Breakthrough Curves of CO_2 and CH_4 on Carbon Molecular Sieves - Experiment and Modelling

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Introduction

Carbon molecular sieves (CMS) are widely used for the refinement of biogas to biomethane [1]. This application is based on kinetic separation due to size selective adsorption in PSA processes [2]. Modern CMS are tuned towards maximum sorption capacities regarding to the component, which is to adsorbed. By means of dynamic measurements, it is possible to examine such materials at realistic process conditions with respect to sorption kinetics and capacities.

In this study breakthrough curves of CO_2, CH_4 in He and their mixtures were measured on Shirasagi MSC CT-300. It can be shown, that an evaluation of the performance of such materials, based on isotherms are not always correct and will lead sometimes to misinterpretation of the whole separation process.

Objectives

Purification of biogas to biomethane necessary for grid feeding:

Typical distribution of main components in biogas / % [3]

CH_4	CO_2	H_2O	H_2S	Other Components
40-75	25-55	<10	<0.5	Balance

Requirements to gas composition according to DVGW G 260 and 262 / % [4]

CH_4	CO_2	H_2O	H_2S	Other Components
acc. to Wobbe index	<6	<50 mg m^{-3}	<5 mg m^{-3}	Balance

H_2S: Removal of H_2S with biological methods (first step), chemical/physical methods

CO_2: **Removal of CO_2 with carbon molecular sieves (PSA process)** or treatment with chemicals (amines)

Test procedures to evaluate the performance of Carbon Molecular Sieves: **Determination of breakthrough at different gas velocities and pressures with dynaSorb BT, modeling and simulation of CH_4 purification.**

Experimental

The experiments were carried out with the commercial available device dynaSorb BT from Quantachrome Instruments at 40 °C. This device is designed for dynamic test routines under process relevant conditions.

As adsorbent the carbon molecular sieve Shirasagi MCS CT-350 from CarboTech AC was used. This material has been especially developed for removal of CO_2 from CH_4 rich gas mixtures. Before the measurements the material was regenerated at 150 °C for 4 h.

The predefined test routines and the mathematical model for evaluation all data are included in the software package of dynaSorb BT.

Mathematical Model – Equations [5, 6, 7]

Mass Balance

$$\frac{\partial C}{\partial t} - D_{ax}\frac{\partial^2 C}{\partial z^2} + u\frac{\partial C}{\partial z} + C\frac{\partial u}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon}\rho_b\frac{\partial \bar{q}}{\partial t} = 0$$

Mass-Transfer Equation

$$\frac{\partial \bar{q}}{\partial t} = K\cdot\left(q^* - \bar{q}\right)$$

Momentum Balance – Ergun Equation

$$-\frac{\partial p}{\partial z} = \frac{150\mu(1-\varepsilon)^2}{\varepsilon^3 d_p^2}u + \frac{1.75(1-\varepsilon)\rho}{\varepsilon^3 d_p}u^2$$

Isotherm Equation

$$q^* = \max\cdot\frac{b\cdot C_g}{\left(1+\left(b\cdot C_g\right)^t\right)^{\left(1/t\right)}}$$

Energy Balance for Fixed Bed (simplified)

$$\rho_b(-\Delta H)\frac{\partial \bar{q}}{\partial t} - \left(C_{p,S}\cdot\rho_b + (1+\varepsilon)C_{p,G}\cdot\rho_g\right)\frac{\partial T}{\partial t} - \frac{4h_w}{D}(T-T_w) = 0$$

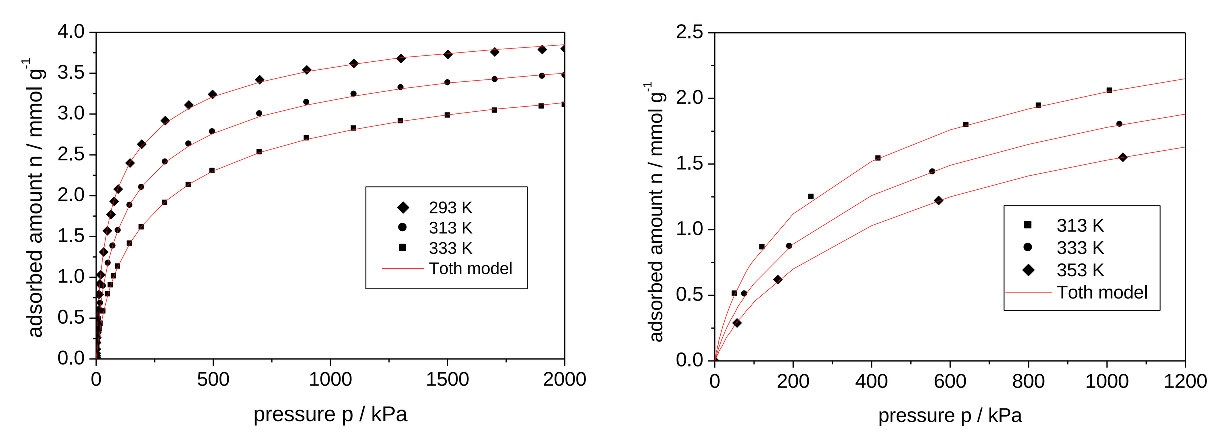
Energy Balance for Adsorber Wall (simplified)

$$\alpha_w h_w(T-T_w) - \rho_w C_{p,w}\frac{\partial T_w}{\partial t} - \alpha_{wL}U(T_w-T_e) = 0$$

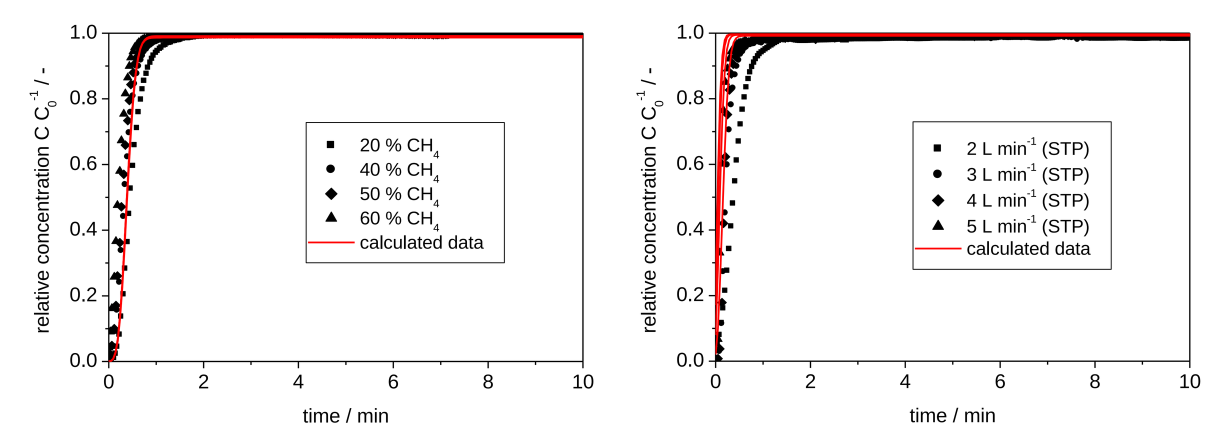
Operation conditions for breakthrough experiments on MSC CT-350 with dynaSorb BT

conditions	CO_2 in He		CH_4 in He		CH_4/CO_2
	V1	*V2*	*V3*	*V4*	*V5*
Temperature [K]	313	313	313	313	313
Pressure [MPa]	0.4	0.4	0.4	0.4	0.4
Fraction CH_4 [%]	-	-	10	**20 - 60**	**20 - 40**
Fraction CO_2 [%]	10	**10 - 60**	-	-	**20 - 40**
Flow rate [cm^3 s^{-1}]	**16.7 – 83.3**	16.7	**33.3 – 83.3**	16.7	33.3

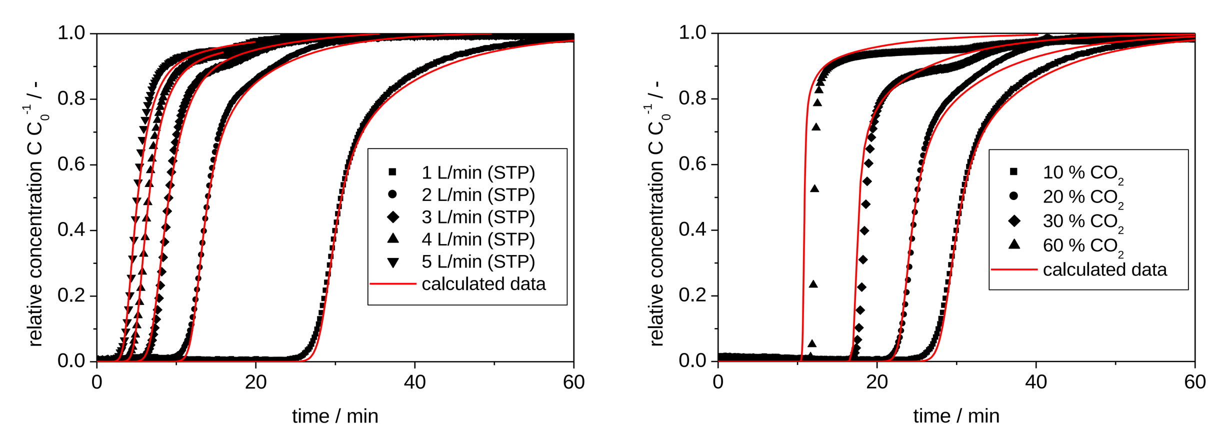
Isotherms of CO_2 and CH_4 on MSC CT-350 from [8]



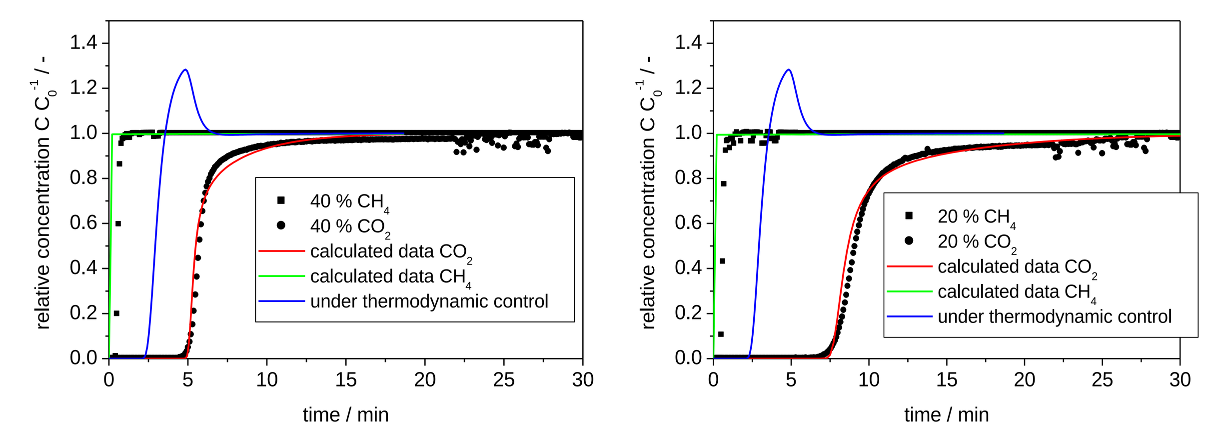
Breakthrough curves of CH_4 on MCS CT-350



Breakthrough curves of CO_2 on MCS CT-350



Breakthrough curves of CH_4/CO_2 on MSC CT-350



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Conclusion

All breakthrough curves of CO_2 show the expected behaviour for a thermodynamic controlled system. However the curves for CH_4 have spontaneous breakthroughs due to the very low kinetic of the CH_4 molecules on MCS CT-350. This different behaviour increases the effective selectivity of the investigated material for the desired separation process considerable. This results in higher selectivity performance compared to the predicted thermodynamic selectivity from isotherms.

Therefore, detailed investigations of kinetics with dynamic methods, i.e. breakthrough experiments, are necessary for a reliable assessment of such materials. The evaluation of isotherms from static methods without considering kinetic effects will lead to considerable misinterpretation of such materials.

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