

Experimental determination of multi-component vapour sorption on active carbon by combined micro-gravimetry and dynamic sampling mass spectrometry

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Experimental methods for direct measurement of multi-component vapour sorption are evaluated in a prototype instrument which combines the gravimetric method for determination of the kinetics and equilibria of the total adsorption and uses mass spectrometry for the analysis of each component. Results are presented for adsorption of water-octane and water-butane on carbon BAX950.

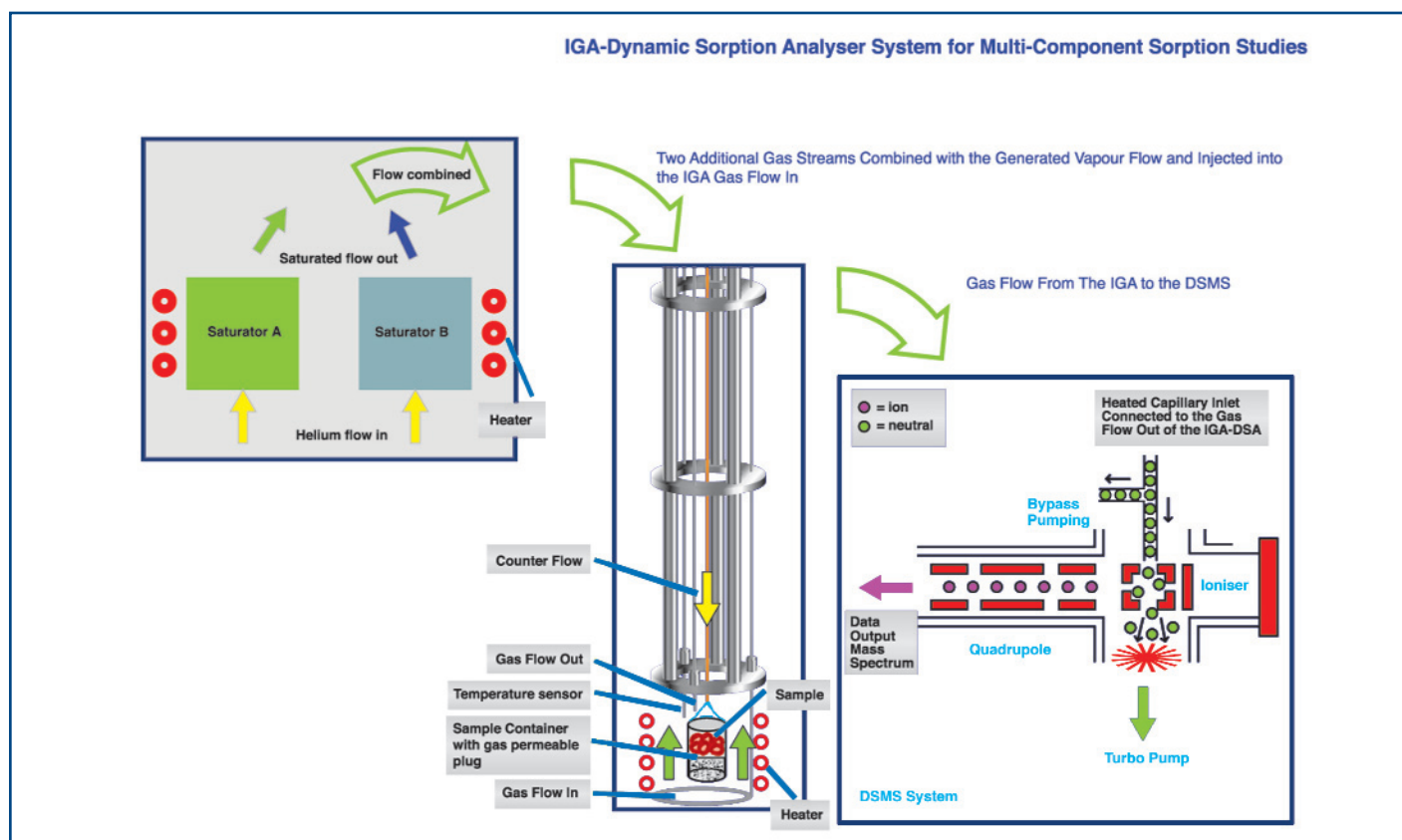
Introduction

Activated carbons are widely used for the removal of environmentally unfriendly species including hydrocarbon vapours. The performance of the carbon bed is inevitably influenced by multi-component adsorption: For example, the presence of water vapour can produce degradation in the breakthrough times of other species [1]. The primary activated carbon adsorption sites for hydrocarbons are hydrophobic sites comprising mainly of the graphene basal plane layers whereas for water these are hydrophilic functional groups. Water molecules can either form isolated clusters which are a potential barrier to hydrocarbon diffusion, or form a continuous surface film depending on the functional group density: Pore volume filling occur at high relative pressure but the density of

the adsorbed water is usually lower than that of the liquid. This has been ascribed to the inability of adsorbed water to form a full 3-dimensional structure in microporosity [2].

Experimental

The gravimetric method is preferred for single component studies not least because it provides a direct, continuous and reproducible measurement of the sample uptake. The use of microgravimetry for multi-component analysis has most commonly involved the van Ness method [3] using a complete set of gas adsorption/concentration isotherms. However, given that equilibration times for e.g., hydrocarbon vapours are orders of magnitude longer, the method is not favourable in relation to the present studies. The fully automated instrument designed for this investigation uses the (Hidden IGA) gravimetric method [4] to continuously weigh the sample in the presence of a carrier gas flow that is regulated upstream at constant total pressure in the balance chamber. The vapours are introduced from a thermostatted vapour generator and fed to a reactor housing the sample that has a separate isothermal jacket (Fig. 1). An independent heating element at the sample position is used for controlled ramp desorption from 0.1-50 °C/min. A





experimental sequences including commutation of isothermal equilibration at 294 ± 0.02 K and flow desorption studies (Figs. 3-9). All these examples use helium as a carrier and pressure regulation is at 1000 ± 1 mbar. In example (a) the predominant factor in obtaining reproducibility is the accuracy of temperature control which is of course critical for all vapour phase experiments. Independent isothermal control by recirculating bath to ± 0.02 K or better is required and the anti-condensation heating of enclosures is regulated within ± 0.1 K.

Mass spectrometer data are normalised to total pressure and then scaled to the equivalent mass rate to enable direct comparison with the differentiated gravimetric measurement (DTG). In the case of isothermal equilibration the comparison is then of mass balance. For example, Fig. 3 shows the displacement of water after the onset of exposure to *n*-octane and the observed gravimetric rate which is reduced in comparison with

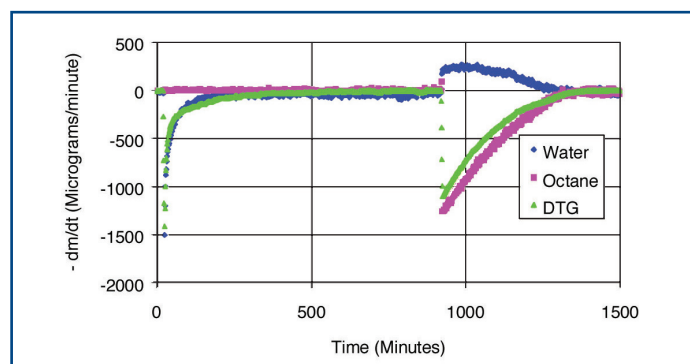


Figure 3: Reaction 'signature' of sequential adsorption of water $p/p_0=0.6$ and octane $p/p_0=0.1$ on BAX950. (The raw gravimetric data is shown in Fig. 5)

Hidden HPR-20 series mass spectrometer is used for gas analysis immediately upstream of the sample position via a heated capillary and direct source inlet. The material used is BAX950 which is a wood-based activated carbon obtained from the Westvaco Corporation, Virginia.

Results

The performance of the system is assessed with the following; the reproducibility of gravimetric response in combined flow of two vapours (Fig. 2), and by operating with different

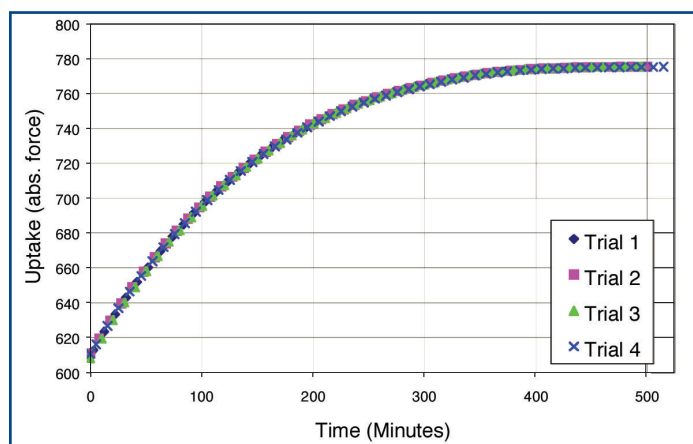


Figure 2: Reproducibility of uptake determination of octane on preadsorbed water



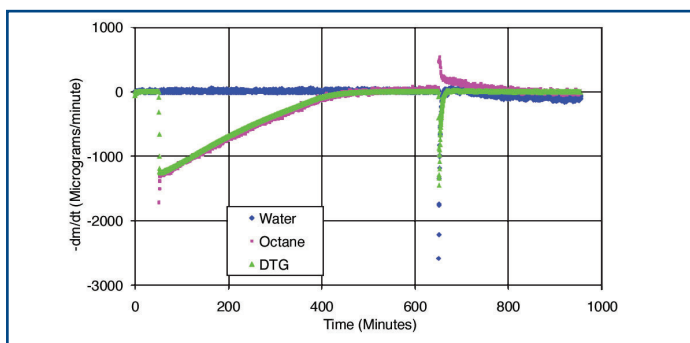
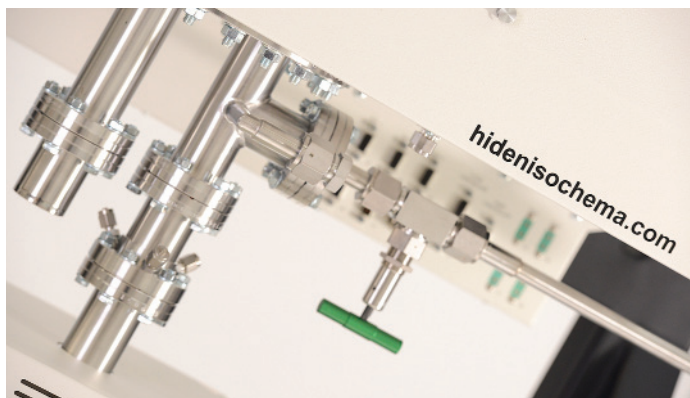


Figure 4: Reaction 'signature' of sequential adsorption of octane $p/p_0=0.1$ and water $p/p_0=0.6$ on BAX950. (The raw gravimetric data is shown in Fig. 5)

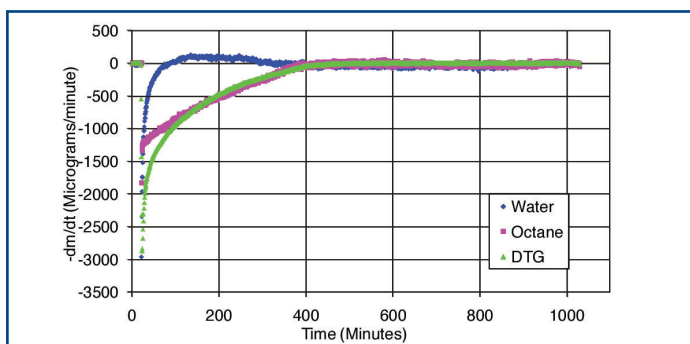


Figure 5: Reaction 'signature' of simultaneous adsorption of octane $p/p_0=0.1$ and water $p/p_0=0.6$ on BAX950.

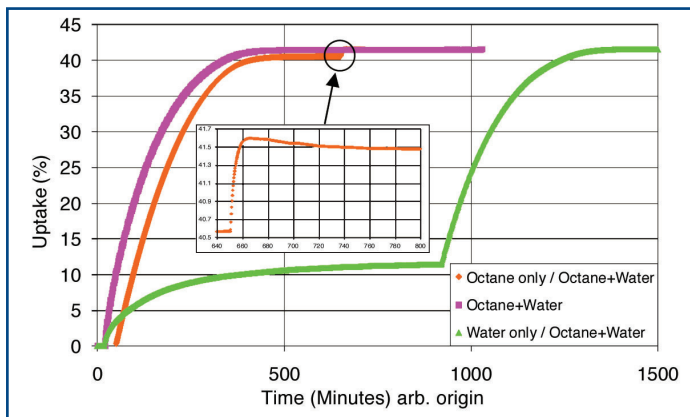


Figure 6: Gravimetric response of commutations of octane $p/p_0=0.6$ and water $p/p_0=0.1$ on BAX 950. (Inset shows detail of the gravimetric response when water is introduced into the octane flow)

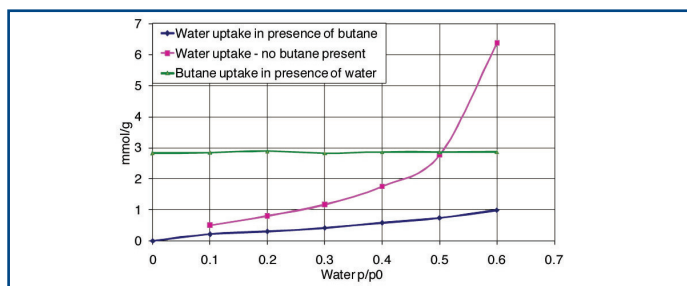


Figure 7: Adsorption of water on BAX950 at 294K with and without the presence of butane at $p/p_0=0.023$ (helium carrier present).

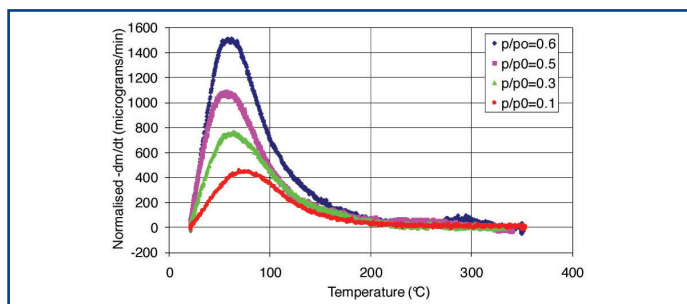


Figure 8: TPD of water from BAX950 following sequential equilibration in butane $p/p_0=0.023$ and water (see legend for p/p_0 details) at 294K

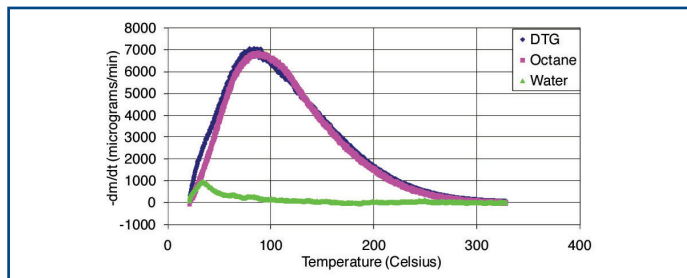


Figure 9: TPD of BAX950 after sequential loading of octane $p/p_0=0.1$ and water $p/p_0=0.8$

the measured n -octane rate. When the exposure sequence is reversed a minor n -octane displacement is seen and the gravimetric signature exhibits relaxation (Figs. 4 and 6). The desorption experiments (Figs. 7, 8 and 9) are similarly scaled and integrated areas used to determine the total uptake of each component.

Conclusions

Flow desorption studies within the limits of operating conditions used thus far have shown an invariance of hydrocarbon loading (within $\sim 1\%$) as humidity is increased and moreover the concentration of adsorbed water is in all cases significantly lower than the pure component isotherm. Commutation of isothermal loading has thus far shown relatively minor change in the hydrocarbon kinetics. This study is currently being extended to a wider concentration range.

References

- [1] C. R. Hall and K. S. W. Sing, Chem. Br. 24 (1988) 670
- [2] N. J. Foley, K. M. Thomas, P. L. Forshaw, D. Stanton, and P. R. Norman, Langmuir 13 (7) (1997) 2083-2089
- [3] H. C. Van Ness, Ind. Eng. Chem. Fundam. 8 (3) (1969) 464-473
- [4] M. J. Benham and D. K. Ross, Z. Phys. Chem. NF 163 (1989) S25-S32

