An analysis of burn-off impact on the structure microporous of activated carbons formation

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Abstract. The paper presents the results on the application of the LBET numerical method as a tool for analysis of the microporous structure of activated carbons obtained from a bituminous coal. The LBET method was employed particularly to evaluate the impact of the burn-off on the obtained microporous structure parameters of activated carbons.

1. Introduction

Microporous carbonaceous materials are widely used as adsorbents, filters, catalyst supports in industries technology [1-4]. In recent years, an increasing attention has been paid to the research into using activated carbon for the storage of gaseous fuels, including natural gas [5-7]. As has been concluded from the research, under specific conditions and with the same storage pressure, the volume of natural gas in a container filled with adsorbent can be even several times higher than the volume of that gas in a container without adsorbent. Consequently, the use of adsorbents for the storage of natural gas enables a reduction in the weight and size of gas containers and the compression of gaseous fuels at a reduced pressure. Another innovative method of energy storage in movable systems consists in hydrogen electrosorption by porous carbon cathode in the process of controlled water electrolysis at ambient temperature and atmospheric pressure [5-7]. Research results obtained so far permit a conclusion that the efficiency of hydrogen stored with the use of this method can exceed the one offered by high-pressure or cryogenic systems.

Since a few years ago, porous carbonaceous materials have been considered for use as the electrode of the electrochemical condenser in which electric charge is stored on the surface of polarised carbon electrode [8-10]. Work has been under way to use such systems to enhance the performance of fuel cells in electrically powered vehicles.

Another promising trend in the large-scale application of carbonaceous adsorbents is the use of carbon molecular sieves for Pressure Swing Adsorption (PSA), which takes advantage of changes in adsorptive properties at varying pressure and consists in repeated fast transient adsorption/desorption from adsorbent bed [11]. Through the suitable control of pressure and directions of the flow of gas
through several adsorbent beds combined together, an effect of considerable gaseous mixture separation can be achieved, maintaining high efficiency of the production process. The PSA method is used in the processes of separating various gaseous mixtures with the use of carbon molecular sieves, including the separation of hydrogen from coal gas or refinery gases, the separation of air into particular components, the separation of carbon dioxide from biogas, the drying of gases, and the enrichment of methane from mine gases.

The middle of the 20th century saw a growing interest in hard coal, or anthracite, and bituminous coal as a raw material in the production of activated carbons. Coal is the most popular precursor owing to its cost-effectiveness and to better mechanical properties of the adsorbents obtained from coal compared to those produced with the use of lignocellulosic materials [12,13]. Interesting research results have been presented in a paper by Carrasco-Marín et al. [14], where bituminous coal from Puertollano (Spain) demineralized with HCl and HF was used to prepare microporous activated carbons. The demineralized coal was pyrolysed in an N2 flow at 1,273 K for 30 min. and activated in a CO2 flow at 1,123 K for different periods of time to achieve different degrees of activation [14]. The activated carbons are referred to in the text as BP followed by a number indicating the percentage burn-off. The particle size of the activated carbons was between 0.15 and 0.25 mm. The development of the microporosity was followed among others by adsorption of N2 at 77 K.

The microporosity of the activated carbons was evaluated by the Dubinin-Astakhov (DA) [15], equation applied to the N2 adsorption isotherms. The Dubinin-Astakhov equation (DA) [15], was more suitable in that case than the Dubinin-Radushkevitch equation [16] because of considerable surface heterogeneity of the activated carbons in question; however, this equation may be insufficient in a number of contexts to accurately determine the impact of burn-off on the formation of the porous structure of activated carbons. Considering the above, an idea has been conceived to analyze the structure of the said activated carbons on the basis of nitrogen adsorption isotherms using a more advanced method of structure analysis, namely the LBET method [17-25].

2. The LBET method

The LBET method, which has been described in detail in the previous works [17-25], was used for the calculations performed as part of this research. The LBET method is based on the original numerical LBET models of adsorption on heterogeneous surfaces, originating from an unique multilayer adsorption theory and the fast multivariant identification numerical procedure of adsorption systems [17-25]. The LBET models have five adjusted parameters: $V_{hA}$ [cm$^3$/g], $Q_{amax}/RT$, $\alpha$, $\beta$ and $B_C$ which can be adjusted by fitting LBET equation to the empirical adsorption isotherm, with a chosen variant of the surface energy distribution function [17-25].

3. Discussion of the obtained results

The results of the numerical analyses carried out for the isotherms of adsorption of nitrogen on the active carbons obtained for the various burn-off were presented in Figures 1-5 and Table 1. In the top right-hand figure, the grey dots ‘•’ mark the spots of the fitted empirical adsorption isotherm, while the black solid line ‘-‘ marks the theoretical isotherm plotted according to the best-fitted variant of the LBET class model. The dotted line represents the theoretical coverage of the first adsorption layer.

The heading of the top figure gives the name of the adsorption system, i.e. the name of the adsorbate (N2) and the symbol of the adsorbent (BP). Next the name and number of the best-fitted LBET class model is given, preceded by a slash. The area of the top chart contains the parameters $Q_{amax}/RT$, $B_C$, $Z_{hA}$, $h$ and the fitting error dispersion $\sigma$. The second figure presents adsorption energy distribution on the adsorbent surface; it contains the value of the volume of monolayer $V_{hA}$ [cm$^3$/g] and the values of the geometrical parameters $\alpha$, $\beta$. 


Fig. 1. The results of the nitrogen adsorption isotherm analyses on activated carbon BP, obtained with burn off 8% and adsorption energy distribution on first layers.

Fig. 2. The results of the nitrogen adsorption isotherm analyses on activated carbon BP, obtained with burn off 18% and adsorption energy distribution on first layers.
Fig. 3. The results of the nitrogen adsorption isotherm analyses on activated carbon BP, obtained with burn off 31% and adsorption energy distribution on first layers.

Fig. 4. The results of the nitrogen adsorption isotherm analyses on activated carbon BP, obtained with burn off 46% and adsorption energy distribution on first layers.
Fig. 5. The results of the nitrogen adsorption isotherm analyses on activated carbon BP, obtained with burn off 72% and adsorption energy distribution on first layers.

Table 1. A selection of results of the analyses carried out using the LBET method and by means of the BET and the DA equations [14].

|       | BP8  | BP18 | BP31 | BP46 | BP72 |
|-------|------|------|------|------|------|
| $h$   | 3    | 9    | 3    | 5    | 1    |
| $V_{hA}$ [cm$^3$/g] | 0.138 | 0.271 | 0.361 | 0.438 | 0.815 |
| $\alpha$ | 0.95  | 0.43  | 0.57  | 0.75  | 0.54  |
| $\beta$ | 1.04  | 1.73  | 1.49  | 1.25  | 1.52  |
| $S_{BET}$ [m$^2$/g] | 306   | 697   | 924   | 1078  | 1632  |
| $W_0$ [kJ/mol]     | 0.140 | 0.309 | 0.414 | 0.487 | 0.742 |

4. Discussion of the obtained results

Based on the research results compiled in Fig. 1–5 and in Table 1, it has been observed that the volume of the first adsorbed layer $V_{hA}$ increases in proportion to a growth in the degree of burn-off; however, the values of the energetic and geometric parameters do not correlate with burn-off, implying that complex mechanisms take place during the activation process. More specifically, it has been evidenced with regard to the activated carbon BP8 that the surface of this material is moderately heterogeneous, with very high and unbranched clusters of adsorbate particles developing in its pores.

The results produced for the sample of BP18 reveal that the surface of this material is strongly heterogeneous, and the clusters formed in its pores are medium-sized and branched. This finding shows that an increase in the degree of burn-off from 8 to 18% resulted in the burning of the walls between adjoining micropores. Moreover, an increase in the degree of burn-off to 31% brought about further growth of $V_{hA}$ concurrently with a significant decrease in surface heterogeneity and an increase in the height of the adsorbate particle clusters formed in the micropores. An increase in burn-off to 46% triggered further increase in the $V_{hA}$ parameter in parallel to an increase in the $h$ parameter. The
adsorbate particle clusters formed in the micropores of the activated carbon BP46 were higher and thinner compared with those developed in the micropores of the activated carbon BP31.

The results obtained for the activated carbon BP72 showed that the value of the $V_{hA}$ parameter of this material was the largest one compared with the remaining analyzed samples, while the value of the heterogeneity parameter $h$ evidenced that the surface of this activated carbon was the most homogeneous one among the samples subject to the analysis. As concluded from a comparison between the $V_{hA}$ parameters obtained using the LBET method and the $S_{BET}$ and $W_0$ parameters obtained by means of the BET and the DA equations, respectively, the values of the said parameters are correlated with regard to the individual samples.

5. Conclusions

The research demonstrated a complex relationship between the structure parameters and the degree of burn-off during the activation process. Still, the tests carried out using the LBET method yielded precise information on the porous structure of the individual samples, including on their surface heterogeneity and pore geometry, which permit accurate determination of preparation conditions in order to produce activated carbons having anticipated properties.

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