

# EQUILIBRIUM AND KINETIC PROPERTIES OF HYDROCARBON VAPOUR ADSORPTION ON ACTIVATED CARBON UNDER DRY AND HUMID CONDITIONS

*M.J.G. Linders<sup>1,2</sup>, L.J.P. van den Broeke<sup>1</sup>, E.P.J. Mallens<sup>2</sup>,  
J.J.G.M. van Bokhoven<sup>2</sup>, F. Kapteijn<sup>1</sup> and J.A. Moulijn<sup>1</sup>*

<sup>1</sup> *Industrial Catalysis - CPT, Delft University of Technology*

*Julianalaan 136, 2628 BL Delft, The Netherlands*

<sup>2</sup> *TNO - Prins Maurits Laboratory,*

*Lange Kleiweg 137, 2280 AA Rijswijk, The Netherlands*

## Introduction

In practical vapour adsorption processes, ranging from industrial adsorption columns to gas mask canisters, water vapour is often present in the feed. In this study the effect of water vapour adsorption on the performance of activated carbon beds is studied. Equilibrium and dynamic sorption are investigated of the organic vapours hexafluoropropene (HFP), methanol, and ethanol, under dry as well as under humid conditions. The results are incorporated into a model, which describes the binary adsorption process of the system water/hydrocarbon in an activated carbon bed.

## Experimental

The adsorbent used is the Norit R1 activated carbon (Norit N.V., The Netherlands). The adsorbent consists of extrudates with an average diameter of 1.0 mm, and an average length of 2.6 mm. The Norit R1 activated carbon was characterised with nitrogen adsorption at 77 K and mercury porosimetry. The activated carbon particles have a bimodal pore size distribution with both macro- and micropores.

For the Norit R1 carbon adsorption isotherms, transient uptake profiles, and breakthrough curves were obtained.

The equilibrium adsorption isotherms of HFP, methanol, ethanol were measured on dried Norit R1 carbon using the head space analysis method. With this method equilibrium isotherms were obtained covering 3 to 4 pressure decades. Shortly, the method is as follows. A known amount of carbon is put into a vial which is sealed gastight with a rubber cap. Subsequently, the adsorptive is injected into the vial. The injected amount is exactly determined by weighing. After equilibration in a thermostatted bath the gas phase concentration of

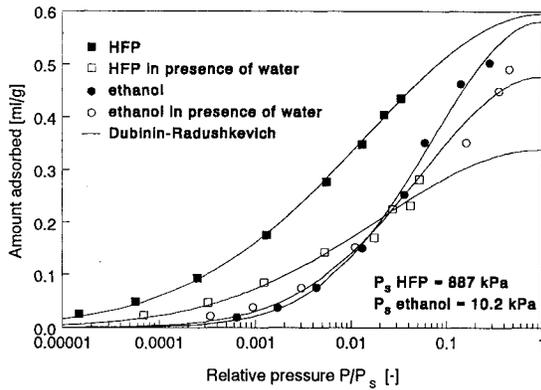
the adsorptive is analysed by gas chromatography. The amount adsorbed on the activated carbon is calculated from a mass balance. In addition to the adsorption isotherms on dried carbon the adsorption isotherms were measured under humid conditions. At a relative humidity of about 60% 0.25 ml water per gram carbon was pre-adsorbed onto the Norit R1 carbon, followed by the adsorption of the component concerned. All the isotherms were measured at a temperature of 303 K.

Transient uptake profiles of the single components were measured with a microbalance (type TG-DSC111, Setaram). The transient experiments were performed under differential conditions, ensuring that all the carbon particles experience the same concentration at the outer surface. From these profiles diffusion coefficients were derived.

Packed bed breakthrough curves have been obtained for HFP and ethanol under dry and humid conditions. In the latter case the carbon was pre-loaded with water by passing helium through the bed at a relative humidity of 80%. After conditioning the carbon bed a HFP or ethanol feed, also at a relative humidity of 80%, was fed to the carbon bed. The experiments were performed at a temperature of 295 K, and a total pressure of 101 kPa. The inlet concentration was 23.0 g/m<sup>3</sup> for HFP, and 6.1 g/m<sup>3</sup> for ethanol. The diameter of the bed was 6.0 mm, and the bed length was 4.0 cm in the case of HFP, and 2.0 cm in the case of ethanol.

## Results and Discussion

In Figure 1 the adsorption isotherms are given of ethanol and HFP. The adsorption isotherms of the single components are compared to the adsorption isotherms determined under humid conditions. It is seen that pre-adsorbed water does not influence the adsorption of ethanol in the low-pressure regime. At higher pressures the ethanol adsorption is somewhat



**Figure 1.** Adsorption isotherms of HFP and ethanol on Norit R1 under dry and humid conditions.

lower as compared to the single component isotherm because the total binary capacity has been reached. Similar results were found for methanol. For HFP, however, it is found that pre-adsorbed water restricts the adsorption of HFP over the whole pressure range. The amount adsorbed HFP decreases by a factor of about two. The adsorption isotherm data were fitted with the Dubinin-Radushkevich relation, given by:

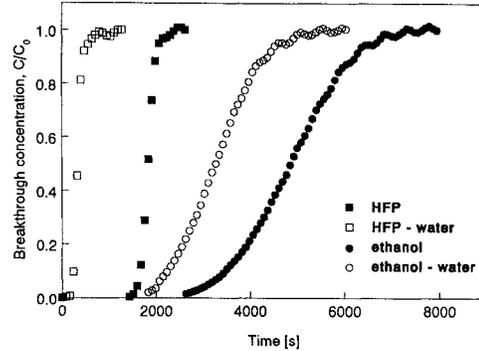
$$\frac{q}{q_{max}} = \exp\left(-B^2 \ln^2\left(\frac{p}{p_s}\right)\right) \quad \text{with:} \quad B = \frac{RT}{\beta E_0}$$

where  $q$  is the amount adsorbed,  $q_{max}$  is the amount adsorbed at saturation,  $p$  is the partial pressure,  $p_s$  the saturation pressure,  $R$  is the gas constant,  $T$  is the temperature,  $\beta$  is the affinity coefficient of the adsorptive, and  $E_0$  is the characteristic energy of the adsorbent. In Table 1 the adsorption parameters are given for the two situations considered. For both components it is found that the presence of water has a larger influence on the capacity  $n_0$  than on parameter  $B$ . Furthermore, it is seen that in the presence of water parameter  $B$  is increased for HFP but decreased for ethanol.

**Table 1.** Adsorption isotherm parameters for HFP and ethanol on Norit R1 at a temperature of 303 K.

	Dubinin-Radushkevich	Single component	In presence of water
HFP	$q_{max}$ (ml/g)	0.60	0.34
	$B$ (-)	0.166	0.180
Ethanol	$q_{max}$ (ml/g)	0.58	0.48
	$B$ (-)	0.264	0.241

The difference between the water/ethanol and the water/HFP system is clearly reflected in the breakthrough behaviour, see Figure 2. The breakthrough time for HFP under humid conditions is decreased by a factor of about six. On the other hand, for ethanol only a decrease of about a factor two is observed in the breakthrough time.



**Figure 2.** Breakthrough curves for HFP and ethanol on Norit R1 under dry and humid conditions.

The transient uptake profiles were used to determine diffusion coefficients. Not surprisingly, it is found that adsorption is a faster process than desorption for components with a favourable isotherm, i.e. for HFP, ethanol, and methanol. This is in contrast to the transient profiles of water, which exhibit a slower adsorption than desorption process. This is due to the unfavourable isotherm of water.

The results of the adsorption isotherms and transient uptake profiles are incorporated into a model that describes the binary adsorption process of the water/hydrocarbon system in an activated carbon bed. Results will be presented comparing simulated and experimental breakthrough curves.

## Conclusions

The effect of water vapour on the performance of activated carbon beds with Norit R1 carbon is demonstrated. The equilibrium amount of adsorbed HFP is reduced in the presence of water, resulting in a lower capacity of the bed and a faster breakthrough of HFP in the activated carbon bed. On the other hand, it has been shown that for methanol and ethanol both the equilibrium amount adsorbed and the breakthrough curves are less affected under humid conditions.