

Effect of the Rate of Pulverized Coal Preheating on Char Reactivity

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Abstract—The effect of the preheating rate of the char particles from Kuznetsk bituminous coal on their specific reaction rate was determined. The experiments were carried out with char samples with mean diameters of 0.15 and 0.35 mm heated to temperatures of 900–1000°C. It was found that the specific surface area of the initial coal, measured by CO₂ adsorption at 273 K, for rapid and slow heat treatments increased more than two times. According to the results of thermogravimetric analysis, it was established that rapid pyrolysis in a muffle furnace led to the production of char whose maximum specific reaction rate was higher than that of the samples after slow pyrolysis.

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The efficient and environmentally appropriate use of coals for the generation of thermal and electrical power and the production of metallurgical coke is a problem of considerable current interest. A possible solution of this problem is the development of scientific fundamentals for a solid fuel preparation technology, which will make it possible to considerably increase the quality of fuel due to its partial gasification. The preliminary thermal preparation of fuel is one of such technologies [1]. On the thermal preparation of fuel, its partial gasification occurs in the burner volume, and a highly reactive mixture, which consists of combustible gases and coal char as the products of gasification, is formed at the inlet of the combustion chamber. As found experimentally [2–7], the pyrolysis temperature, the heating rate, and the pressure at the zone where volatile matter release and burning have an effect on the char reactivity and lead to changes in its structure. High-rank coals remain less sensitive to such a thermal activation/deactivation.

A pyrolysis temperature increase and a decrease of the coal heating rate led to a decrease in the chemical reaction activity of char with reactant gases [2–5]. Senneca and Salatino [8] also noted a similar effect based on calculations performed with the use of bituminous coal sample; in this case, as the diameter of particles was increased, thermal deactivation came

into play at a lower temperature and at a smaller degree of conversion of the sample.

Data on changes in the properties of coals upon heating [9], on the dynamics of volatile matter release upon thermal destruction [10], and on changes in the porous structure of char during combustion [11] are widely available in the publications of Russian researchers; however, it is difficult to combine them for an integrated consideration of the effects on reactivity. As a successful example, Maistrenko et al. [12] reported in 1990 the results of an integrated study for anthracite concerning the effect of pyrolysis temperature on the subsequent rate of conversion in an atmosphere of CO₂ and O₂.

From a practical point of view, coal from the Kuznetsk Basin is of considerable current interest for the development of promising technologies with an integrated gasification combined cycle [13]. The conditions of pyrolysis in the gasifier influence the thermal preparation of char, and they should be taken into account in the determination of kinetic characteristics and the development of the numerical model of the installation.

The aim of this work was to experimentally evaluate the effects of the temperature and pyrolysis rate of Kuznetsk coal particles on the chemical activity and specific surface area of the resulting char.

Table 1. Technical characteristics of the initial coal

Sample	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf}	Q_s^{daf} , MJ/kg
	wt %			daf, %					
Kuznetsk flame coal	5.5	15.9	44.8	75.6	5.7	1.8	0.6	16.3	29.7

EXPERIMENTAL

The chosen flame coal from the Kuznetsk Basin was crushed in a ball drum mill. The standard procedures of proximate and granulometric analysis and all of the subsequent experiments with the prepared samples were carried out using the following three facilities: a muffle furnace, a thermogravimetric analysis (TGA) instrument, and an analyzer for the determination of the specific surface area of reaction. Table 1 summarizes data on the proximate and ultimate analysis of coal.

The heat treatment of coal under the conditions of slow and rapid heating was performed with the aid of two furnaces:

(1) A TGA furnace (NETZSCH STA F3 instrument) was used for low-rate preparation. A weighed sample of 8–12 mg was placed on the TG-DSC holder and heated up to a temperature of 900°C at a rate of 25 K/min in an atmosphere of high-purity argon. After heating and 20 min exposure, the furnace was cooled to a temperature of 400°C. In case of sample preparation for studying the specific surface area, the program was the same with the exception of the last segment, in which the furnace continued to be cooled to room temperature in an atmosphere of argon.

(2) A SNOL 7.2/1100 muffle furnace with a temperature regulator was used for the rapid pyrolysis. The furnace was heated up to two selected temperatures (900 and 1000°C); a closed crucible was placed in the operating area, and the furnace was closed. The sample exposure time was 7 min (by analogy with GOST [State Standard] R 55660–2013), the furnace temperature after the placement of a cold crucible was balanced for in less than 3 min. In this case, the heating rate was 200–300 K/min, i.e., higher by an order of magnitude than that in TGA. Sklyar [1] described a similar method of high-speed preparation, which is close to a standardized procedure. Note that it is possible to attain much higher heating rates of about 9000 K/min with the use of alternative heating modes (by high-frequency currents [14] or by electric current [15]).

Figure 1 shows the temperature program of sample preparation. Based on the results of preparatory procedures, a set of char samples of different sizes and thermal preparation technologies was obtained (Table 2). Table 2 also summarizes data on the fraction of volatile matter ($V_{\text{prep}}^{\text{daf}}/V^{\text{daf}}$) released upon the sample preparation, as compared with the result of proximate analysis. Note that the yield of volatile matter from the selected coal increased with the maximum pyrolysis temperature. Upon the slow pyrolysis, the fraction of

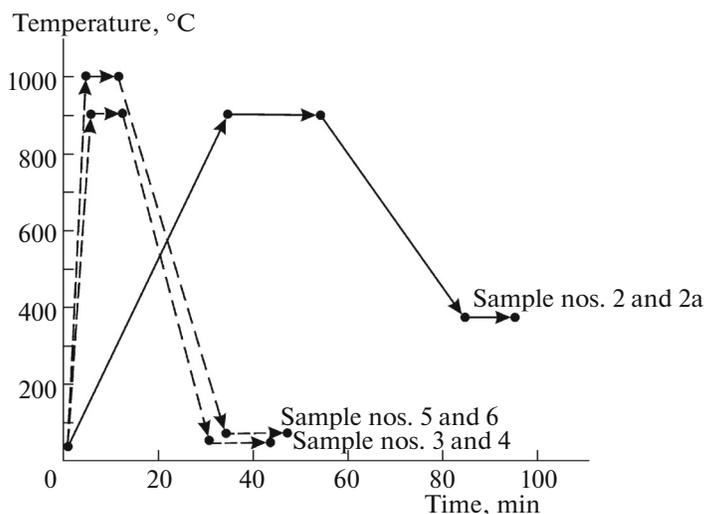


Fig. 1. Temperature program of the char samples preparation: solid and dashed lines refer to slow heating and rapid heating and pyrolysis, respectively.

Table 2. Characteristics of the initial coal and tested chars

Sample no.	Coal/char	Particle diameter, mm	Char preparation conditions	Fraction of volatiles released upon the preparation of char $V_{\text{prep}}^{\text{daf}}/V^{\text{daf}}$
1	Initial coal	<0.5	—	—
2	Char	0.2–0.5	In TGA with slow heating (25 K/min) to 900°C in an inert atmosphere and an exposure of 7 min	0.79
2a	The same	0.1–0.2	In TGA with slow heating (25 K/min) to 900°C in an inert atmosphere and an exposure of 7 min	0.76
3	»	0.2–0.5	High-speed heating in a closed crucible. Furnace temperature, 900°C; exposure time, 7 min	0.99
4	»	0.1–0.2	High-speed heating in a closed crucible. Furnace temperature, 900°C; exposure time, 7 min	1.15
5	»	0.2–0.5	High-speed heating in a closed crucible. Furnace temperature, 1000°C; exposure time, 7 min	1.03
6	»	0.1–0.2	High-speed heating in a closed crucible. Furnace temperature, 1000°C; exposure time, 7 min	1.5

released volatiles was 20% smaller than that upon the rapid pyrolysis at the same maximum heating temperature. The differently directed effects on the fraction of released volatiles in the samples of different sizes can be explained by random error related to the insufficiently constant parameters of the tested material.

The experiments on the determination of the reaction rate properties of the prepared char samples were carried out on an STA F3 TGA instrument. The analyzer has high resolution of 1 μg and 0.1 K with respect to mass and temperature, respectively. The maximum permissible error of the measurement of weight losses was no greater than 10%. On slow heating (nos. 2, 2a) the sample preparation and the experiment were carried out consecutively in a TGA furnace, whereas the preparation with rapid pyrolysis (nos. 3–6) was performed in a muffle furnace; thereafter, the samples were transferred into the TGA furnace.

The specific surface areas and pore sizes were measured with the aid of an Autosorb-6B-Kr instrument (Quantachrome Instruments, the United States) for sample nos. 1, 2, and 3–6. The samples were prepared in a FLOVAC Degasser instrument (Quantachrome Instruments, the United States) for the removal of moisture and adsorbed gases from the surface and the pore volume. The preparation conditions were the following: a vacuum (the absolute pressure was no higher than 6 Pa) with programmed heating. The steps of heating were 80 and 120°C, and the final temperature, which was chosen based on the sample properties, was 150°C (for initial coal no. 1) or 350°C for the chars

(nos. 2, 3–6). The heating rate between the steps was 1 K/min. The exposures at the steps were 0.5 h at 80 and 120°C, 12 h at 150°C, and 3 h at 350°C. The exposure time at the final stage of heating was chosen for the achievement of a final dynamic vacuum of 1.5 Pa. Cooling to room temperature after heating within a thermal cup took no shorter than 1.5 h. The adsorption isotherms were measured with the use of carbon dioxide adsorbate at 273 K (the melting point of ice at a normal pressure) and for sample no. 2 with the nitrogen adsorbate at 77 K.

RESULTS AND DISCUSSION

Figure 2 shows the curves of conversion for the samples of char reacting with atmospheric oxygen. In all of the experiments, the furnace heating rate at the stage of air supply was 7.5 K/min. For the samples prepared in the TGA furnace (nos. 2, 2a), only the section of conversion in an atmosphere of air is given (*d–e*). The curves of conversion for sample nos. 3–6 include the section of heating and isothermal exposure in argon (*a–b–c*). A considerable weight loss was not detected on heating in argon. Switching to air occurred at point (*c*), and (*c–d–e*) is the section of char combustion.

The burning of all of the samples was complete at a temperature of about 600°C. A discrepancy between the residual ash contents of the samples of different fractions was no greater than 4%, and it was determined by the heterogeneity of the initial samples obtained upon size grading.

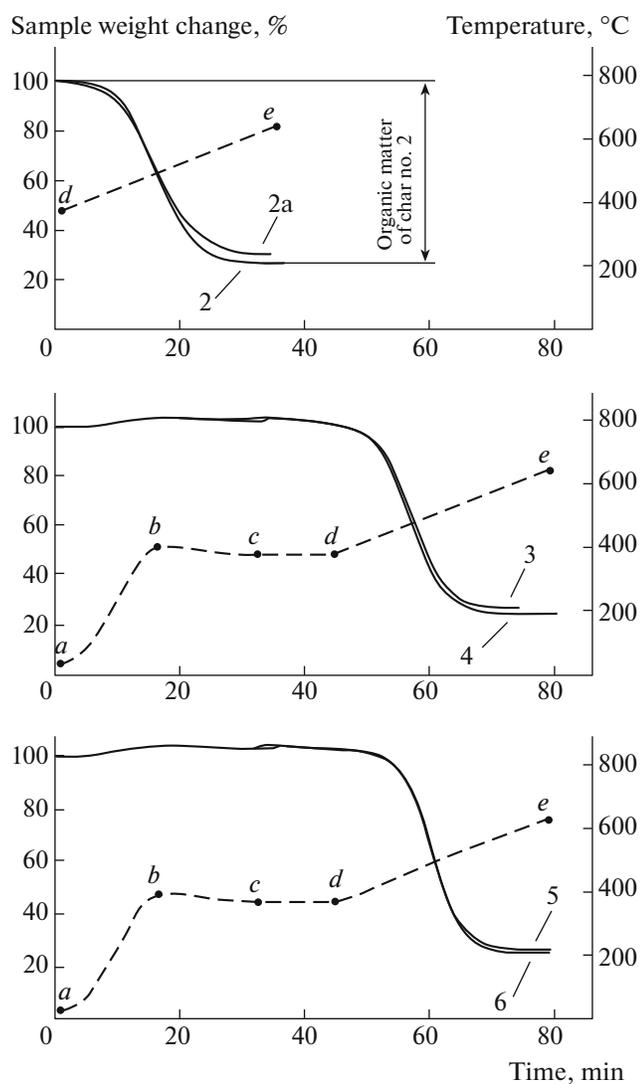


Fig. 2. Coal chars conversion curves: Solid lines, chars weight losses of sample nos. 2, 2a, and 3–6; dashed lines, sample temperature.

It is difficult to visually compare the conversion of the test samples based on the initial weight loss curves. A picture obtained upon the conversion of data to the specific reaction rate of the sample organic matter is more descriptive. The specific reaction rate on an initial weigh basis R_0 (1/s) was calculated based on the initial TGA data from the equations

$$R_0 = \frac{1}{m_0} \frac{dm}{d\tau} = \frac{dX}{d\tau}, \quad X = \frac{m_0 - m_\tau}{m_0},$$

where m_τ is the current organic mass of the sample (g), dm is the loss of mass (g) in the period $d\tau$ (s), m_0 is the mass of organic matter (g), and X is the degree of conversion. The mass of organic matter was determined from the indications of the TGA analyzer as the loss of

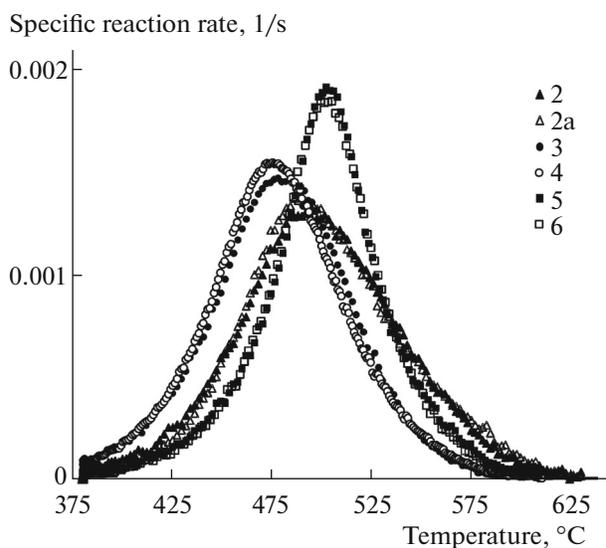


Fig. 3. The temperature dependence of the specific reaction rate (R_0) for sample nos. 2, 2a, and 3–6.

mass from the point of air supply switching on to the end of burning out.

Figures 3 and 4 show the dependences of the specific reaction rate of char reacting with atmospheric oxygen. Figures 3 and 4 clearly distinguish between the conversion in the initial and final periods and in the major portion, respectively.

The rate of preliminary pyrolysis exerted an effect throughout the entire conversion curve. A maximal specific reaction rate reached in the samples (nos. 3–6) after rapid pyrolysis was higher than that in the samples obtained in TGA on slow pyrolysis (nos. 2, 2a). In the range $0.3 < X < 0.9$, the conversion rate was higher in the samples prepared in the muffle furnace. In a comparison with the results of the combustion of anthracite char [12], which was obtained at different pyrolysis temperatures under slow heating conditions, it is possible to note that the specific rate of bituminous coal conversion was higher at the same preparation temperature. The reaction rate of anthracite decreased with the preparation temperature, but such a relationship was not found in the experiments.

The shapes of conversion curves for the particles of different sizes and the same thermal preparation method (2–2a, 3–4, and 5–6) indicate that the effect of the pulverized coal particle size on the reaction rate is insignificant in this temperature range.

The trial measurement of nitrogen adsorption isotherms at 77 K for sample no. 2 showed the presence of a hysteresis loop (Fig. 5), that is, the occurrence of capillary condensation in mesopores and the presence of ultramicropores in the sample, in which adsorption occurs with a high activation energy. The adsorption of

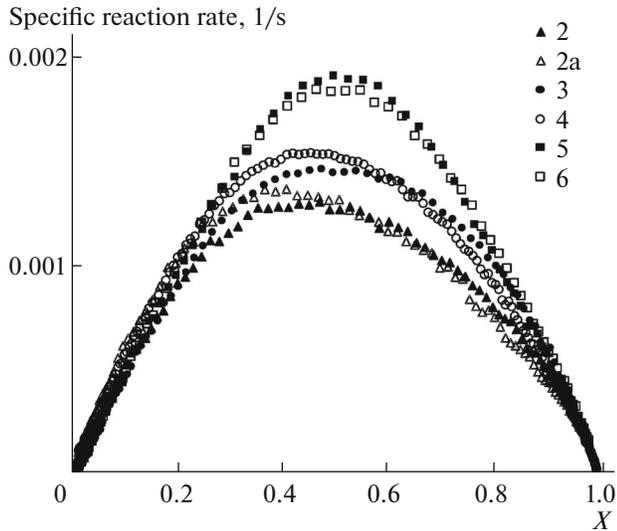


Fig. 4. Specific reaction rate (R_0) as functions of the conversion degree for sample nos. 2, 2a, and 3–6.

nitrogen on the sample occurred extremely slowly; the first points of the isotherm were obtained a day after the start of measurements. The adsorption of carbon dioxide at 273 K was chosen as a more acceptable alternative to nitrogen for determining the textural characteristics of this set of samples. At this temperature, the adsorption occurred much more rapidly. Figure 6 shows the carbon dioxide adsorption isotherms at 273 K.

The value of adsorption considerably increased as the adsorption temperature was increased; this fact confirmed the hypothesis of activated adsorption on the samples of char. A comparison of the adsorption isotherms indicated that, in general, all of the chars exhibited close values of adsorption, and the samples prepared at 1000°C had lower values. The value of adsorption on the initial coal was substantially lower than that on the chars.

The textural characteristics of the tested samples and the pore size distribution curves (Fig. 7) were calculated by carbon dioxide adsorption at 273 K. It is necessary to note that the measurement method with the use of CO_2 adsorption at 273 K and subatmospheric pressures makes it possible to measure only micropores (<2 nm). From the distributions, it is evident that test sample nos. 2 and 3–6 had similar distribution curves, and pores with widths of 0.35, 0.5, and 0.8 nm were present in the samples. A smaller specific pore volume and a smaller contribution of pores with a width of 0.35 nm to the total volume characterized the textural properties of initial coal sample no. 1.

The experimental values of the specific surface areas of reaction for the initial coal and chars are

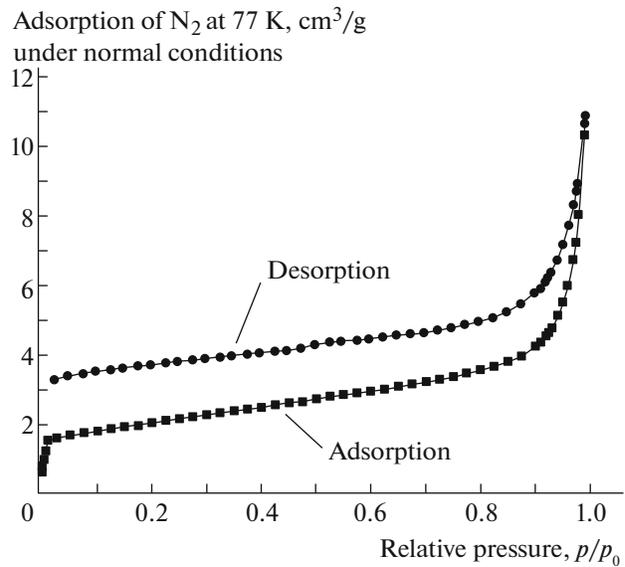


Fig. 5. Isotherm of nitrogen adsorption on sample no. 2 at 77 K. Preparation temperature, 150°C; time, 12 h.

within a characteristic range for coals on the adsorption of CO_2 (Fig. 8). Table 3 summarizes the generalized textural characteristics.

The more intense release of volatile matter implies the formation of voids with large cross sections inside a particle; the surface area of these voids is smaller than that of micropores. This is the reason for a decrease in the specific surface area of tested char sample nos. 5 and 6.

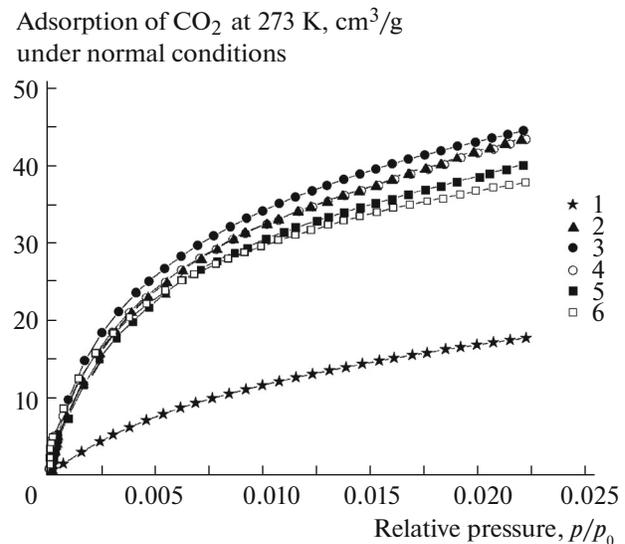


Fig. 6. Carbon dioxide adsorption isotherms on coal sample no. 1 and char samples nos. 2–6 at 273 K. Preparation temperature, 350°C; time, 3 h.

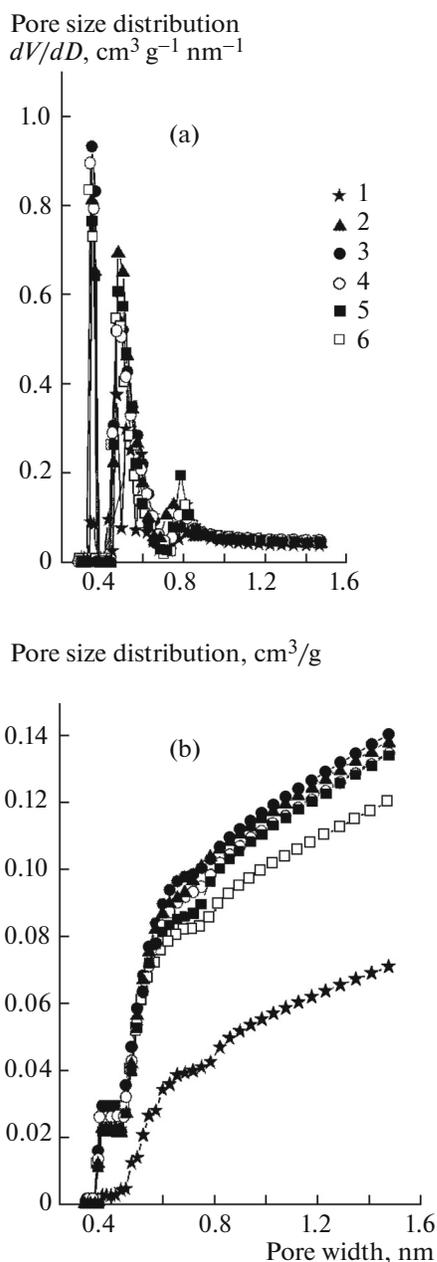


Fig. 7. Pore size distributions in coal sample no. 1 and char samples nos. 2–6: (a) differential dV/dD and (b) integral. Calculation method, NLDFT based on a slit-pore model; the adsorption of CO_2 on carbon at 273 K.

CONCLUSIONS

The above analysis allowed us to estimate the influence of the preliminary thermal preparation of the initial coal on the chemical activity and a change in the specific surface area of coal char.

The specific surface area of the initial coal increased from 221 to 437–507 m^2/g , as measured with the aid of the CO_2 adsorption at 273 K. The reaction surface areas had close values for the particles of

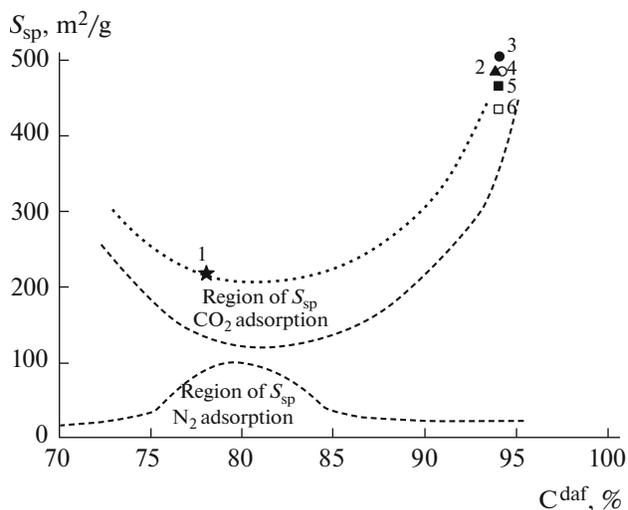


Fig. 8. Specific surface areas of coal pores by the CO_2 and N_2 adsorption [16]: (1) initial coal and (2–6) the char samples.

different sizes with different exposure times; a tendency toward decreasing the specific surface area with the increase of preparation temperature and violates release was established.

The maximum rate of reaction of char with atmospheric oxygen in a conversion range from 0.3 to 0.9 was found higher in the samples prepared under the conditions of rapid pyrolysis at 1000°C . At the initial stage of burning at $X < 0.3$, these samples start burning more slowly than the others, and the samples prepared at 900°C under the conditions of rapid heating exhibited a maximum rate of burning. The slow heating of coal led to the production of the least reactive char.

Thus, is necessary to consider sample preparation procedures in the construction of a numerical model and in the experimental determination of the kinetic properties of fuel in the case that the pyrolysis tem-

Table 3. Textural characteristics of the char samples. The NLDFT calculation method based on a slit-pore model; the adsorption of CO_2 on carbon at 273 K

Sample no.	Specific pore volume (pores smaller than 1.47 nm), cm^3/g	Specific surface area S_{sp} , m^2/g	Maximum in a pore size distribution curve dV/dD , nm
1	0.072	220.9	0.479
2	0.138	488.5	0.349
3	0.140	506.9	0.349
4	0.136	487.2	0.349
5	0.134	467.5	0.349
6	0.121	436.6	0.349

perature is maximally close to the conditions of a real power plant.

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