A thermodynamic model for the adsorption of heavy hydrocarbons on silica alumina gel in natural gas processing

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Introduction

Beside light hydrocarbons natural gas includes hydrocarbons of higher molecular weight, which are valuable raw materials for chemical industry. A common method for hydrocarbon recovery is fixed bed adsorption in cyclic temperature swing adsorption processes (TSA). To optimize the design of these processes a deep knowledge of the thermodynamics of ad- and desorption is necessary. The Chair of Thermal Process Engineering at the University of Duisburg-Essen and the adsorbent manufacturer BASF cooperate to measure cumulative breakthrough curves in a fixed bed adsorber at different temperatures to calculate adsorption isotherms and isosteric heats of adsorption.

By comparison of equilibrium capacities and heats of adsorption different mechanisms e.g. of C_6 hydrocarbons can be found and linked to their different molecular structure and properties. We evolve an adsorption equilibrium model using the adsorption potential of the Freundlich equation to get a global description of a temperature dependent field of isotherms on heterogeneous surfaces. Using this model it is also possible to estimate the adsorption enthalpy as a function of loading and temperature. By comparing results of the model and of the isosteric method with an independent calorimetric measurement the validity and limits of the calculation methods can be discussed.

Experimental Methods

Apparatus:

- Test gas from thermal mass flow controller (adsorptive + N_2 matrix gas)
- Dosing of heavy hydrocarbons by a bubbler system
- Vertical fixed bed adsorber
- Quasi-continuous analysis by micro-gas-chromatograph (µ-GC)
- Temperatures up to 300°C, pressure 1.3 bar

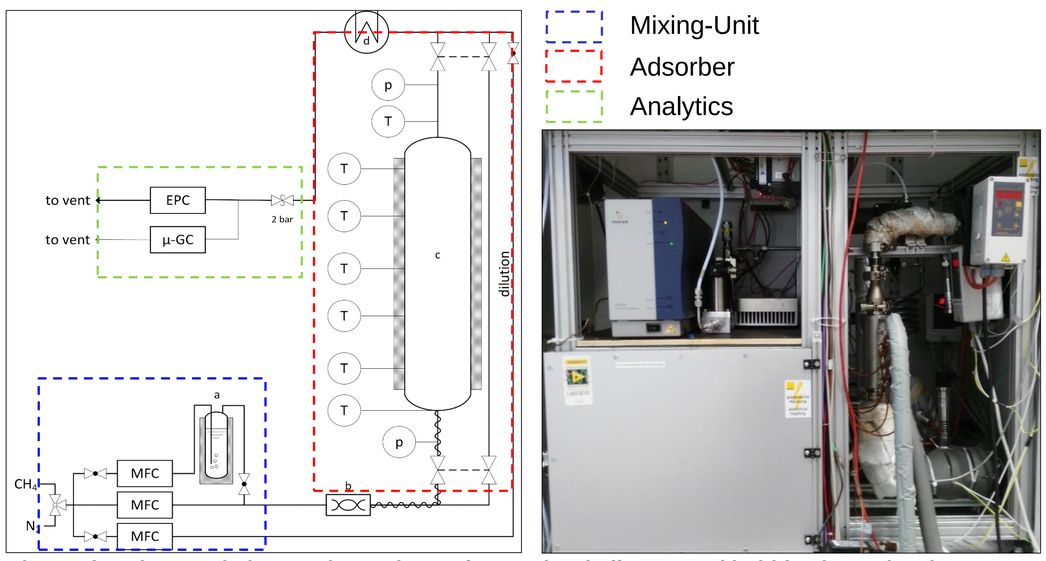

Fig. 1: Flowsheet and picture of experimental setup (a: shell tempered bubbler, b: static mixer, c: shell tempered adsorber column, d: air cooler)

Methods:

- Cumulative breakthrough experiments between 25°C - 75°C → isotherms

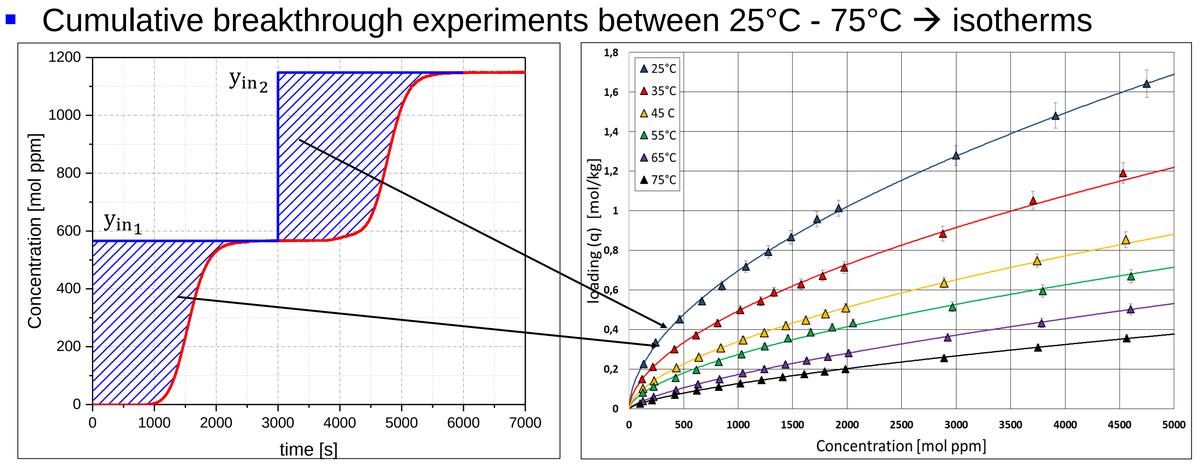

Fig. 1: Calculation of adsorption isotherms from cumulative breakthrough curves

- a) Calculation of isosteric heats of adsorption from experimental data

$$\Delta h_{Ads} = R \cdot \frac{\partial ln(p_A)}{\partial \frac{1}{T}}\bigg|_q$$

- b) Global fitting of temperature-dependent Freundlich parameters between 25°C and 75°C $\quad q_{(T)} = k_F(T) \cdot p_A^{n(T)}$

→ Estimation of temperature dependent adsorption enthalpy

Results and Discussion

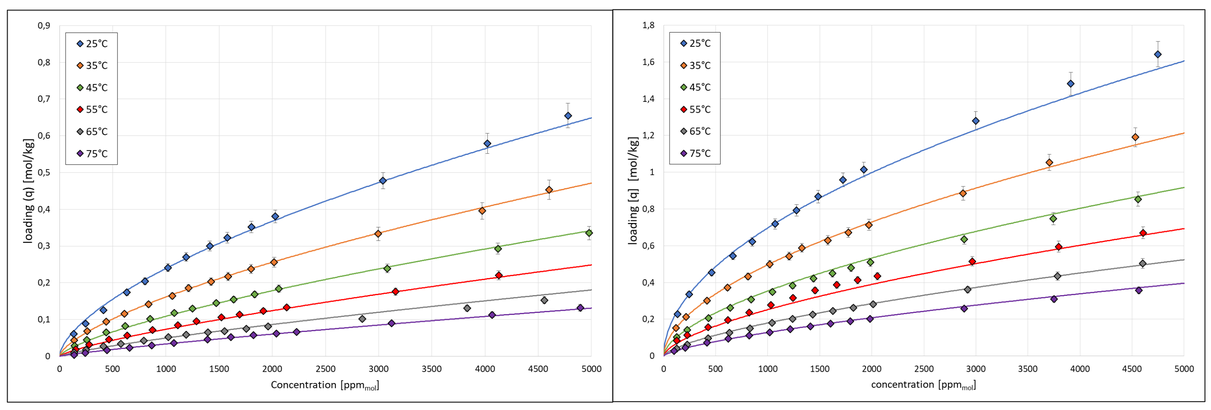

Fig. 2: Adsorption isotherms of n-hexane (left diagram) and benzene (right diagram) on Sorbead H at different temperatures (25 °C - 75 °C). (lines: fit with global model)

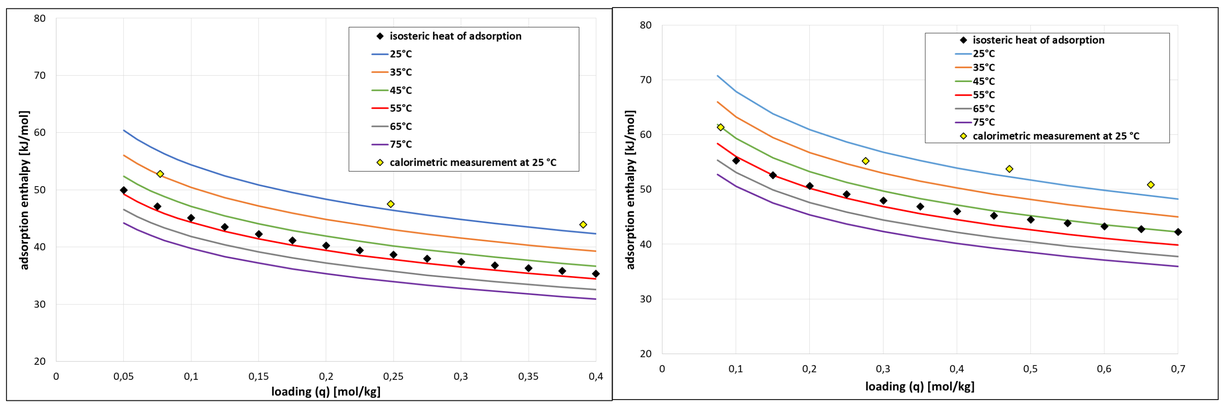

Fig. 3: Comparison of different adsorption enthalpies (isosteric heat of adsorption, temperature-dependent model, calorimetric measurement at 25°C) of n-hexane (left diagram) and benzene (right diagram) on Sorbead H at different loading

- Temperature dependent model describes the whole temperature range between 25°C and 75°C
- Excellent fit of experimental data by temperature-dependent Freundlich-model
- Higher loadings of benzene in comparison to n-hexane

- Higher adsorption enthalpy of benzene fits to higher capacity
- Isosteric heat of adsorption averages temperature dependent enthalpies
- Good approximated enthalpy at 25 °C by the temperature dependent model
- Estimation of temperature dependency of adsorption enthalpy possible
- Benzene shows stronger temperature dependency than n-hexane

Resume and Prospect

The adsorption of C_6 hydrocarbons on sililca alumina gels is measured in a temperature range between 25°C and 75°C. By fitting temperature-dependent parameters of the Freundlich isotherm a good prediction of the equilibrium capacity is possible in the experimental temperature range. Additionally, an estimation of the temperature dependency of the adsorption enthalpy can be obtained. By calorimetric measurement the validity of the model is proved at 25°C. Furthermore a comparison with the isosteric heat of adsorption shows the limitations of the isosteric method where a temperature-independent adsorption enthalpy is assumed.

By comparing the adsorption of the aromatic benzene with the aliphatic n-hexane a higher capacity, higher adsorption enthalpy, and more pronounced temperature dependency occurs.
The experiments will be extended to hydrocarbons of higher molecular weight and other silica alumina gels. The predicted temperature dependency of the adsorption enthalpy should be verified by calorimetric measurements at higher temperatures. Based on a deep knowledge of heavy hydrocarbon adsorption on silica alumina gels new adsorbents will be designed for a more effective separation.

Acknowledgments

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