

The Determination of the Pore Size Distribution of an Activated Carbon using Dubinin-Astakhov Analysis of CO₂ Adsorption at 273 K

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Abstract

The pore size distribution (PSD) of an activated carbon has been determined by the analysis of a CO₂ adsorption isotherm measured at 273 K using a Hidden Isochema IGA-001 Intelligent Gravimetric Analyser. The data were analysed in the Hidden Isochema *IGASwin* software package and the PSD that was obtained shows a maximum at a pore dimension of approximately 0.6 nm, indicating that the pores in this material are predominantly in the microporous regime.

Introduction

Activated carbons are porous carbonaceous materials that serve a broad range of practical applications including catalysis, gas purification and separation, and other vapour and liquid phase adsorption-based technologies. The pore structure, as well as the specific surface area, of these materials can vary greatly between carbons activated using different methods and under differing conditions, and it depends also on the choice of raw material. Activated carbons can contain pores in the macro- ($d > 50$ nm), meso- ($50 \text{ nm} > d > 2$ nm) and microporous ($d < 2$ nm) regimes, according to the IUPAC classification [1]. The pore structure of a particular carbon is crucial to its practical application and so the determination of the pore size distribution (PSD) is an important characterization measurement in the study of these materials. In addition, activated carbons are non-crystalline materials that cannot be characterized easily by X-ray powder diffraction. As a result, alternative methods for the determination of their microstructure are of significant interest. The measurement of the adsorption behaviour of different probe molecules, and the subsequent analysis of the data to obtain a PSD, is one of the alternative methods that can complement small angle scattering and other characterisation techniques. So-called 'classical' methods of pore size distribution determination include Dubinin-Astakhov (DA), Dubinin-Radushkevich (DR) and Horvov-Kawazoe (HK) Analysis [2].

CO₂ Adsorption

PSD measurements are commonly performed using nitrogen and, to a lesser extent, argon at their respective boiling points (77 and 87 K). At these low temperatures, kinetic limitations can prevent the achievement of equilibrium during isotherm determination, particularly in the case of microporous materials. Therefore, for the characterization of the pore structure of activated carbons it is valuable to perform complementary measurements using another probe molecule such as carbon dioxide. The critical temperature of CO₂ is 304 K and its boiling point is 195 K. Measurements performed at these higher temperatures are not so susceptible to such kinetic limitations and

equilibrium is therefore reached relatively rapidly. The problems can therefore be greatly reduced by the performance of CO₂ adsorption measurements. A convenient measurement temperature for this purpose is 273 K [3]; however, the saturation pressure of CO₂ at this temperature is approximately 3.5 MPa, and so the required measurement pressures for a given relative pressure (p/p^0) are higher than those required for nitrogen and argon at their respective boiling points. This has advantages because low relative pressure measurements can be performed at more manageable absolute pressures, but the higher relative pressure measurements ($p/p^0 > 0.03$) require above ambient pressure measurement capabilities. The IGA range of gravimetric gas sorption instruments, which offer an upper operating pressure of 2.0 MPa, are ideally suited to the pressure range required for this purpose.

It is also worth noting that the determination of CO₂ uptake is of crucial importance in the study of carbon capture by coals and other porous media, and so the type of measurement presented here will also be of interest to researchers in this field.

Dubinin-Astakhov (DA) Analysis

Dubinin-Astakhov (DA) analysis is based on Polanyi's potential theory, which views adsorption in terms of the adsorption potential of the material. For a given gas-solid system the adsorption potential can be determined empirically by measuring its temperature-independent 'characteristic curve'. Dubinin and Astakhov [4] proposed the following equation as the characteristic curve, which expresses the fractional filling of the micropore volume (W/W_0) in terms of A , the Polanyi 'adsorption potential' and E , the characteristic energy of the system,

$$\frac{W}{W_0} = \exp\left[-\left(\frac{A}{E}\right)^n\right] \quad (1)$$

where n is an empirical constant. This is a generalization of the earlier proposal by Dubinin and Radushkevich [5] in which $n = 2$.

The adsorption potential, A , is given by the following expression,

$$A = -RT \ln\left(\frac{p}{p^0}\right) \quad (2)$$

where p/p^0 = the relative pressure of the adsorbate, R is the gas constant and T is the temperature.

In DA analysis, equation (1) is fitted to the adsorption data, expressed in terms of p/p^0 , by the least squares minimization of W_0 , E and n .

The values obtained from the least squares minimization can then be used to determine the pore size distribution of the material through the application of the following expression,

$$\frac{d\left(\frac{W}{W_0}\right)}{dr} = 3n\left(\frac{D}{E}\right)^n r^{-(3n+1)} \exp\left[-\left(\frac{D}{E}\right)^n r^{-3n}\right] \quad (3)$$

where D/r^3 is the form of the adsorption potential, for a dispersion interaction energy, D , and a pore radius, r .

In this Application Note we demonstrate the use of the *IGASwin* software package to determine the pore size distribution of an activated carbon using DA analysis of CO₂ adsorption data. The adsorption data were measured using a Hiden Isochema IGA-001 gravimetric gas sorption analyser.

Experimental Details

Apparatus

The IGA-001 gravimetric analyser is an ultra-high vacuum (UHV) system with a fully automated microbalance and a pressurized gas delivery system that operates up to pressures of 2.0 MPa (20 bar). This allows the accurate measurement of gas adsorption and desorption isotherms, and the corresponding adsorption or desorption kinetics at each pressure step. It can be used to measure a range of different gases over a broad temperature range. The approach to equilibrium is monitored and analysed in real-time using the *IGASwin* software. The balance and pressure control system is fully thermostatted and the long-term stability of the balance is $\pm 1 \mu\text{g}$, with a weighing resolution of 0.2 μg . The sample environment for these measurements consisted of a recirculating fluid bath that allows a temperature regulation accuracy of $\pm 0.05 \text{ }^\circ\text{C}$ in the range 0 - 80 $^\circ\text{C}$ (273 - 353 K). The stainless steel reactor in which the sample was suspended is equipped with a integral heater for the degassing of samples at temperatures of up to 500 $^\circ\text{C}$ (773 K). When combined with a turbomolecular pump and an oil-free membrane backing pump, this allows the pretreatment of samples under high vacuum conditions.

Measurement Details

A commercial activated carbon sample (52.1 mg, wet mass) was loaded into the IGA-001, and degassed at a temperature of 150 $^\circ\text{C}$ (423 K) until the weight reading had stabilized. The sample was then cooled and the temperature allowed to stabilize at 0 $^\circ\text{C}$ (273 K). The carbon dioxide pressure was then controlled at a series of pressures while the mass change was monitored. The data were fitted in real time using the linear driving force model (F1 in the *IGASwin* software),

$$u(t) = \Delta u \left(1 - \exp \left[- \left(\frac{t}{k} \right) \right] \right) \quad (4)$$

where $u(t)$ is the uptake at a time, t , Δu is the overall uptake for the sorption step, and k is the time constant.

During the real-time data fitting process, Δu is estimated together with the time constant. At each sorption step, 99% of the estimated value Δu was reached before proceeding to the next point, and the time-out for each step was set to 30 minutes.

Results

Figure 1 shows the adsorption isotherm measured using the IGA-001. The starting (dry mass) weight of the sample after degassing was 47.9 mg. The figure shows the data corrected for buoyancy (Archimedes' Principle) effects in *IGASwin*, with the pressure axis expressed in terms of the saturation pressure of carbon dioxide at the measurement temperature. The data points marked by green circles are the sorption steps during which the real time fit to the linear driving force model did not converge and the instrument moved on after reaching the time-out period of 30 minutes.

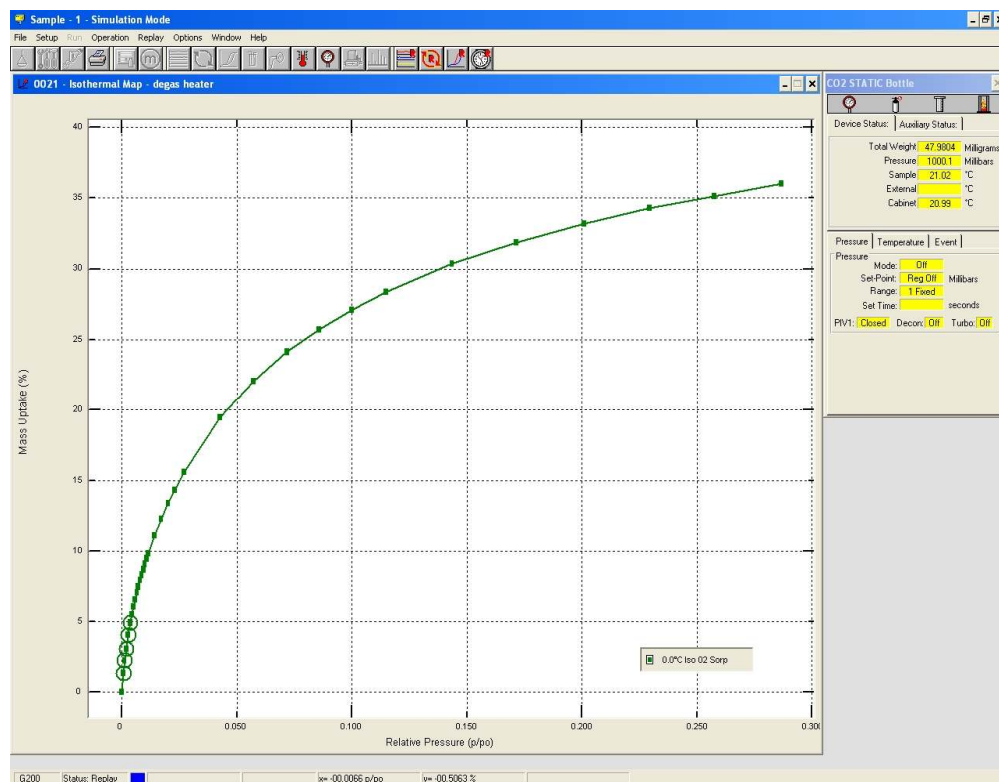


Figure 1. The buoyancy-corrected data showing the gravimetric determination of carbon dioxide adsorption on the activated carbon at 273 K, plotted as % mass uptake vs relative pressure. (Screenshot from the *IGASwin* instrument control and data analysis package version 1.03.176)

Dubinin-Astakhov (DA) Analysis

After correcting the adsorption data for buoyancy effects, and plotting mass uptake as a function of relative pressure, the DA analysis was performed in *IGASwin* by using the PSD Analysis fitting routines included in the software. A least squares minimization of the DA parameters resulted in convergence at $W_0 = 40.05\%$, $E = 8,182 \text{ J mol}^{-1}$ and $n = 1.89$. This fit is shown in Figure 2.

The fitted parameters are then used to calculate the pore size distribution (PSD) using equation (3). The value of the dispersion interaction energy, D , is entered as the

parameter *DA Interaction Constant* and has units of $\text{kJ nm}^3 \text{mol}^{-1}$. For CO_2 this value is typically $1.5 \text{ kJ nm}^3 \text{mol}^{-1}$, and for N_2 it is $2.96 \text{ kJ nm}^3 \text{mol}^{-1}$.

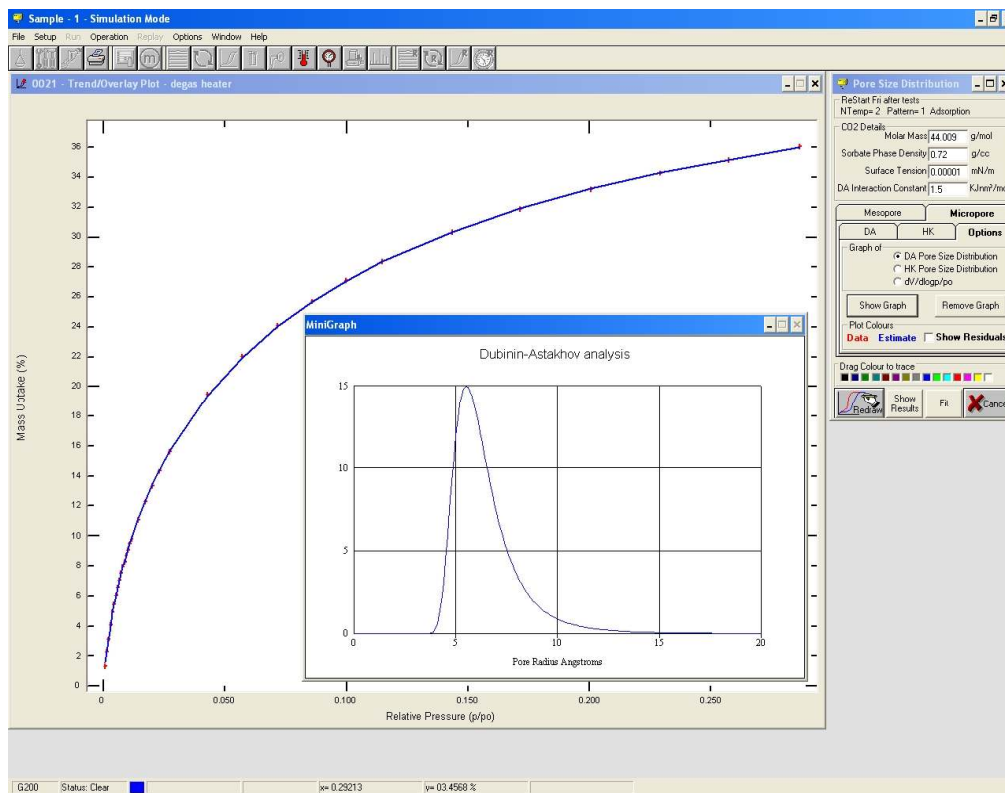


Figure 2. The determined pore size distribution, plotted as a function of pore radius in the *IGASwin* software. (Screenshot from the *IGASwin* instrument control and data analysis package version 1.03.176)

The calculated PSD is shown in Figure 2, together with the fitted isotherm data. The numerical data from the PSD calculation can be readily exported from *IGASwin*, if required. It can be seen that the peak in the pore size distribution calculated from this data is at approximately 0.6 nm. The pore size distribution is therefore in the microporous category, as defined in the IUPAC classification scheme [1].

Conclusion

The pore size distribution of an activated carbon has been determined by the analysis of a CO_2 adsorption isotherm measured at 273 K using a Hiden Isochema Intelligent Gravimetric Analyser. The measurement pressure range required for this analysis is ideal for the 0 - 20 bar operating pressure of the IGA-001 gas sorption analyser and the *IGASwin* software package allows the straightforward analysis of sorption data by the method proposed by Dubinin and Astakhov [4]. The pore size distribution calculated for the activated carbon sample using this method showed a maximum at a pore dimension of approximately 0.6 nm, indicating that the pore dimensions are predominantly in the microporous category in the IUPAC classification scheme.

References

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