

Modeling of dynamic sorption processes

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Outline überarbeiten!



- 1. Introduction
- 2. Scope of Modeling / Simulations
- 3. Modeling / Simulation

Input Parameter

- Mass and Energy balances
- LDF approach

Isotherms

Choice of energy and overall mass balance

- 4. Influence of most important parameters
- 5. Working with the model Examples
- 6. Conclusion







1. Dynamic gas sorption – a multi-scale process





Mesoscopic

adsorbent

Microscopic

adsorption

• Size of Adsorber

3

• Shape of Adsorber

Macroscopic

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

Textural Properties

heat of adsorption

adsorptive

transport into particle

- Surface Characteristics
- Accessibility

1. General Remarks I

Different segments of a breakthrough curve



time

Determination of technical usable sorption capacity

• Can be used as **benchmark** for separation performance of adsorbents



time

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

• Determination of saturation capacity

• By assuming of thermodynamic controlled system \rightarrow Measurement of **isotherms** possible



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1. General Remarks II - Equilibria



2 component mixture: CO₂/He (non-adsorbable carrier)

 \rightarrow Pure component equilibria

- 2 component mixture: CO₂/CH₄ (adsorbable)
 - \rightarrow Partial loading for CO₂ (mixture data)



- 3 component mixture: CO₂/CH₄/He (non-adsorbable carrier)
- Weakly adsorbed component (CH₄) is displaced by stronger adsorbed component (CO₂)

 \rightarrow partial desorption

- → role up effect (evaluation difficult!)
- 3 component mixture: CO₂/CH₄/N₂ (adsorbable)

 \rightarrow Ternary equilibrium data

Parametric Studies & Kinetics

- Quantifying kinetic parameter from breakthrough curves
- Understanding of Sorption Characteristics on Fixed Bed Adsorbers under industrially relevant conditions
- Experimental time can be drastically reduced and parametric studies can be easily performed
- Estimation of role-up effects and dynamic of co-adsorption phenomena
- Calculation of so called **Constant Pattern Profiles**
- Calculation of PSA-cycles based on Mass- and Energy Balances
- Can support Upscaling or Process design



2. Scope of Simulation II



Example: CO₂ Adsorption on D55/1.5



Observations:

- 1) Desorption curve flatter than Adsorption curve
- 2) Desorption time higher than Adsorption time
- 3) Adsorption time 5.78 min (c_{out}< 0.2 %)

Questions concerning:

- 1) Kinetic parameter (k_{LDF})
- 2) Total pressure during each step

3) Adsorption/Desorption times

4) Purge flow during Desorption

Adsorption: 5% CO₂ in N₂ at 40°C, 5 bar, 2000 ml/min on D 55/1.5

Desorption: Purging with 2000 ml/min N_2 at 40°C, 5 bar

3. Modeling – necessary Input Parameter





Cycle duration, pressure range...

Red:properties of adsorbent/adsorptive systemBlack:properties of adsorber and adsorber wall



Mass Transfer coefficient k_{LDF}



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

3. Modeling – Mass and Energy balances





* M.S. Shafeeyan et. al, Chem. Eng. Res. Des. 92 (2014)



Example for Diffusion - Equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \longrightarrow \frac{C_z^{t+1} - C_z^t}{\Delta t} = D \frac{C_{z+1}^{t+1} - 2C_z^{t+1} + C_{z-1}^{t+1}}{\Delta z^2}$$

Transfer of Partial Differential Equation (PDE) to algebraic Equations

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ -D\frac{\Delta t}{\Delta z^2} & 1 + 2D\frac{\Delta t}{\Delta z^2} & -D\frac{\Delta t}{\Delta z^2} & 0 & 0 \\ 0 & -D\frac{\Delta t}{\Delta z^2} & 1 + 2D\frac{\Delta t}{\Delta z^2} & -D\frac{\Delta t}{\Delta z^2} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & -1 & 1 \end{pmatrix} (\vec{C}(t+1)) = (\vec{C}(t))$$

Large Algebraic Equation System

- Vector length depends on height of Adsorber and size of Δz
- Number of steps depends on Time and Δt

$$-D\frac{\Delta t}{\Delta z^2}C_{z+1}^{t+1} + \left(1+2D\frac{\Delta t}{\Delta z^2}\right)C_z^{t+1} - D\frac{\Delta t}{\Delta z^2}C_{z-1}^{t+1} = C_z^t$$

Important Comments for Mass balance

- Three solver parameter Δz , Δt and ratio Δt / Δz^2
- Depending on stiffness of PDE solver converge to correct solution and sufficient accuracy mostly for:

\rightarrow small Δz and

- $\rightarrow \Delta t \ll \Delta z$
- \rightarrow Not always guaranteed convergence
 - → Especially for very steep isotherms

Dynamic Simulation	atagina. In			
File Clipboard Units mass balances energy b	oalances Help			
global Parameters Adsorptives Calculation Table (si	mulated data) Chart (simulated data)	Reactorprofiles PSA-C	Advorbent	
			mass [g]	75.30 📄 from experimental data
			particel diameter [mm]	3.0
height [cm]	20.0		bed porosity	0.30
inner diameter [cm]	3.0		particle porosity	0.30
gas flow [ml (STP) /min]	1001 👘 u constant 🔻	from experimental data	heat capacity [J/K/o]	0.88
axial dispersion [cm2/min]	16.43 🔔 user defined 🔻			
environmental temperature [°C]	39.8 💌 isothermal 🔻	from experimental data	Carrier Gas	
pressure [bar]	5.0	from experimental data	molecular weight [g/mol]	30.0
wall thickness [mm]	3		heat capacity [J/K/g]	1.01
density wall [g/cm3]	7.90			
heat transfer Solid-Gas [W/m2/K]	20.0			
heat transfer bed-wall [W/m2/K]	50.0		height of temperature sensors	
heat transfer wall env. [W/m2/K]	400.0		height of temperature sensor 4 [cm]	16.0
heat capacity wall [J/K/g]	0.477		height of temperature sensor 3 [cm]	12.0
axial heat dispersion [J/K/min/cm]	0.20		height of temperature sensor 2 [cm]	8.0
			height of temperature sensor 1 [cm]	4.0



- No knowledge of script language
- Simple input form for parameter
- Overview of used isotherm model
- No knowledge of solver necessary
- Usage of own Δz , Δt values possible
- Output of stoiciometric values
- Comparison of calculations with Experiment

Dynamic Simulation					-	
File Clipboard Units mass balances energy	gy balances Help					
global Parameters Adsorptives Calculation Table	e (simulated data) Chart (simulat	ted data) Reactorprofiles	PSA-Calculations		_	isotherm model
		Adsorptiv 1	adsorptive 2	adsorptive 3	adsorptive 4	SIPS 🔹
input concentration (process cond.) [Vol.%]	1.0000000	4.98	0	0	0	
effective mass transfer coeff. [1/min]	10.000	20	0	0	0	
molecular Weight [g/mol]	44.0	44	0	0	0	
afinity constant [1/bar]	2.000	0.42795	0	0	0	$(K \cdot p)^{t}$
maximal loading [mg/g]	0.300	230.504	0	0	0	$q_{eq} = q_{\max} \cdot \frac{(r \cdot p)^{\epsilon}}{1 + (K \cdot p)^{\epsilon}}$
Toth/Sips/Freundlich exponent	1.000	0.79585	0	0	0	
heat of sorption [kJ/mol]	20.00	15.966	0	0	0	
temperature dependence of maximal loading	0.000	0.745844	0	0	0	Multicomponent LAI
temperature dependence of exponent	0.000	0.317224	0	0	0	
						number of components
		Set value	Set value	Set value	Set value	1
		/ edit values	edit values	edit values	/ edit values	



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🧏 Dynamic Simulation							
File Clipboard Units mass balances energy bala	ances Help						
global Parameters Adsorptives Calculation Table (simul	lated data) Chart (simulated data) Re	actorprofiles PSA-Calculations					
calculate breakthrough curve	fitting of experime	ital data	calculated parameter				
estimation of solver parameters	utomatic selected Curve	e for Fitting	Reactor Volume [cm3]	141.37			
reliability factor (increase for exact solutions) 1.0	 Adsorptiv 	1	gas velocity (id) [cm/min]	109.5			
x-step size (recommendation (max.): =0.50000)	00 💼 🔿 adsorptiv	e 2	app. particle density [g/cm3]	0.761			
observation height [cm] (max. 20 cm)	adsorptiv	e 3	skeleton density [g/cm3]	1.087			
time resolution factor 1.0	adsorptiv	e 4	stoich. time Adsorptiv 1 [min]	25.57			
t/x^2-ratio (recommendation (max.): =0.008949)	8949 💼	sfer gas wall	stoich. time adsorptive 2 [min]	0.00			
number of calculations (corr. time: =76.71 min) 1714	4 🔿 heat tran	sfer wall env	stoich. time adsorptive 3 [min]	0.00			
required calculation number for 3 x stoich. time: 1714			stoich. time adsorptive 4 [min]	0.00			
number x-direction (vector size) 40			equ. loading Adsorptiv 1 [g/g]	0.033			
 semi-implicit (Lax-Wendroff) mplicit (Upv 	wind)		equ. loading adsorptive 2 [g/g]	0.000			
			equ. loading adsorptive 3 [g/g]	0.000			
init solver Calculate X cano		it exp. Data	equ. loading adsorptive 4 [g/g]	0.000			
	Iteration						



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 Experiment

3. Modeling - Isotherm models





3. Modeling - Energy and overall balances



3. Modeling - Further Simplifications





 \rightarrow Blow-Down within Desorption

Influence of isotherm on breakthrough





Influence of u and c_{in}



time Increasing of velocity *u*:

Breakthrough shifts to lower times, often breakthrough becomes steeper

 $\frac{\partial \overline{q}_i}{\partial t} = k_{eff} \cdot \left(q_i^* - \overline{q}_i \right)$



Increasing of C_{in}:

- Curved isotherm: breakthrough shifts A) to shorter times, curves becomes steeper
- Linear isotherm: breakthrough time B) remains constant

time

Influence of c_{in} on breakthrough depends on shape of isotherm!



For small $D_{ax} \rightarrow$ steepness of breakthrough curves approaches limit



^keff

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For very small $k_{\rm eff}$ spontaneous breakthrough can occur

For small D_{ax} steepness of breakthrough curves tended to a limit





Influence of thermal effects

Temperature

Heat Balance Gas / Adsorbent



Increasing of sorption heat:

Breakthrough shifted to shorter times because sorption capacity=FKT(T) Mass transfer zone becomes bigger, low slope to input concentration Non-isothermal results differ considerably from isothermal results Heat effects have to be considered in most cases (*i.e.* high sorptive concentrations).



Influence of thermal effects (heat transfer parameter)



Increasing of inner heat transfer h_w results in decrease of temperature maximum Increasing of outer heat transfer U_g results in faster cooling rates

Big influence of these parameters on history of temperature inside adsorber



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





Replacement effects



SIPS model (from isotherms):

5. Working with the model – Example II



- Q (equivalent to $-\Delta H_{\Theta=0.5}$)
- Q _{CO2}: 15.9 kJ mol⁻¹
- Q _{CH4}: 11.9 kJ mol⁻¹

Fitting Heat Transfer Coeff.

- $h_w : \sim 30 \text{ W m}^{-2} \text{ K}^{-1}$ (Gas, Fixed Bed/Wall)
- U_g: ~ 400 W m⁻² K⁻¹ (Wall/Liquid)

Input Q in energy balance

Replacement effects – Temperature profiles Use of integral heat of adsorption with



5% CO₂ 15% CH₄ in He at 20°C, 5 bar, 2500 ml/min on D 55/1.5

- Input nue in energy Input nue Input nue CH₄ induced higher temperature effect
 - Model can describe temperature profiles qualitatively
 - Underestimation of temperature peaks
 - Experiment shows mostly sharper temperature profiles
 - \rightarrow differences due to simplification of no radial gradients
 - \rightarrow radial gradients in experiment expected due to external liquid cooling





Replacement effects



Replacement effects – Temperature profiles

Use of integral heat of adsorption with SIPS model (from isotherms):

 $q_{s} = q_{\max} \cdot \frac{(K_{i} \cdot c_{i})^{t_{i}}}{1 + \sum_{j=1}^{n} (K_{j} \cdot c_{j})^{t_{j}}}$ $K_{i} = K_{i,0} \cdot \exp\left(\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_{0}}\right)\right)$ $q_{\max,i} = q_{\max,i,0} \cdot \exp\left(\chi_{i}\left(1 - \frac{T}{T_{0}}\right)\right)$ $t_{i} = t_{i,0} + \alpha_{i}\left(1 - \frac{T_{0}}{T}\right)$

- Q (equivalent to $-\Delta H_{\Theta=0.5}$)
- Q _{CO2}: 25.1 kJ mol⁻¹
- Q _{CH4}: 17.5 kJ mol⁻¹

Fitting Heat Transfer Coeff.

- $h_w : \sim 23 \text{ W m}^{-2} \text{ K}^{-1}$ (Gas, Fixed Bed/Wall)
- $U_g : \sim 500 \text{ W m}^{-2} \text{ K}^{-1}$ (Wall/Liquid)



Input hw in energy



- CO₂ induced higher temperature effect
- Model can describe temperature profiles quite well
- Slightly underestimation of temperature peaks
 - ightarrow differences due to simplification of no radial gradients
 - ightarrow radial gradients in experiment expected due to external liquid cooling





Kinetic Separation





Kinetic Separation



5% CO₂ 15% CH₄ in He at 20°C, 5 bar, 2500 ml/min on MSC-CT-350

balance



Kinetic separation – Temperature profiles

Use of integral heat of adsorption with SIPS model (from isotherms):

 $q_{s} = q_{\max} \cdot \frac{(K_{i} \cdot c_{i})^{t_{i}}}{1 + \sum_{j=1}^{n} (K_{j} \cdot c_{j})^{t_{j}}}$ $K_{i} = K_{i,0} \cdot \exp\left(\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_{0}}\right)\right)$ $q_{\max,i} = q_{\max,i,0} \cdot \exp\left(\chi_{i}\left(1 - \frac{T}{T_{0}}\right)\right)$

- $t_i = t_{i,0} + \alpha_i \left(1 \frac{T_0}{T} \right)$
- Q (equivalent to $-\Delta H_{\Theta=0,5}$)
- Q _{CO2}: 21.5 kJ mol⁻¹
- Q _{CH4}: 9.6 kJ mol⁻¹

Fitting Heat Transfer Coeff.

- $h_w : \sim 40 \text{ W m}^{-2} \text{ K}^{-1}$ (Gas, Fixed Bed/Wall)
- U_g : ~ 450 W m⁻² K⁻¹ (Wall/Liquid)

Input Q in energy



5% CO₂ 15% CH₄ in He at 20°C, 5 bar, 2500 ml/min on MSC- CT-350

- $\frac{1}{100} \frac{1}{100} \frac{1}$
 - \rightarrow CH₄ no contribution to temperature profiles due to slow kinetic
 - Model can describe temperature profiles qualitatively
 - Underestimation of first temperature peak
 - ightarrow differences due to simplification of no radial gradients
 - ightarrow radial gradients in experiment expected due to external liquid cooling



Adsorption and Desorption



3I INSTRUM

Regeneration / PSA



5% CO₂ 95% N₂ at 40°C, 5 bar, 2000 ml/min on D 55/1.5

Model after Fitting

- Isotherms (MCSIPS)
- Kinetic parameter (k_{LDF})
- Heat Transfer Parameter

→ Model can consider slower Desorption due to curved isotherm Parameter from Experiment and general requirements:

- Adsorption time 5.78 min
- Adsorption pressure 5 bar
- Feed Flow 2000 ml/min
- Purge Flow 500 ml/min pure N₂
- Desorption in counter current flow
- Max. CO₂ content in product 1%

Question concerning:

1) Desorption pressure?

Regeneration / PSA



- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 Cycles



Cycle times for Experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow Down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N₂
- Pressurization from 4.6 bar to 5 bar with Feed
- Measurement of 5 cycles

Calculations with p_{DES} = 1 bar

Predictions by modeling:

Regeneration conditions not strong enough \rightarrow CO₂ impurity in effluent flow increases from cycle to cycle to ~ 3 %



Regeneration / PSA



- Adsorption time 5.78 min
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3P NSTRUMENTS

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Predictions were confirmed by experiment

Regeneration / VPSA



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Calculations with p_{DES} = 0.5 bar

Predictions by modeling:

 Regeneration conditions good enough
 → CO₂ impurity in effluent flow increases from cycle to cycle, but still below target (<1%)

Regeneration / VPSA



Cycle times for modeling:

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- Measurement of 5 cycles

But: modeling divers from experiment!

- Cycle Steps in modeling strong simplified
- Variations experiment from model mainly in desorption part
 - → Modeling can help to reduce experimental effort
 → final evaluation only by experiment!

C₃H₈ removal from CH₄ (partial pressure range 0.01 bar and 0.50 bar)

Selection of activated carbon with different BET-Surfaces, but from same raw material

- AC 1 BET ~1800 m²/g
- AC 2 BET ~1300 m²/g



Often AC with higher BET will be selected by user which is not always the best decision!

 \rightarrow according to isotherms AC 2 is better for low C₃H₈ concentrations

 \rightarrow for high C₃H₈ concentrations AC 1 is better

C_3H_8 removal from CH_4 (partial pressure range 0.01 bar and 0.50 bar)

Selection of activated carbon with different BET-Surfaces, but from same raw material

- AC 1 BET ~1800 m²/g
- AC 2 BET ~1300 m²/g



Breakthrough experiments and simulations very sensitive for low concentrations!

 \rightarrow Observations made from isotherms were confirmed by dynamic experiments and calculations

Calculation of Constant Pattern Profiles

For favored isotherms (TYP I-Isotherms) a Constant Pattern Behavior can occur

- Shape of breakthrough will not change for longer elongation times or adsorber heights, respectively
- Based on compensation of flattening and rising effects
- Height for Constant Pattern = FKT(Shape of Isotherm, Dispersion, Kinetics)



5% CO₂ in He at 40°C, 5 bar, 1000 ml/min on D 55/1.5

Experiment carried out at 20 cm, simulations were performed for different heights

- \rightarrow Slopes at C/C₀=0.5 were used to evaluate steepness of breakthrough curves
- \rightarrow Constant pattern Behavior can be expect above 20 cm bed height





Limitations of simplified model – Water on Activated Carbon

Difficult to calculate breakthrough due to shape of isotherm, good isotherm model fit necessary!



1 bar, 4000 ml/min on D 55/1.5

- Isotherm fit with an empiric Dualsite Langmuir-SIPS equation
- Heat of adsorption 60 kJ/mol
- Heat for condensation 40.8 kJ/mol

- \rightarrow Description of the curve qualitatively possible
- ightarrow Isothermal calculation failed for this example
- \rightarrow Stronger deviations for condensation part

5. Conclusions

- Gas-Flow Methods allow Characterization under **application-related conditions**
- Information regarding Kinetics can be obtained by fitting of mass- and energy balances
- Modeling can be helpful for interpretation dynamic sorption processes
- PSA process design can supported by Simulations
- Modeling can lead to **considerable decrease of experimental effort**
- Simulation model can used for investigations of Constant Pattern Behavior

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Thank You!





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