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Influence of Active Carbon Modification on Its Porous Structure and Heat Effects of Methanol Vapours Adsorption

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Methanol adsorption of the active carbon seems to be very interesting for use in thermodynamic systems such as heat pumps and transformers as well as cooling systems. The porous structure of commercial active carbon modified by successive removal of external layers from a particle surface as produced by abrasion in a spouted bed and by demineralization was evaluated on the basis of the nitrogen adsorption data and those for methanol. The modifications improve densimetric characteristics and heat effects of methanol adsorption. Porous structure parameters obtained for nitrogen and methanol agreed reasonably well and Dubinin-Radushkevich approach can be a useful method for characterization of these systems. The methods for calculation of heat effects of methanol adsorption in a wide range of temperature and pressures are discussed.

Key words: active carbon, methanol adsorption, microporosity, heat of adsorption

Adsorption processes have been proposed for heat management as a consistent alternative to vapour compression systems. Gas adsorption phenomenon is strictly correlated to energy transfer and transformation, because they are regulated by temperature and pressure. Taking into account these properties and combining endothermic desorption with exothermic adsorption processes in closed cycles, it is possible to realize several attracting features for both heat pump and heat transformers applications [1–4]. Adsorption systems show some advantages: many adsorbents are not submitted to any change of volume during the sorption processes, as in solid absorption; it does not need a rectifying column as in liquid absorption. Moreover, adsorption techniques allow cycling large amounts of the refrigerant liquid.

In the design of adsorption refrigeration/heat pump systems, the characteristics of both adsorbent – adsorbate (refrigerant) pairs and adsorption cycles play an important role in various kinds of applications. A number of suitable adsorbents can be used to sorb refrigerants from the air with the simultaneous release of energy. At present two pairs dominate in refrigeration systems: zeolite – water and active carbon – methanol. It seems that the last one appears to be the most promising medium for the heat storage systems [5–6], because methanol is easily desorbed from active carbon

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when it is heated and this pair is best adapted to operating cycles with small evaporating temperature variation (up to 313 K).

The aim of this study was to test the improvement of the properties of commercial active carbon for adsorption refrigeration systems. The methods of successive removal of external layers from a particle surface and demineralization of active carbon were used for the preparation of samples. Characterization of the pore structure as well as densimetric properties of the modified samples were also undertaken to establish a link between pore structure and methanol capacity. Methods for description of methanol equilibrium data in a wide range of temperature and pressures are proposed.

EXPERIMENTAL

A commercial granulated active carbon of type N (Poland) obtained by activation of hard coal with steam was subjected to working in a spouted bed [7–8]. As a result of this process, samples of different abrasion ranges were obtained. Both the initial sample and two additional samples abraded at 33% and 66% were also treated with concentrated HCl and HF acids, and then washed with distilled water. Figure 1 shows schematically the methods used for modification of active carbon.

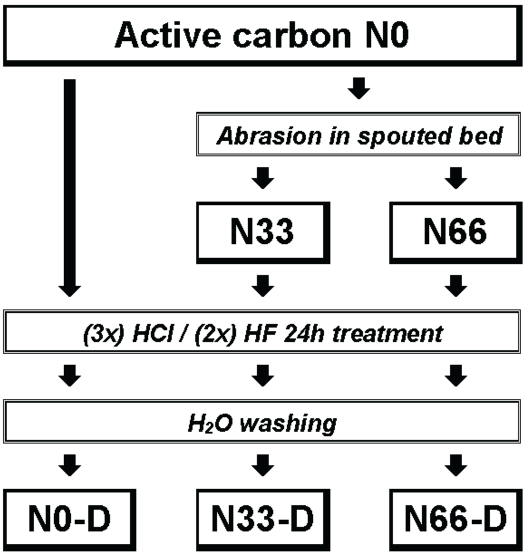

Figure 1. The methods of active carbon modification.

To characterize the changes in properties of active carbons, densimetric and physicochemical measurements were made. The samples were characterized by nitrogen adsorption at 77 K (Sorptomatic 1900), the apparent density was measured using a mercury pycnometer at 0.1 MPa, and the true (skeletal) density was measured on a helium pycnometer (AccuPyc).

Parameters characterizing micropore structure: micropore volume (W_o), characteristic energy of adsorption (E_o) were calculated from Dubinin-Radushkevich equation [9] and next micropore width was evaluated according to Mc Enaney [10]: $x_{mi} = 2.345\exp(-0.0666\,E_o)$. Volume of mesopores ($V_{me}$) and its surface area ($S_{me}$) were estimated according to Dollimore and Heal method [11]. Specific surface area (S_{BET}) was determined from BET equation [12]. The results of measurements and calculations are listed in Table 1.

Table 1. Parameters characterizing the active carbon samples obtained from nitrogen (77 K) adsorption and density measurements.

Property	N0	N33	N66	N0-D	N33-D	N66-D
True density, d_{He} [gcm^{-3}]	2.209	2.180	2.134	2.099	2.063	2.056
Apparent density, d_{Hg} [gcm^{-3}]	0.851	0.949	0.951	0.701	0.791	0.945
Particle porosity, ε_p [cm^{3}cm^{-3}]	0.615	0.565	0.554	0.666	0.617	0.540
Total pore volume, V_{po} [cm^{3}g^{-1}]	0.722	0.595	0.583	0.950	0.779	0.552
Volume of micropores, W_o [cm^{3}g^{-1}]	0.334	0.299	0.252	0.391	0.359	0.273
Characteristic energy, E_o [kJmol^{-1}]	17.70	19.30	21.60	18.10	18.90	21.50
Micropore width, x_{mi} [nm]	0.72	0.65	0.56	0.70	0.67	0.56
Volume of mesopores, V_{me} [cm^{3}g^{-1}]	0.133	0.085	0.052	0.151	0.094	0.061
Mesopores surface area, S_{me} [m^{2}g^{-1}]	102	76	46	111	79	60
BET surface area, S_{BET} [m^{2}g^{-1}]	803	724	596	944	838	615
Ash content, A^a [%]	20.67	20.28	15.2	0.38	0.42	0.61

Methanol adsorption isotherms were measured volumetrically using a device for simultaneous determination of isotherms and kinetics of adsorption [13]. A manometric pressure stabilizer of manostate type guaranteed that the measurements were isobaric, and a system of thermostates ensured that the process was isothermal. The measurements were carried out between 273–373 K (corresponding values of relative pressures 0.00025–0.33).

RESULTS AND DISCUSSION

Samples obtained by attrition in spouted bed show different physicochemical properties within carbon particle. These radial changes in the texture result from the nature of the activation process. During abrasion, highly converted external layers (with a greater proportion of macropores and ash content) were removed [8]. Simultaneously the shape and density of particles were changed. On the other hand, demineralization causes leaching of inert mineral substance. Both procedures used change distinctly the porous structure and densimetric characteristics of active carbon, and in the consequence its sorption properties with respect to methanol.

For the description of adsorption equilibrium in microporous materials with a polymodal distribution of pore dimensions, such as the active carbons, we used the well-known Dubinin-Radushkevich isotherm:

$$a = W_o \rho_s \exp\left\{-D\left[T \ln\left(\frac{p_o}{p}\right)\right]^2\right\} \qquad D = \left(\frac{R}{\beta E_o}\right)^2 \tag{1}$$

in which W_o is the specific micropore volume, E_o is the characteristic energy of adsorption, R is the gas constant, p_o is the saturated vapour pressure of the adsorbate at absolute temperature T, p is the partial pressure of the adsorbate vapour, β is the similarity coefficient and ρ_s is the density of adsorbed phase.

The density of methanol in the adsorbed state below the boiling point has been determined according to Dubinin-Nikolaev [14] as a density of liquid phase. For temperature above the boiling point of adsorbate, the density of adsorbed phase (ρ_s) was calculated from the Benson equation:

$$\rho_s = \rho_{nbp} - \frac{\rho_{nbp} - \rho_c}{T_c - T_{nbp}}(T - T_{nbp}) \tag{2}$$

where: ρ_{nbp} is the density of the liquid adsorbate at normal boiling point T_{nbp}, ρ_c is the density at critical temperature T_c ($\rho_c = 1/b$; b is the van der Waals equation constant).

The adsorption isotherms of methanol vapours for sample N0D, as well as plots in generalized coordinates of the Dubinin-Radushkevich equation, are presented in Figure 2.

All of the samples readily adsorb methanol, giving reversible isotherms of type I. A small step observable for some isotherms at low pressures is probably due to a specific interaction with polar surface groups. D-R plot shows reasonable linearity over the range of relative pressure up to about 0.14p$_0$, as well as temperature independence.

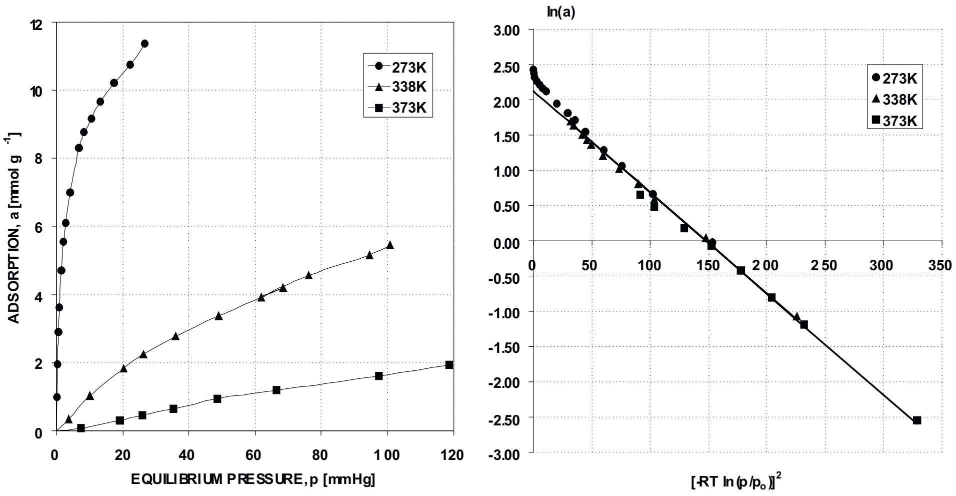

Figure 2. Methanol adsorption isotherms and DR plots for active carbon sample N0D.

The values of specific micropore volume, the characteristic energy of adsorption and the micropore width obtained from isotherms are summarized in Table 2.

Table 2. Parameters characterizing the micropore structure of active carbon samples calculated from methanol adsorption isotherms.

Parameter	N0	N33	N66	N0D	N33D	N66D
Volume of micropores, W_o [cm^{3}g^{-1}]	0.340	0.303	0.258	0.388	0.362	0.279
Characteristic energy, E_o [kJmol^{-1}]	17.15	19.54	21.25	17.82	18.95	21.61
Micropore width, x_{mi} [nm]	0.70	0.61	0.56	0.67	0.63	0.56

The results obtained for methanol in a wide range of temperatures are in excellent agreement with those presented for nitrogen in 77 K; this demonstrates the possibility of application of D-R equation for analysis of adsorption equilibrium data for system under study. Next, the energy released in the adsorption process was analyzed. The isosteric heat of adsorption (q_{st}) can be derived from the Gibbs isotherm, that reduces to a constant adsorbed mass function (isoster of adsorption), which is given as:

$$\left(\frac{\partial \ln p}{\partial T}\right)_a = \frac{q_{st}}{RT^2} \tag{3}$$

For the saturation condition ($p = p_o$), the q_{st} term in (3) can be replaced by the latent heat H. Then, the D-R equation becomes:

$$\frac{\partial \ln p}{\partial T} = \frac{\partial \ln p_o}{\partial T} + \ln\left(\frac{p_o}{p}\right)\left\{\frac{1}{T} + \frac{\alpha}{2D}\left[T \ln\left(\frac{p_o}{p}\right)\right]^{-2}\right\} \tag{4}$$

where α is the coefficient of thermal expansion of the liquid adsorbate.

Multiplying each term of the differential equation (3) by RT^2, the isosteric heat q_{st} can be obtained as a function of pressure and temperature:

$$q_{st} = H + RT \ln\left(\frac{p_o}{p}\right) + \left[\frac{\alpha RT}{2D}\right]\left[T \ln\left(\frac{p_o}{p}\right)\right]^{-1} \tag{5}$$

The run of isosteric heat of adsorption for sample N0D is presented in Fig. 3.

For all systems under study, the isosteric heat of adsorption was higher than the heat of condensation and of the sufficient magnitude to be characterized as physical adsorption.

The above-mentioned expression is possibly adequate for calculations of the thermodynamic properties of the active carbon – methanol systems. It was considered that it would be sufficient for numerical calculations of adsorption data for a given sample as a method facilitating and speeding up the calculation for various operative conditions.

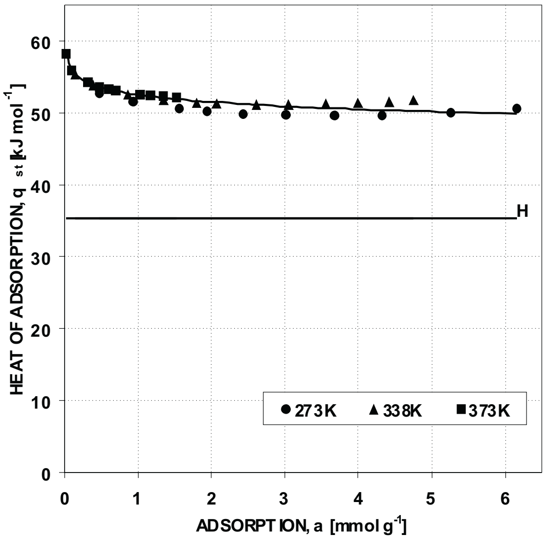

Figure 3. Isosteric heat of adsorption *vs.* amount adsorbed for active carbon sample N0D.

The hypothesis, that these data could be represented by the potential theory, was also tested. The potential theory of adsorption is simply expressed by:

$$W = F(\varepsilon) \tag{6}$$

where W, F and ε denote the volume of adsorbed gas, the universal adsorption function and the adsorption potential, respectively. The adsorption potential ε of adsorbate molecules from the gas phase to the solid surface is evaluated by the following formula:

$$\varepsilon = -RT\ln(p/p_o) \tag{7}$$

The universal adsorption functions (also called the „characteristic curve”) for the selected systems under study calculated from experimental adsorption data are presented in Fig. 4.

The procedure proposed gives a good representation of the data. Analysis of the data for a given temperature results in a temperature-independent characteristic curve. Thereby, if the characteristic curve for an adsorbate is known, then the adsorption values of that adsorbate can be predicted at any pressure and temperature. Only one adsorption isotherm is necessary to obtain the characteristic curve and this is sufficient to describe the adsorption at all other temperatures and pressures.

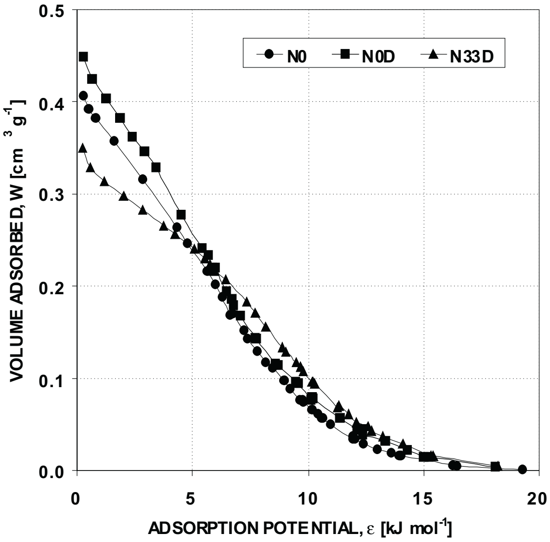

Figure 4. Characteristic curves for methanol adsorption on selected active carbon samples.

CONCLUSIONS

The data obtained in this work should serve the sorption equilibrium and thermodynamic quantities needs in many engineering applications of low-grade heat, especially those concerning solar energy. Considering the cooling adsorption system purpose, the active carbon – methanol pair seems to be very adequate.

Methanol is a good working liquid, because: it can evaporate at a temperature largely below 273 K; its enthalpy of vaporization is high, its molecule is so small, that it can be easily adsorbed in micropores; its normal boiling point is much higher than room temperature; its working pressure is always lower than atmospheric.

For refrigerating applications, the adsorbent must have a high adsorption capacity at ambient temperature and low pressures and a small capacity of adsorption at high temperatures and pressures.

Above conditions are fulfilled for systems under study, and the method proposed for active carbon preparation gives the possibility to control both porous structure and packing properties of the active carbon bed.

The approach proposed in description of equilibrium data in a wide range of temperatures and pressures is very convenient to use in numerical calculations and the simplicity of the procedures allows a rapid screening of many active carbon types in different conditions.

Active carbon adsorption cycles have great promise for small refrigeration systems. The porosity characteristics of available carbons give a reasonable performance compared to the maximum that can be achieved with physical adsorption. Also, an improvement in the mechanical strength and conductivity of adsorbent is needed and the actual design of the total system, including heat exchangers, still needs to be considered in order to realise these systems.

Acknowledgments

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