Study of the porous structure of carbon sorbents based on Kuzbass coal at various stages of metamorphism

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Abstract. The work is devoted to the investigation of the porous structure of carbon sorbents prepared on the basis of long-flame, gas, low-caking and lean coal of Kuzbass. Carbon sorbents were obtained by alkaline activation with potassium hydroxide at 800 °C and a KOH/coal (RKOH) ratio of 0.5 g/g. Using the method of low-temperature nitrogen adsorption (analyzer ASAP-2400), the values of the textural characteristics of carbon sorbents based on coal of different stages of metamorphism were determined: pore volume, micropore volume and specific surface area. It is shown that the carbon sorbents obtained in this work are predominantly microporous (more than 80% by volume). A carbon sorbent based on long-flame coal has the greatest texture characteristics; its specific surface area is 1220 m²/g and a pore volume of 0.54 cm³/g.

1. Introduction
It is known that carbon sorbents can be prepared from a wide range of different carbon-containing natural, synthetic and artificial materials [1]. However, in coal-mining regions, such as Kuzbass, it is coal that can become an affordable and acceptable raw material for the production of carbon sorbents. To prepare carbon sorbents, it is advisable to use the least popular coal grades in coke production: long-flame, gas, low-caking and lean. All of the above grades of coal are mined at coal enterprises in Kuzbass.

In previous works [2-6] it was shown that alkaline activation (thermolysis in the presence of alkali) of coals of different nature leads to the formation of a developed porous structure of the obtained carbon sorbents. The use of potassium hydroxide as an activator in the process of alkaline activation of coals leads to a significant increase in the specific surface area of the prepared carbon sorbents [7].

The aim of this work was to investigate the textural characteristics of carbon sorbents obtained by alkaline activation from coal of various stages of metamorphism.

2. Experimental

2.1 Coal characteristics
The work used coal samples of four grades (long-flame "LF", gas "G", weakly caking "WC" and lean "L"), selected at the coal mining enterprises of Kuzbass. Samples with a particle size of 0.2-0.5 mm
were prepared from the initial coal of each grade by successive grinding and quartering and dried in air. Analytical studies were carried out for coal samples with a particle size of less than 0.2 mm. Determination of technical characteristics was carried out in accordance with the standards ISO 602-74, 562-74 (technical analysis) and ISO 625-75 (elemental composition). Analysis for the sulfur content in the organic mass of coal was carried out according to GOST 8606-93. Petrographic analysis of the studied samples was carried out on an automated complex for assessing the grade composition of coals SIAMS 620. The investigated characteristics of the original coals are presented in Table 1.

| Coal grade | Vitrinite reflectance | Technical analysis, % | Elemental composition, % per daf | Atomic ratio |
|------------|----------------------|-----------------------|----------------------------------|--------------|
|            | \( R_{0,\%} \)    | \( W^d \) | \( A^d \) | \( V^{def} \) | \( S^d \) | C | H | (O+N+S) | C/H | O/C |
| «LF»       | 0.57                 | 4.5 | 3.4 | 43.3 | 0.5 | 80.2 | 5.6 | 14.2 | 0.84 | 0.13 |
| «G»        | 0.64                 | 2.2 | 3.1 | 43.3 | 0.3 | 81.8 | 5.6 | 12.6 | 0.82 | 0.12 |
| «WC»       | 1.25                 | 1.9 | 6.0 | 19.5 | 1.0 | 87.5 | 4.5 | 8.0  | 0.62 | 0.07 |
| «L»        | 1.88                 | 0.5 | 8.4 | 14.1 | 0.6 | 90.3 | 4.1 | 5.6  | 0.54 | 0.05 |

The results of technical analysis show that the initial coals are characterized by low ash content (3.1-8.4%) and moisture (up to 4.5%), with an increase in the stage of metamorphism, the content of heteroatoms in coals decreases from 14.2% (grade "LF") to 5.6% (grade "L"). Sulfur in coal samples was found in an amount of no more than 1%.

2.2 Preparation of carbon sorbents
The preparation of carbon sorbents was carried out by the method of alkaline activation according to the modified procedure of [8, 9]. In the process of preparing sorbents, coal with a particle size of 0.2-0.5 mm was used. Potassium hydroxide was used as an alkaline reagent.

A mixture of coal and potassium hydroxide was prepared at an alkali / coal mass ratio of \( R_{KOH} = 0.5 \text{ g/g} \). Mixing was carried out in a Pulverisette 6 ball mill (Fritsch, Germany). A steel drum was loaded with a mixture of coal and alkali to 1/3 of its volume. Steel balls with a diameter of 8 mm, occupying 1/3 of the volume, were used as the acting bodies. The process was carried out for 80 seconds, achieving an even distribution of coal and potassium hydroxide in the mixture.

The carbon-alkali mixture was heated in ceramic crucibles with an average heating rate from room temperature to operating temperature of \( \sim 9 \) °C/min. Alkaline activation was carried out at a temperature of 800 °C for 60 minutes under isothermal conditions. After thermolysis, the sorbents were cooled to room temperature in an inert medium. Large agglomerations of sintered sorbent particles were crushed to a particle size of <1 mm, then washed from the remaining potassium hydroxide with distilled water, 0.1 N hydrochloric acid solution, and then with distilled water until the medium was neutral. The washed sorbents were dried in an oven at 105 ± 5 °C to constant weight. The process of preparing sorbents for the ratio \( R_{KOH} = 0 \) (carbonization without alkaline activation) was similar to the process of obtaining sorbents with alkaline activation, except for the mixing stage. To study the texture characteristics, samples with a particle size of 0.2-0.5 mm were prepared from a sorbent of non-uniform size.

2.3 Porous structure
The study of the porous structure of the obtained carbon sorbents was carried out on an ASAP-2400 analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA). The characteristics of the porous structure (specific surface area - \( S_{BET} \), m²/g, total pore volume - \( V_{t} \), cm³/g, micropore volume - \( V_{μ} \), cm³/g) were determined from nitrogen adsorption isotherms at 77 K in the range of equilibrium
relative nitrogen vapor pressures from 0.005 to 0.99 p/p₀. Before carrying out measurements, to completely remove the sorbed impurities, the sorbent samples were evacuated at a temperature of 200 °C for 12 hours and a residual pressure of no more than 0.001 mm Hg.

The Brunauer-Emmett-Teller (BET) model was used to determine the specific surface area of the sorbents. The t-plot method was used to calculate the volume of micropores using the Harkins-Jura equation. These methods make it possible to calculate the characteristics of the porous structure of carbon sorbents prepared from fossil coals [10].

**Discussion of results**

Table 2 shows the characteristics of the porous structure of the prepared carbon sorbents (S\textsubscript{BET} - specific surface area, V\textsubscript{o} - total pore volume, V\textsubscript{μ} - micropore volume). The technique used does not accurately determine the low values of pore volumes in coal carbonates, therefore, only the specific surface area was measured in this work.

| No | Initial coal grade | R\textsubscript{KOH}, g/g | Sorbent yield, % | S\textsubscript{BET}, m\textsuperscript{2}/g | V\textsubscript{o}, cm\textsuperscript{3}/g | V\textsubscript{μ}, cm\textsuperscript{3}/g |
|----|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1  | «LF»              | 0               | 62              | 35              | -               | -               |
| 2  | «LF»              | 0.5             | 51              | 1220            | 0.54            | 0.48            |
| 3  | «LF»              | 0.5             | 63              | 30              | -               | -               |
| 4  | «G»               | 0.5             | 55              | 840             | 0.41            | 0.33            |
| 5  | «G»               | 0.5             | 84              | 17              | -               | -               |
| 6  | «WC»              | 0.5             | 72              | 420             | 0.16            | 0.15            |
| 7  | «L»               | 0.5             | 89              | 15              | -               | -               |
| 8  | «L»               | 0.5             | 78              | 260             | 0.12            | 0.11            |

From the data given in the table it can be seen that carbonization of coal at 800 °C allows obtaining sorbents with low textural characteristics, and the resulting specific surface area does not exceed 15-35 m\textsuperscript{2}/g. Alkaline activation with potassium hydroxide leads to a significant increase in textural characteristics. The specific surface area of carbon sorbents of coal grade "LF" with alkaline activation is 35 times higher than with carbonization without alkali, and sorbents of coal grade "L" 17 times higher.

When potassium hydroxide is used with an R\textsubscript{KOH} ratio of 0.5 g/g, the yield of sorbents is reduced compared to carbonization without the addition of alkali. For different grades of bituminous coals, the sorbent yield is different, which is shown in Figure 1. As a parameter characterizing the grade of coal in Figure 1 and subsequent figures, the atomic ratio H/C was chosen in the work (Table 1). The H/C ratio decreases with an increase in the degree of metamorphism of the initial coal (Table 1), along with this, the yield of sorbents decreases (Figure 1), which in turn can be associated with a decrease in the yield of volatile V\textsubscript{daf} (Table 1).
Figure 1. The yield of sorbents from coal upon activation with potassium hydroxide with an $R_{KOH}$ ratio of 0.5 g/g (2) and without the use of activation with potassium hydroxide (1).

With a change in the degree of metamorphism of coal from grade "LF" (H/C = 0.84) to grade "L" (H/C = 0.54), the specific surface area of the prepared sorbents decreases. The highest value of the specific surface area is possessed by the sorbent obtained from coal grade "LF", it is 1220 m$^2$/g. With a decrease in the H/C ratio in the initial coal, the specific surface area of the sorbents prepared by activation with potassium hydroxide at an $R_{KOH}$ ratio of 0.5 g/g decreases almost linearly (Figure 2).

The pore volume of the prepared sorbents behaves in a similar way, an increase in which with increasing H/C of the initial coal is shown in Figure 3.

Figure 2. Specific surface area of carbon sorbents from coal upon activation with potassium hydroxide in the ratio $R_{KOH}$ 0.5 g/g.
Figure 3. Values of the total pore volume \( V_0 \), micropore volume \( V_\mu \) and the difference in pore volumes \( V_0 - V_\mu \) of carbon sorbents from coal upon activation with potassium hydroxide in the ratio \( R_{KOH} 0.5 \, g/g \).

It is worth noting that the sorbents prepared from the coals of grades "WC" and "L" are characterized by a high relative content of micropores (almost the entire volume of pores is represented by micropores). At the same time, the porous structure of the sorbent made of LF coal is characterized by the total volume of macro- and mesopores of 0.06 cm\(^3\)/g. The largest pore volume with a diameter of more than 2 nm \( (V_0 - V_\mu) \) is observed for the sorbent based on coal "G" (0.08 cm\(^3\)/g). Nevertheless, all samples of sorbents obtained by alkaline activation at 800 °C are predominantly microporous, which is also shown by the example of a sorbent from brown coal in [6].

Conclusion

By the method of alkaline activation with potassium hydroxide at a KOH/coal ratio of 0.5 g/g and a temperature of 800 °C, carbon sorbents were prepared from coals of grades "LF", "G", "WC", "L".

The study of the textural characteristics of carbon sorbents by the method of low-temperature nitrogen adsorption was carried out, the values of the pore volume, micropore volume and specific surface area were determined. It was found that the sorbents prepared in this work are predominantly microporous. The sorbent based on LF carbon has the greatest textural characteristics, its specific surface is 1220 m\(^2\)/g and pore volume is 0.54 cm\(^3\)/g.

The use of the alkaline activation method leads to a significant increase in the textural characteristics of the prepared sorbents in comparison with carbonization without alkali. The specific surface area of sorbents made of "LF" grade coal is 35 times higher with alkaline activation than with carbonization, and sorbents made of "L" grade coal by 17 times.

Acknowledgment

The work was carried out within the framework of a state assignment (project AAAA-A17-117041910147-2).

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