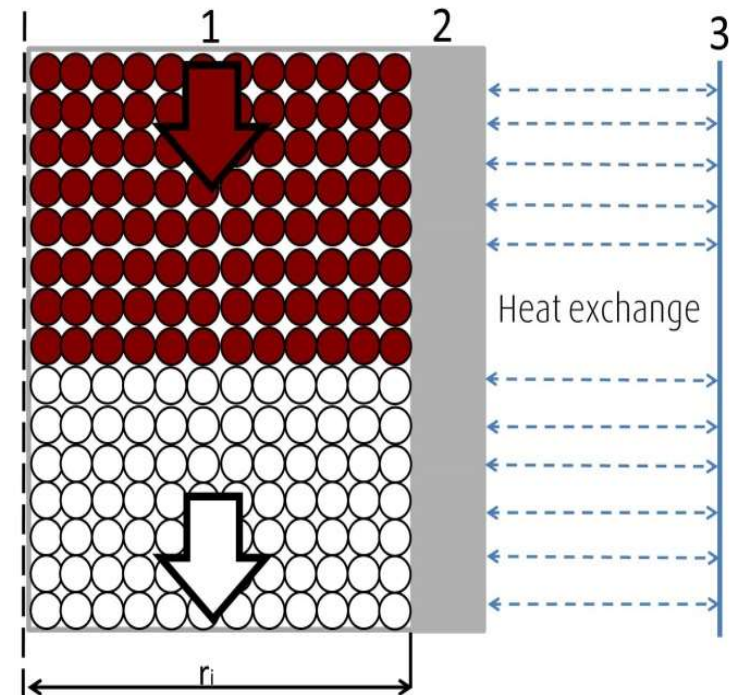
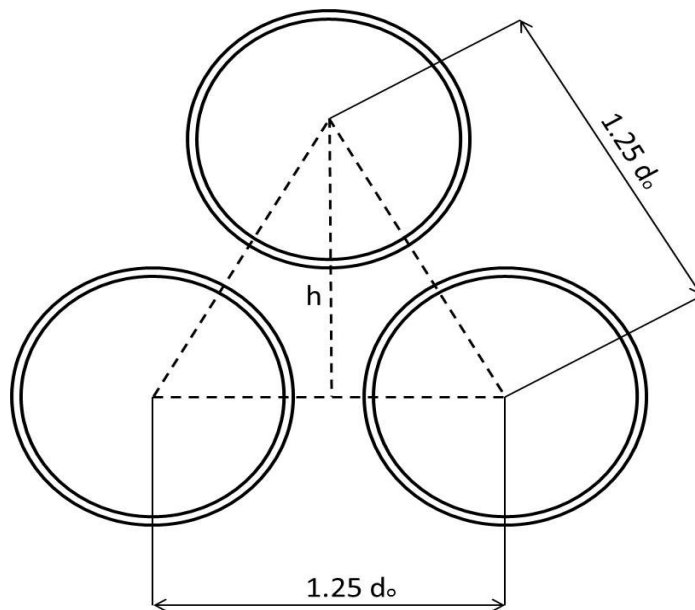
- Two separated flow channels
- Heat exchange between channels
- Cooling/heating fluid in the shell
- Adsorbent in the tubes
- Indirect heating with a utility fluid, e.g. water



5. Sophisticated Simulations

Simulation of Tube Bundle Adsorber (Linde AG)

- One tube of the tube bundle system
- Numerical study using COMSOL Multiphysics®
- Simulated dry flue gas: 15% CO₂ and 85% N₂
- Geometry: Axial symmetrical 2D model coupled to a 1D model
- Surface to volume ratio ϕ estimated from unit cell



5. Sophisticated Simulations

Wall:

$$\frac{\partial T_{wall}}{\partial t} = \nabla \left(\frac{\lambda}{\rho_{wall} c_{p,wall}} \nabla T \right)$$

Adsorbent + gas (local thermal equilibrium and linear driving force):

$$\frac{\partial \widetilde{c}_i}{\partial t} = \overbrace{\nabla(D_i \nabla c_i)}^{Dispersion} - \overbrace{\nabla(u_z \cdot c_i)}^{Convection} - \rho_s \overbrace{\frac{1 - \epsilon}{\epsilon} \frac{\partial q_i}{\partial t}}^{Adsorption}$$

$$\frac{\partial((\rho_g c_{pg} \epsilon + (1 - \epsilon) \rho_s c_{ps}) T)}{\partial t} = \nabla(\lambda_{eff} \nabla T) - \epsilon \cdot \nabla(u \rho_g c_{pg} T) + (1 - \epsilon) \rho_s \sum \Delta H_{ads,i} \frac{\partial q_i}{\partial t}$$

$$\frac{\partial c}{\partial t} + \nabla(uc) = - \sum \rho_s \frac{1 - \epsilon}{\epsilon} \frac{\partial q_i}{\partial t}$$

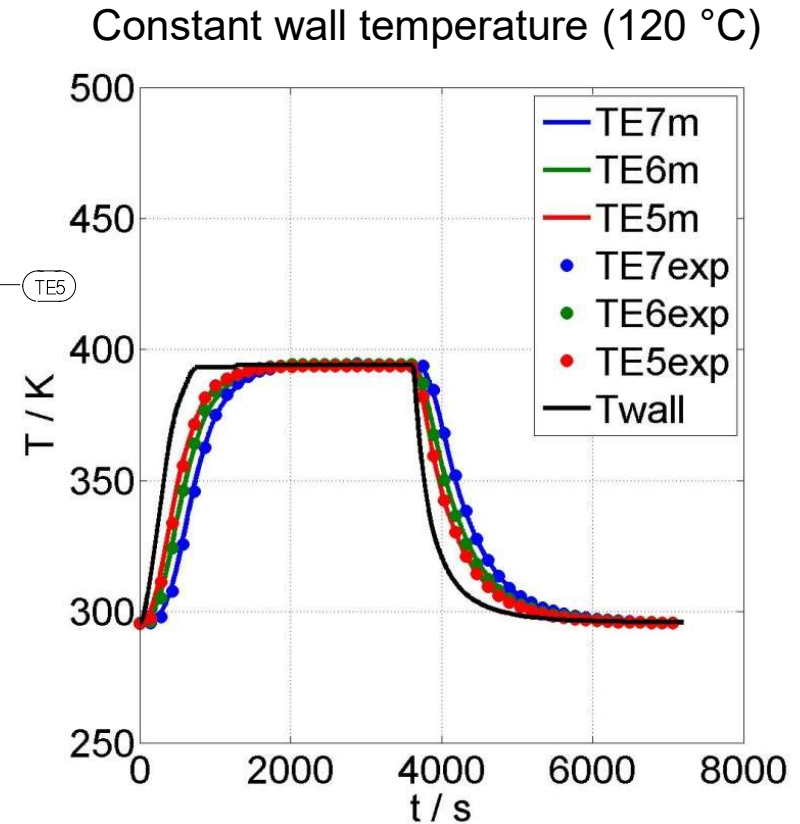
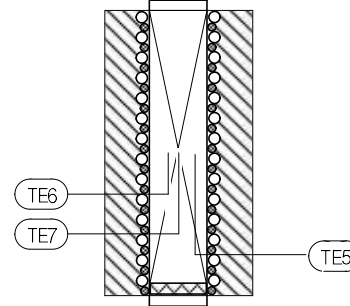
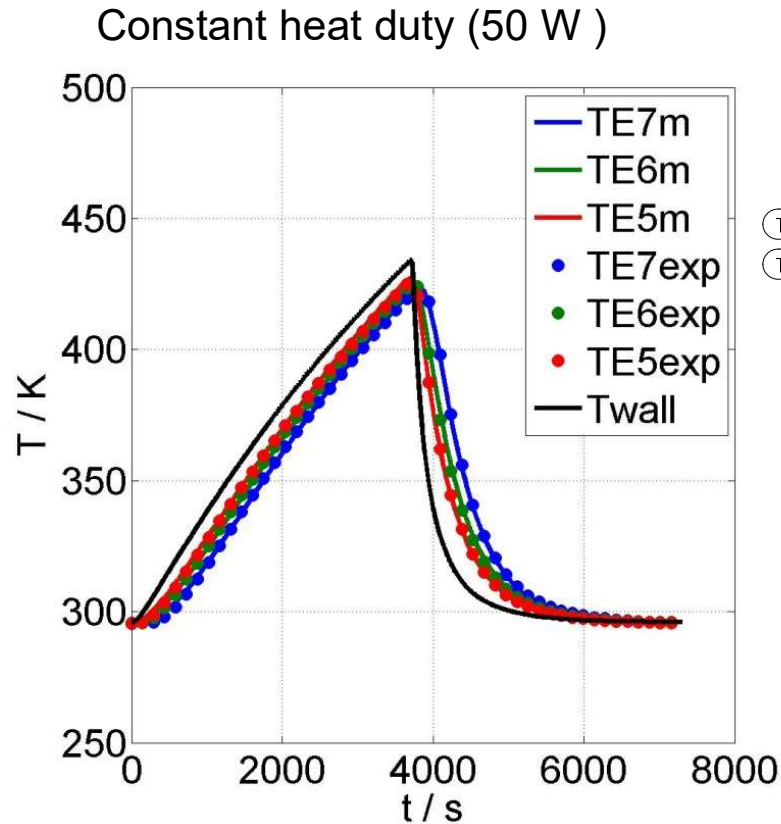
$$-\nabla p = (150 \frac{(1 - \epsilon)^2 \eta_g}{\epsilon^3 d_p^2} + 1.75 \frac{1 - \epsilon \rho_g}{\epsilon^3 d_p} u_0) \cdot u$$

$$\frac{\partial q_i}{\partial t} = k_{LDF}^* \frac{1 - \epsilon}{\epsilon} (q_{eq} - q_i)$$

Heat transfer fluid:

$$\frac{\partial T_{Hex}}{\partial t} + u_{z,Hex} \frac{\partial T_{Hex}}{\partial z} = \frac{\partial}{\partial z} \left(\lambda_{Hex} \frac{\partial T_{Hex}}{\partial z} \right) + \phi \alpha_{Hex} (T_{Hex} - T_{wall}(r = r_o))$$

5. Sophisticated Simulations



$$\lambda_p = 0.391 \frac{W}{mK}, Bi = 1.17 \frac{W}{mK}$$

$$\lambda_p = 0.395 \frac{W}{mK}, Bi = 1.08 \frac{W}{mK}$$

→ **Good agreement** between experiments and simulations

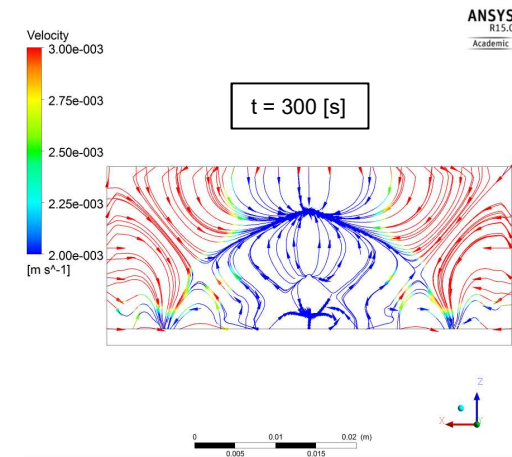
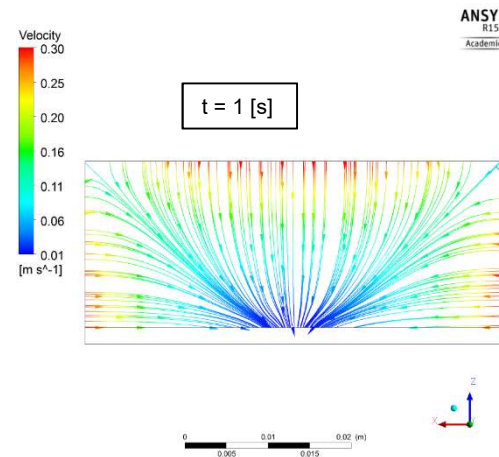
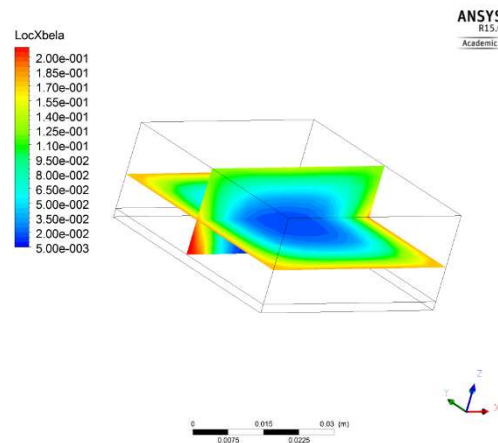
5. Sophisticated Simulations

Adsorptive Air Conditioning (Bosch)

Concept:

- Foam as Basic Structure
- Coating with SAPO 34
- Water as Adsorptive

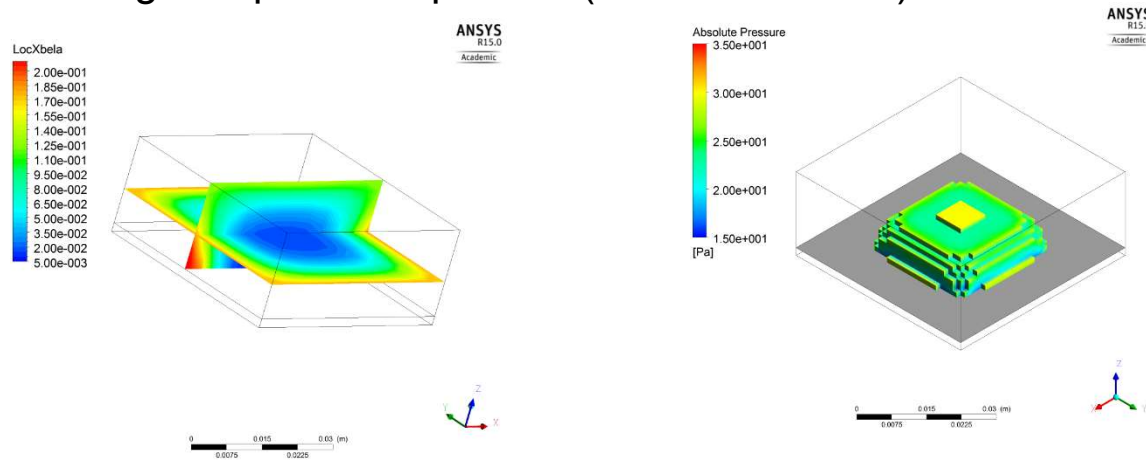
- CFD-Simulation with Ansys®



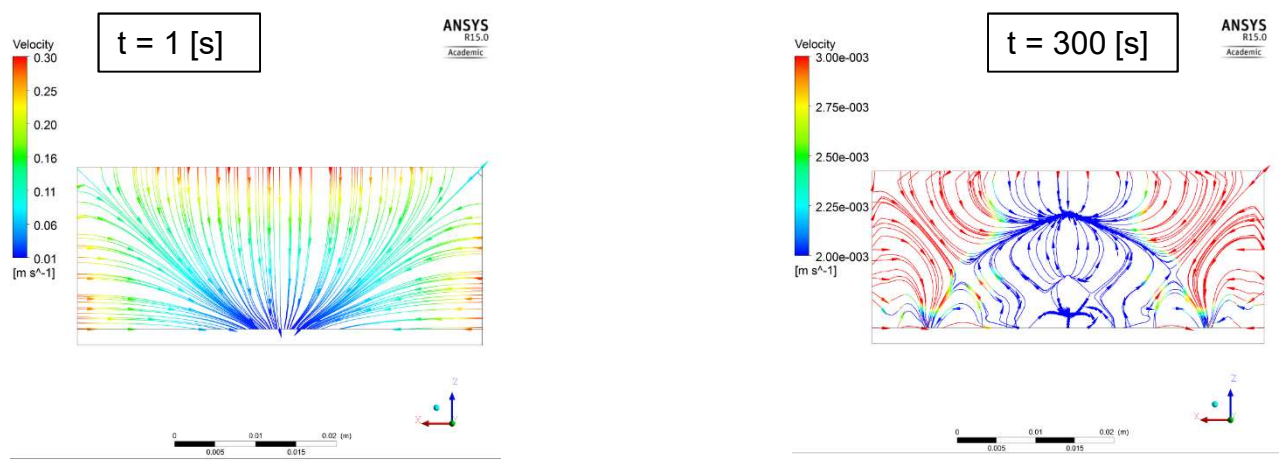
5. Sophisticated Simulations

Simulation Results

- Loading and pressure profiles (CFD-Simulation)



- Flow profile (CFD-Simulation)



6. Summary



State of the Art in Simulation

- Mathematical Equations are well known
- Performance of Computers is sufficient
- Missing Data on Adsorption-specific Properties
- Missing Data on Multi-component Adsorption
- Missing Data on Adsorption Kinetics

Recent Research Activities

- 2D and 3D Simulations
- Coupling of Adsorption and CFD
- Computer-based Calculation of Adsorption-specific Data
- Simulation of Complete Adsorption Processes (ADS-DES-COOL)

7. Recent Selected Publications



Simulation of Adsorption Processes

- B. Burrichter / C. Pasel / M. Luckas / D. Bathen, Parameter study on the adsorptive drying of isopronanol in a fixed bed adsorber, Sep. & Pur. Tech. 132 (2014), S. 736-743
- B. Burrichter / C. Pasel / M. Luckas / D. Bathen, Experimental and theoretical study on the adsorptive drying of primary alcohols in a fixed bed adsorber, Sep. & Pur. Tech. 145 (2015), S. 39-49
- G. Salazar Duarte / B. Schürer / C. Voss / D. Bathen, Modeling and simulation of a tube bundle adsorber for the capture of CO₂ from flue gases, Chem.Ing.Tech. 88 (2016) 3, S. 336-345
- S. Bruckner / T. Demmer / M. Ganswind / D. Bathen, Modeling of water adsorption in a SAPO 34 coated aluminum foam, Chem.Ing.Tech. 89 (2017) 6, S. 757-764

Characterisation of Adsorbents

- M. Helmich / M. Luckas / C. Pasel / D. Bathen, Characterization of microporous activated carbons using the molecular probe method, Carbon 74 (2014), S. 22-31
- J. Treese / C. Pasel / M. Luckas / D. Bathen, Chemical Surface Characterization of Activated Carbons by Adsorption Excess of Probe Molecules, Chem.Eng.Tech. 39 (2016) 6, S. 1144-1150
- C. Bläker / C. Pasel / M. Luckas / F. Dreisbach / D. Bathen, Investigation of load-dependent heat of adsorption of alkanes and alkenes on zeolites and activated carbons, Microporous and Mesoporous Materials 241 (2017), S. 1-10

Thank you for your attention!

Prof. Dr.-Ing. Dieter Bathen



dieter.bathen@uni-due.de

www.uni-due.de/verfahrenstechnik



bathen@iuta.de

www.iuta.de



bathen@jrf.nrw

www.jrf.nrw