Study of the textural characteristics of carbon sorbents prepared by alkaline activation

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Abstract. The paper investigates the textural characteristics of carbon sorbents prepared by alkaline activation of brown coal from the Tisul deposit. The texture characteristics (specific surface area - $S_{BET}$, m$^2$/g, total pore volume - $V_T$, cm$^3$/g, mesopore volume - $V_{mes}$, cm$^3$/g and volume of micropores - $V_{mi}$, cm$^3$/g) of carbon sorbents were measured on an ASAP-2020 analyzer. The production of carbon sorbents was carried out by activating coal impregnated with potassium hydroxide at a KOH/coal ($R_{KOH}$) ratio of 0.5 g/g; 1 g/g and 2 g/g. The activation of brown coal was carried out at three different temperatures - 700 °C, 750 °C and 800 °C. It is shown that the $R_{KOH}$ ratio has a greater effect on the texture characteristics of carbon sorbents, as compared to the effect of the alkaline activation temperature. Alkaline activation at an $R_{KOH}$ ratio of 2 g/g makes it possible to obtain carbon sorbents with the highest values of textural characteristics. High-temperature alkaline activation (800 °C) has a positive effect on the formation of a common pore space of carbon sorbents based on brown coal from the Tisulsky deposit for all studied $R_{KOH}$.

1. Introduction
Due to the uniqueness of their physical and chemical properties, carbon sorbents have a wide range of applications in solving various environmental problems. Carbon sorbents are prepared from a wide range of different carbon-containing natural, synthetic and artificial materials [1]. Low-metamorphosed brown coals [2], which are relatively cheap and affordable raw materials, can be used as a raw material for the production of carbon sorbents.

The high yield of volatiles and the presence of a large number of oxygen-containing groups make brown coal effective in carrying out the process of alkaline activation [3]. These features of brown coals allow the use of small amounts of alkali when activated. Thus, the alkaline activation method can be used to obtain carbon sorbents with high values of the characteristics of the porous structure.

For each activating reagent, there is an optimal temperature range at which the activation process is most effective, for example, for phosphoric acid - 400-500 °C, for zinc chloride - 500-600 °C, for alkali metal hydroxides - 700-900 °C [4].

The most effective reagent in the alkaline activation reaction of coals is potassium hydroxide [5]. The interaction of brown coal with potassium hydroxide begins already at room temperature [6]. In the range 200-400 °C, various reactions of coal with alkali take place: heterolysis of C – O and polarized C – C bonds of framework-forming chains [7], formation of humates [8]. In the range of 400-600 °C, the reactions of alkaline dehydrogenation [9] and dealkylation [10] are additionally realized. At 600-800 °C, the processes of potassium reduction to metal begin to occur, its intercalation into the interlayer space of crystallites, catalysis of secondary reactions $\text{C}+\text{H}_2\text{O} \rightarrow \text{CO}+\text{H}_2$, $\text{C}+\text{CO}_2 \rightarrow 2\text{CO}$ [11].
Therefore, the purpose of this work was to study the influence of the temperature of alkaline activation of brown coal from the Tisul deposit on the characteristics of the porosity of the resulting carbon sorbents.

2. Experimental

2.1. Coal characteristics

We used brown coal from the Kaychakskiy open-pit mine of the Tisulsky deposit, located in the Kemerovo region. A sample of coal with a particle size of 0.2-0.5 mm was prepared from the initial coal by successive grinding and quartering and dried in air. For analytical studies, an analytical sample with a particle size of less than 0.2 mm was prepared from it. Characteristics studies were carried out in accordance with the standards ISO 602–74, 562–74 (technical analysis) and ISO 625–75 (elemental composition). The investigated characteristics of the coal from the Tisul deposit are presented in Table 1.

| Technical analysis, % | Elemental composition, % per daf | Atomic ratio |
|-----------------------|----------------------------------|--------------|
| W^a                   | A^d                             | V^daf        | C   | H   | (O+N+S) | H/C | O/C |
| 11.5                  | 10.4                            | 46.7         | 70.4| 4.4 | 25.2     | 0.75| 0.27|

According to the results of technical analysis, it can be seen that the original coal is characterized by a fairly high ash content (10.4%) and moisture content (11.5%), a high content of heteroatoms (25.2% per daf). The analysis for the sulfur content in the organic mass of coal was carried out according to GOST 8606-93. Sulfur in the organic mass of coal was found only in trace amounts.

Thermal analysis of the initial coal was carried out on a Netzsch STA 409 thermal analyzer under the following conditions: sample weight 40 mg; platinum-iridium crucible; inert medium - nitrogen; heating up to 1000 °C at a rate of 10 °C/min. During the analysis, weight loss (TG,% ) and rate of weight loss (DTG,% /min) were recorded. The research results are presented in Figure 1.

![Figure 1. Thermal analysis of brown coal from the Tisul deposit.](image)

The temperature dependence of the rate of change of mass (DTG) has two main peaks (reverse peaks due to weight loss). The first one at T = 105.2 °C is mainly associated with the desorption of
higrosopic moisture. The second peak at \( T = 434 \, ^\circ\text{C} \) is associated with the decomposition of the organic mass of coal. This temperature value, at which the maximum weight loss is observed, is expectedly lower for brown coal than for LF coals (\( T = 444 \, ^\circ\text{C} \)) [12, 13].

In the temperature range most acceptable for alkaline activation (700-800 \( ^\circ\text{C} \)), the decrease in the organic mass of coal is almost linear and without extremes. At temperatures above 800 \( ^\circ\text{C} \), there is practically no weight loss, and the residual weight tends to a value of 54\% of the initial one.

2.2. Preparation of sorbents

The sorbents were prepared by the method of alkaline activation (thermolysis of coal in the presence of potassium hydroxide) according to the method described in [14-16]. Coal with a particle size of 0.2-0.5 mm was used, which was soaked for 24 hours with a potassium hydroxide solution. Then the mixture was dried in an oven at 105 ± 5 \( ^\circ\text{C} \) until complete drying. Thus, a homogeneous mixture of potassium hydroxide and coal was obtained. The amount of alkali was taken so that the mass ratio of KOH/coal (\( R_{\text{KOH}} \)) was equal to - 0.5 g/g; 1 g/g; 2 g/g. The carbon-alkali mixture was heated in closed crucibles in a muffle furnace. The maximum heating temperature (TA) was varied and amounted to 700 \( ^\circ\text{C} \), 750 \( ^\circ\text{C} \), and 800 \( ^\circ\text{C} \). The heating process consisted of two stages: an increase in temperature at a rate of 7-9 \( ^\circ\text{C}/\text{min} \) to TA and isothermal holding for 1 hour. Then the crucibles were removed and placed in a desiccator for cooling. The caked solid reaction products were ground to a particle size of <1 mm, then they were sequentially washed from alkali 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 \( ^\circ\text{C} \) to constant weight. The prepared sorbents are a heterogeneous powder consisting of particles of various sizes; therefore, sorbents with a particle size of 0.2–0.5 mm were prepared for the study of textural characteristics.

2.3. Porous structure

The study of the porous structure of sorbents (specific surface area - \( S_{\text{BET}}, \, \text{m}^2/\text{g} \), total pore volume - \( V_{\Sigma}, \, \text{cm}^3/\text{g} \), mesopore volume - \( V_{\text{me}}, \, \text{cm}^3/\text{g} \) and volume of micropores - \( V_{\text{mi}}, \, \text{cm}^3/\text{g} \)) was carried out on an ASAP-2020 analyzer. The characteristics of the porous structure of the sorbents were determined from the isotherms of low-temperature (77 K) nitrogen adsorption in the range of equilibrium relative nitrogen vapor pressures from 10\(^{-3}\) to 0.995 p/p\( _0 \). Before carrying out measurements, to completely remove the sorbed impurities, the sorbent samples were evacuated at a temperature of 200 \( ^\circ\text{C} \) for 12 hours and a residual pressure of \( 5 \times 10^{-3}\) 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. Mesopore volume was calculated using the Barrett-Joyner-Halenda (BJH) method. These methods make it possible to calculate the characteristics of the porous structure of carbon sorbents prepared from fossil coals [17].

3. Discussion of results

Table 2 shows the characteristics of the porous structure of sorbents (\( S_{\text{BET}} \) - specific surface area, \( V_{\Sigma} \) - total pore volume, \( V_{\text{mi}} \) - micropore volume, \( V_{\text{me}} \) - mesopore volume).
Table 2. Characteristics of sorbents prepared from brown coal from the Tisul deposit at different activation temperatures ($T_A$) and mass ratios of KOH / coal ($R_{KOH}$).

| No | Sorbent sample | $T_A$, °C | $R_{KOH}$, g/g | $S_{BET}$ m$^2$/g | $V_\Sigma$, cm$^3$/g | $V_{ms}$, cm$^3$/g | $V_{mes}$, cm$^3$/g |
|----|----------------|-----------|----------------|-------------------|-------------------|------------------|------------------|
| 1  | C$_{700}^{0.5}$ | 700       | 0.5            | 540               | 0.29              | 0.18             | 0.1              |
| 2  | C$_{700}^{1}$   | 700       | 1              | 650               | 0.38              | 0.21             | 0.17             |
| 3  | C$_{700}^{2}$   | 700       | 2              | 1090              | 0.49              | 0.36             | 0.07             |
| 4  | C$_{750}^{0.5}$ | 750       | 0.5            | 730               | 0.36              | 0.24             | 0.11             |
| 5  | C$_{750}^{1}$   | 750       | 1              | 820               | 0.46              | 0.23             | 0.2              |
| 6  | C$_{750}^{2}$   | 750       | 2              | 1220              | 0.55              | 0.4              | 0.08             |
| 7  | C$_{800}^{0.5}$ | 800       | 0.5            | 760               | 0.39              | 0.25             | 0.12             |
| 8  | C$_{800}^{1}$   | 800       | 1              | 910               | 0.49              | 0.3              | 0.2              |
| 9  | C$_{800}^{2}$   | 800       | 2              | 1230              | 0.56              | 0.4              | 0.1              |

Analysis of the data obtained shows that an increase in the amount of added potassium hydroxide upon alkaline activation of brown coal from the Tisul deposit, regardless of the activation temperature $T_A$, leads to an increase in all textural characteristics of the prepared sorbents.

Sorbents obtained with a KOH/coal ratio of 2 g/g at the temperatures under study are microporous (the proportion of micropores in the total pore volume exceeds 70%) with a small content of mesopores. While at $R_{KOH} = 1$ g/g, an increased content of mesopores is observed, with the maximum amount at $T_A = 750$ °C. The high activation temperature, as well as the large amount of alkali, promote the development of micropores in the coal. The milder conditions created by a decrease in temperature and a decrease in the amount of injected alkali contribute to the development of not only micropores, but also mesopores. It should be noted that low $R_{KOH}$ ratios do not allow the activation of coal and at $R_{KOH} = 0.5$ g/g, the values of the porosity characteristics of the obtained sorbents are not high.

The peculiarities of the influence of the temperature of the alkaline activation process on sorbents prepared from carbon-alkaline mixtures of various compositions are illustrated in Figures 2-4.

The values of the total pore volume shown in Figure 2 do not linearly increase with increasing temperature, gradually approaching the maximum value. Analyzing the behavior of the curves, it can be assumed that there is a maximum temperature at which the total pore volume reaches its maximum value. The existence of such a point is also shown by the data of thermal analysis of the initial coal (in Figure 1, the rate of weight loss at temperatures above 850 °C tends to zero).

The effect of $R_{KOH}$ on the total pore volume is mainly reduced to a change in the position of the temperature dependences, and an increase in the amount of potassium hydroxide in the carbon-alkali mixture has practically no effect on their appearance.

For the dependences of the total pore volume on the temperature of alkaline activation (Figure 2), the following tendency is observed: sorbent C$_{800}^{0.5}$ ($V_\Sigma = 0.39$ cm$^3$/g) and sorbent C$_{700}^{1}$ ($V_\Sigma = 0.38$ cm$^3$/g) have practically the same values of total pore volume, as well as sorbent C$_{800}^{1}$ ($V_\Sigma = 0.49$ cm$^3$/g) and sorbent C$_{700}^{2}$ ($V_\Sigma = 0.49$ cm$^3$/g). This feature indicates a comparable effect of the above factors (an increase in $T_{max}$ from 700 °C to 800 °C and an increase in $R_{KOH}$ from 0.5 g/g to 1 g/g and from 1 g/g to 2 g/g) on the total pore volume in carbon sorbents based on brown coal from the Tisulsky deposit.
The values of the volume of micropores of carbon sorbents at different activation temperatures are shown in Figure 3.

![Figure 2](image1.png)

**Figure 2.** Values of the total pore volume ($V_\Sigma$) of sorbents prepared from coal from the Tisul deposit by alkaline activation at various temperatures and mass ratios of KOH/coal ($R_{\text{KOH}}$): (1 - $R_{\text{KOH}}$ = 0.5 g/g; 2 - $R_{\text{KOH}}$ = 1 g/g; 3 - $R_{\text{KOH}}$ = 2 g/g).

![Figure 3](image2.png)

**Figure 3.** Values of the volume of micropores ($V_{\text{mi}}$) of sorbents prepared from coal from the Tisul deposit by alkaline activation at various temperatures and mass ratios of KOH/coal ($R_{\text{KOH}}$): (1 - $R_{\text{KOH}}$ = 0.5 g/g; 2 - $R_{\text{KOH}}$ = 1 g/g; 3 - $R_{\text{KOH}}$ = 2 g/g).

For sorbents obtained at $R_{\text{KOH}}$ = 1, the values of micropore volumes differ to a small extent from the values for sorbents prepared at $R_{\text{KOH}}$ = 0.5 at all studied activation temperatures. The dependence at $R_{\text{KOH}}$ = 1 has an atypical growth pattern: with an increase in temperature from 700 °C to 750 °C, the increase is not significant, but from 750 °C to 800 °C, a sharp increase in the volume of micropores is observed.
Figure 4. The values of the volume of mesopores ($V_{me}$) of sorbents prepared from coal from the Tisul deposit by alkaline activation at various temperatures and mass ratios of KOH/coal ($R_{KOH}$) (1 - $R_{KOH} = 0.5 \text{ g/g}$; 2 - $R_{KOH} = 1 \text{ g/g}$; 3 - $R_{KOH} = 2 \text{ g/g}$).

Also, the dependence of the volume of mesopores (Figure 4) for the same sorbents prepared at $R_{KOH} = 1$ behaves in an unusual way, differing from other curves by the presence of a maximum at an activation temperature of 750 °C.

However, with the above-mentioned features of the behavior of the volumes of micropores and mesopores, for sorbents obtained at $R_{KOH} = 1 \text{ g/g}$, the dependence of the total pore volume does not differ in any way from similar dependences for sorbents prepared with other $R_{KOH}$.

The volume of micropores and mesopores under the studied conditions is dominated by the amount of potassium hydroxide during alkaline activation, while temperature has a weak effect.

Alkaline activation at a ratio of $R_{KOH} = 1 \text{ g/g}$ contributes to the production of carbon sorbents with high values of mesopore volume from brown coal from the Tisul deposit. The maximum value of the volume of mesopores is observed at an activation temperature of 750 °C. At a temperature of 800 °C, predominantly microporous sorbents can be prepared.

4. Conclusion

Sorbents based on brown coal from the Tisul deposit impregnated with potassium hydroxide solution at different KOH/coal ($R_{KOH}$) ratio - 0.5 g/g were prepared by alkaline activation at temperatures of 700 °C, 750 °C and 800 °C; 1 g/g and 2 g/g. The influence of the temperature of alkaline activation on the formation of the porous structure of the prepared sorbents was studied. It was shown that the temperature of alkaline activation has a smaller effect on the characteristics of the sorbents compared to the amount of potassium hydroxide used.

The influence of temperature in the range of 700-800 °C has a greater effect on the formation of pores in the process of alkaline activation at a KOH/coal ratio of 1 g/g. Sorbents with the maximum mesopore volume were obtained for this ratio at a temperature of 750 °C. High-temperature alkaline activation (at 800 °C) has a positive effect on the formation of a common pore space in sorbents based on brown coal from the Tisul deposit for all studied $R_{KOH}$.

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