Adsorption of Components of Biofuel on Activated Carbon

M. Lange[(1)], A. Möller[(1)], R. Gläser[(1)], E. Schieferstein[(2)], J. U. Keller[(3)]

[(1)]Institut für Nichtklassische Chemie e.V., Leipzig/Germany

[(2)] Fraunhofer-Institut UMSICHT, Oberhausen/Germany

[(3)] Institute of Fluid- and Thermodynamics, University of Siegen, Siegen/Germany

E-Mail: lange@inc.uni-leipzig.de Homepage: http://www.uni-leipzig.de/inc

Introduction

Otto-engine-powered vehicles have a fuel vapor retention system, which is installed in the vent line of the tank (see Fig. 1). This system applies activated carbon (AC) to avoid emissions of polluting gases in the environment. At certain engine parameters the AC container is flushed with fresh air and desorption is caused by concentration gradient.

Bioethanol is already used as alternative fuel, especially in Sweden, USA and Brazil.[1] In Europe it is mainly added to gasoline, e.g., in Germany the fraction of the ethanol amount is recently increased up to 10 % (E10).[2-4]

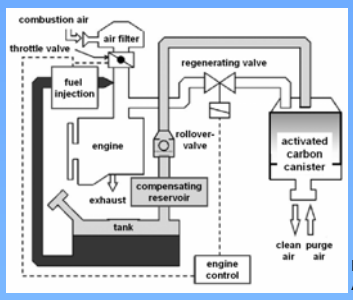

Fig. 1: functional set-up of the AC-filter in a vehicle[5]

The retention system has been designed for (standardized) gasoline, but neither for use with E5 or E10.

For this purpose, it is necessary to study the adsorption behavior of the individual components of biofuel and their mixtures to get more information of the adsorption behavior of the AC, if exposed to gas mixtures evaporating from E10 or related mixtures with higher proportions of alcohol.

Experimental / Material

Adsorption isotherms of methanol, ethanol and *n*-alkanes as well as certified gasoline were measured on the activated carbon BAX1100 (Westvaco) at 283 K, 297 K and 308 K by using a gravimetric magnetic suspension balance (Rubotherm, Germany). Moreover, coadsorption measurements of *n*-hexane–ethanol mixtures on BAX1100 were performed at 283 K. The Tóth equation (eq. 1) was used for the mathematical description and calculation of the isosteric heat of adsorption.

$$N = N_{max} \cdot \frac{b \cdot p}{\left[1 + (b \cdot p)^t\right]^{\frac{1}{t}}} \qquad (1)$$

Fig. 2: Gravimetric system for measurement of vapor adsorption equilibria with static measuring method (left) or flow measurement method (right) on a magnetic suspension balance (center, Rubotherm).

Textural properties of BAX1100:

In Table 1 are the textural properties of BAX1100.

Tab. 1: Specific Surface Area (BET), Pore volume (* Gurvich rule, ** method of Horvath and Kawazoe, *** method of Dubinin and Raduskevich, **** method of BJH) and Specific Volume

	A_{BET} / m^2 g^{-1}	V_{Pore} * / cm^3 g^{-1}	V_{micro} / cm^3 g^{-1}	V_{meso} **** / cm^3 g^{-1}	V_{spec} / cm^3 g^{-1}
BAX1100	1326	0,97	0,57 **	0,53	0,542
			0,50 ***		

The N_2-isotherm at 77 K and Pore Size Distribution of BAX1100 are presented in Fig. 3.

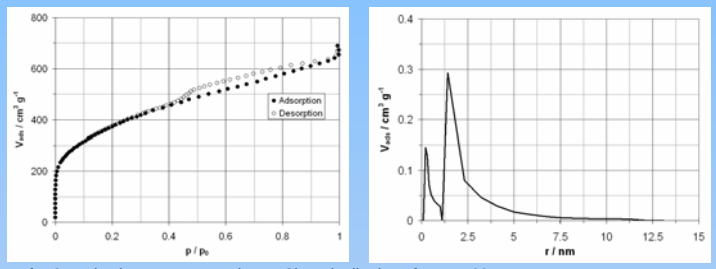

Fig. 3: N_2-isotherm at 77 K and Pore Size Distribution of BAX1100.

Results

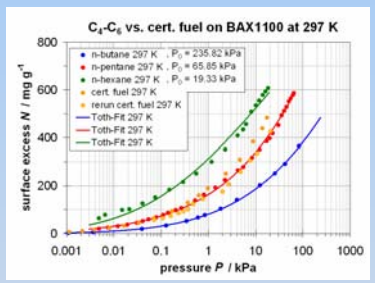

Fig. 4: Adsorption isotherms of certified fuel (orange) in comparison with *n*-butane (blue), *n*-pentane (red) and *n*-hexane (green) on BAX1100 at 297 K.

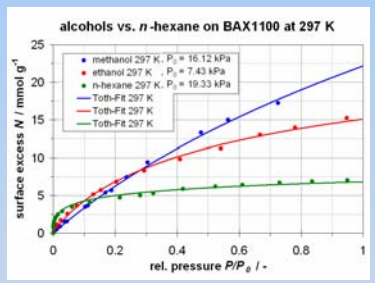

Fig. 5: Adsorption isotherms of *n*-hexane (green) in comparison with methanol (blue) and ethanol (red) on BAX1100 at 297 K.

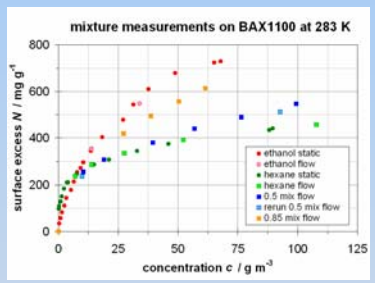

Fig. 6: Adsorption isotherms of *n*-hexane–ethanol mixtures on BAX1100.

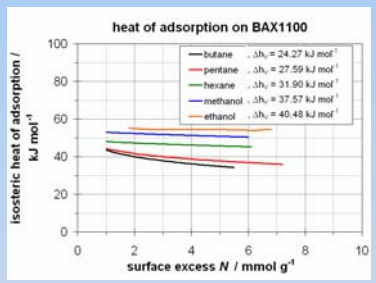

Fig. 7: Isosteric heat of adsorption of *n*-alkanes and alcohols on BAX1100

➔Comparison of adsorption isotherms of accredited fuel compared to *n*-alkanes to find a appropriate model fluid for gasoline.

➔It is evidenced that the adsorption behavior of gasoline corresponds with *n*-pentane in lower pressure region and at higher pressures it approximates to *n*-hexane.

➔All measured adsorption isotherms demonstrate Typ-I behavior by IUPAC-classification.

➔Methanol offers the highest adsorption capacities for saturation pressure range on BAX1100 explainable by its molecular size.

➔Mixture measurements for E50 (50:50 – ethanol:*n*-hexane) and E85 (85:15 – ethanol:*n*-hexane) flanked by the pure vapor isotherms of ethanol and *n*-hexane

➔E85 approaches the pure ethanol isotherm while E50 is strongly attracted to pure *n*-hexane isotherm

➔The Tóth model provides data for heat of adsorption (h_{Ads}) of methanol, ethanol and *n*-alkanes on BAX1100

➔Binding energies ($h_B = h_{Ads} - \Delta h_V$) for alcohols (~ 15 kJ mol^{-1}) are lower than for *n*-alkanes (~ 19 kJ mol^{-1})

Summary

- Pure vapor isotherms of methanol, ethanol and *n*-alkanes on activated carbon BAX1100 (Westvaco) at 283 K, 297 K and 308 K were measured gravimetrically up to its saturation pressure
- Adsorption behavior of accredited gasoline resembles *n*-pentane in the low pressure range and approaches the isotherm of *n*-hexane for higher pressures
- At low pressure *n*-hexane is adsorbed best, however, in saturation pressure range methanol and ethanol show higher adsorption capacities in consequence of their molecular size.
- Adsorption isotherms of *n*-hexane–ethanol mixtures at 283 K, measured with the flow measurement method, are comprehensible in their adsorption behavior
- Tóth equation describes the experimental data in a good manner. Thus, the heat of adsorption of methanol, ethanol and *n*-alkanes were presented.
- *n*-alkanes have a major attraction to BAX1100 compared to alcohols given by the binding energy (h_B)

References

[1] FNR – Fachagentur Nachwachsende Rohstoffe e.V. (Hrsg.), 2007, 3. Auflage: Biokraftstoffe. Gülzow: FNR.

[2] FNR – Fachagentur Nachwachsende Rohstoffe e.V. (Hrsg.), 2010: Biokraftstoffe – Basisdaten Deutschland. Stand: Juni 2010. Gülzow: FNR.

[3] Richtlinie 2009/28/EG des europäischen Parlaments und des Rates.

[4] Bundes-Immissionsschutzgesetz (BImSchG) § 37a Abs. 3.

[5] J. Sohnemann, Diss., 2005, Dortmund

Acknowledgement

The authors thank the *Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AiF-FV No.: 16211)* for financial support.

Printed in the computer centre of University of Leipzig