Determination of the parameters of the porous structure of carbon sorbents based on Kuzbass fossil coals by the method of low-temperature nitrogen adsorption

Y N Dudnikova, I Yu Zykov, S A Sozinov and Z R Ismagilov

Federal Research Center of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Science,
18 Sovetskiy Ave., 650000, Kemerovo, Russia
E-mail: dudnikova.yuliya80@mail.ru

Abstract. The paper presents a technique for measuring the parameters of the porous structure of carbon sorbents obtained on the basis of Kuzbass fossil coals using an ASAP 2020 "Micromeritics" analyzer. The conditions for sample preparation were selected, which make it possible to record reproducible isotherms of low-temperature adsorption-desorption of nitrogen (77K) by the studied samples of carbon sorbents based on fossil coal of various grades. The textural characteristics of the porous structure of carbon sorbents were determined, such as the specific surface area ($S_{BET}$, m$^2$/g), the total pore volume ($V_S$, cm$^3$/g), the volume of micro- and mesopores ($V_{micro}$, $V_{meso}$, cm$^3$/g) of the studied carbon sorbents. The textural characteristics of the porous structure of carbon sorbents were calculated from the obtained isotherms of low-temperature (77K) nitrogen adsorption-desorption. The textural characteristics of carbon sorbents were calculated by various methods implemented by the software of the ASAP 2020 analyzer "Micromeritics": BET, Langmuir, DFT, t-Plot, Dubinin-Radushkevich, Dubinin-Astakhov, MP-method, Horvath-Kawazoe, BJH and Dollimore-Heal. The obtained values of the textural characteristics of the porous structure of carbon sorbents, calculated by various methods, make it possible to obtain more detailed information about the objects of study and to determine the scope of their further application.

1. Introduction
One of the most important indicators of the quality of carbon sorbents is their porous structure. The accepted parameters of the porous structure are total volume (the sum of pore volumes of all varieties, cm$^3$/g of sorbent); the limiting volume of the sorption space, which is the sum of the volumes of the sorbing pores ($V_{micro} + V_{meso}$, cm$^3$/g); pore size (width, diameter, nm) [1-3]. The developed porous structure of coals determines the high adsorption capacity and, consequently, the efficiency of their use [4-7]. Therefore, the study of the properties of the porous space of carbon sorbents is an urgent scientific and practical task, since the results of such studies make it possible to determine the mechanisms of sorption and the field of application of carbon sorbents [8-12].

Carbon sorbents based on fossil coals are complex objects, since they are mixed sorbents, and their porous structure is polymodal. In this regard, the question of conducting research on the surface and
porous structure of such sorbents by modern methods, using the latest analytical and research equipment is relevant.

However, the existing GOST standards for determining the specific surface area of various materials, for example, GOST 25699.2-90 “Technical carbon for rubber production. Methods for determining the specific outer surface area” establishes a method for determining the specific outer surface of carbon black for rubber production; GOST 23401-90 “Metal powders. Catalysts and carriers. Determination of the specific surface area ”- a method for determining the specific surface area of metal powders, catalysts and carriers from 0.05 to 1000 m²/g by thermal desorption of nitrogen (argon), demonstrates outdated instrumentation of the methods. In addition, at the moment there is no GOST for the determination of the specific surface area and parameters of the porous structure of carbon sorbents based on fossil coals using modern equipment, for example, an ASAP 2020 surface area and porosity analyzer "Micromeritics". Thus, it can be stated that there is an urgent need to develop new and adapt existing methods for measuring the parameters of the porous structure of carbon sorbents.

2. The essence of the research methodology
The study of the parameters of the porous structure was carried out on an ASAP 2020 analyzer "Micromeritics". The gas adsorption analyzer ASAP 2020 is designed to measure the specific surface area (sorption capacity) using physically and chemically sorbed gases for dispersed and porous materials, and to further determine their characteristics: integral specific surface area, pore volume and size, distribution of pore volume and surface over their effective dimensions for physical sorption according to standard measurement methods.

The ASAP 2020 analyzer is an automatic device, the principle of which is based on the adsorption and desorption of gases on the external and internal surfaces of the studied samples of dispersed and porous materials.

Before carrying out measurements, the test sample is placed in an ampoule, installed on the preliminary preparation port and degassed in vacuum at an elevated temperature in order to remove gases and vapors absorbed by it from the surface of the test material (thermal training of the sample). Then the ampoule with the sample is placed on the measuring port, cooled to the boiling point of liquid nitrogen (77K) and filled with a sorbable gas - sorbate, which is nitrogen (krypton, carbon dioxide, etc.).

From the isotherms of physical adsorption and desorption obtained as a result of measurements by specially developed measurement methods, the textural characteristics of dispersed and porous materials are determined, including the integral specific surface area by the BET (Brunauer-Emmett-Taylor), Langmuir, pore volume, pore size, distribution pore size, etc. The measurement error is 5-7%.

The following reagents are required for measurements:
1. Gaseous nitrogen of high purity 99.999% and liquid GOST 9293-74 (ISO 2435-73);
2. Helium TU 0271-001-45905715-02.

To select the degassing parameters, it is necessary to set the degassing temperature by varying the temperature from 105 - 450 °C with a resolution of 1 °C (the recommended temperature for oxide materials is 150 °C, for microporous materials and zeolites - 350 - 400 °C). The interval is selected according to the results of thermogravimetric studies and (or) according to the physicochemical properties of a particular sample. In this case, it is necessary to set the heating rate (1 - 10 °C/min).

To register the nitrogen adsorption-desorption isotherm, it is necessary:
- indicate the range of relative pressures;
- carry out a quick degassing and a leak check;
- set the values of pressure and degassing time;
- indicate the need to measure the free volume;
- indicate the need for Po measurement during the analysis (isotherm survey);
- set the mode of step-by-step nitrogen dosing at low pressure;
- set the time to reach equilibrium;
- indicate the need to fill the ampoule with nitrogen after measurement;
- set the parameters of the report.

When determining the parameters of the porous structure: specific surface area, total pore volume, volume of micro- and mesopores, their size distribution, it is necessary to take into account that:

- measurements of adsorption isotherms are carried out only for dispersed (powdered) samples;
- the minimum required amount of a sample with unknown characteristics is 1 g (if the specific surface area of the sample is more than 150 m²/g, then the minimum amount is 0.5 g; if the specific surface area exceeds 300 m²/g, then the minimum amount is 0.1 g), and the maximum amount of the sample is - 3-7g (depending on the bulk density of the material);
- before measurement, samples are necessarily degassed in vacuum when heated, therefore the sample must first be dried in a drying oven, because during degassing, no toxic or contaminating substances should be released. In addition, the sample should not react with a glass measuring tube, and should be stable for a long time under specified conditions: there should be no destruction, particle agglomeration, phase transitions, sublimation at low pressures;
- the minimum specific surface area of the material used for measurement – 15 m²/g (may vary depending on the nature of the surface and the composition of the sample);
- determination of the specific surface area by the BET method for materials with a microporous structure is not physically justified due to the assumptions of the theory;
- when measuring nitrogen adsorption from the gas phase, the determination of the pore size distribution is possible for pores with a diameter (width) of 0.39 - 50 nm (when using the BJH method up to 300 nm, depending on the sample).

3. Discussion of results

In the presented work, studies of the porous structure of carbon sorbents obtained from fossil coals were carried out using an ASAP 2020 "Micromeritics" analyzer. As a result, the conditions for degassing and measurements were selected, namely: the studies were carried out by the method of low-temperature adsorption of nitrogen after evacuating the samples at 200 °C for 12 hours and a residual pressure of less than 0.5 • 10⁻³ mm. Hg. The specific surface area of the samples under study was obtained from the analysis of the adsorption-desorption isotherms of N₂ at -196 °C (77 K). The nitrogen adsorption-desorption isotherms were measured in the range of equilibrium relative vapor pressures from 10⁻³ to 0.995 P/P₀.

The main parameters of the porous structure of carbon sorbents: specific surface area (S_BET, m²/g), total pore volume (V_Y, cm³/g), volume of micro (V_microl, cm³/g) - and mesopores (V_meso, cm³/g) and average diameter pores (D_pores, Å) of the samples are shown in Table 1.

In addition, the software of the ASAP 2020 analyzer allows one to calculate the texture characteristics of carbon sorbents by various methods, the results of which are shown in Table 2.

| Table 1. Parameters of the porous structure of carbon sorbents |
|-------------------------------------------------------------|
| Sample No. | Sample                      | S_BET, m²/g | V_Y, cm³/g | V_microl, cm³/g | V_meso, cm³/g | D_pores, Å |
|-----------|-----------------------------|-------------|------------|-----------------|---------------|------------|
| 1         | Carbon sorbent No. 1        | 330         | 0.18       | 0.07            | 0.06          | 21.6       |
| 2         | Carbon sorbent No. 2        | 1100        | 0.75       | 0.32            | 0.43          | 26.9       |
| 3         | Carbon sorbent No. 3        | 1600        | 0.77       | 0.40            | 0.17          | 19.5       |
The specific pore surface area was calculated using the Brunauer-Emmett-Taylor (BET), Langmuir, and density functional theory (DFT) methods. The specific surface area of micropores was assessed by the comparative t-Plot method and the MR method, as well as using the Dubinin-Radushkevich and Dubinin-Astakhov methods.

The volume of micropores was determined using the comparative t-Plot method and the MR method, DFT, as well as using the Dubinin-Astakhov and Horvath-Kawazoe method. Mesopore volume was determined using the Barrett-Joyner-Halenda (BJH) and Norvath-Kawazoe method.

The average pore diameter was estimated according to the formula $D_p = \frac{4V_{ads}}{S}$, according to the BET, BJH, Dollimore-Heal and MP method. Mesopore volume was calculated from the size distribution of mesopores (BJH and Dollimore-Heal method).

### Table 2. Textural characteristics of carbon sorbents

| Textural characteristics | Characterization method | CS No.1 | CS No.2 | CS No.3 |
|--------------------------|-------------------------|---------|---------|---------|
| Specific surface area, m$^2$/g | Single point | 300 | 1100 | 1600 |
| | BET | 300 | 1100 | 1600 |
| | Langmuir | 300 | 1300 | 1800 |
| | DFT | 300 | 1400 | 1400 |
| | t-Plot | 200 | 800 | 1000 |
| Specific surface area of micropores, m$^2$/g | Dubinin-Radushkevich | 300 | 1200 | 1700 |
| | MP-Method | 400 | 1300 | 2000 |
| | Dubinin-Astakhov | 300 | 1000 | 1500 |
| Specific surface area of mesopores, m$^2$/g | BJH | 70 | 300 | 200 |
| | Dollimore-Heal | 60 | 300 | 200 |
| Total pore volume, $V_p$, cm$^3$/g | 0.18 | 0.32 | 0.40 |
| | t-Plot | 0.14 | 0.35 | 0.64 |
| | DFT | 0.13 | 0.43 | 0.61 |
| | Dubinin-Astakhov | 0.17 | 0.55 | 0.73 |
| | MP-Method | 0.18 | 0.59 | 0.78 |
| | Horvath-Kawazoe | 0.06 | 0.43 | 0.17 |
| Micropore volume $V_{micro}$, cm$^3$/g | BJH | 0.06 | 0.43 | 0.16 |
| | Dollimore-Heal | 0.06 | 0.41 | 0.16 |
| | BET | 21.6 | 26.9 | 19.5 |
| | BJH | 35.4 | 54.5 | 36.7 |
| | Dollimore-Heal | 36.9 | 53.6 | 38.7 |
| | MP-Method | 4.5 | 4.2 | 3.7 |

Figures 1 - 3 show the adsorption-desorption isotherms of nitrogen by carbon sorbents No. 1, No. 2, No. 3, respectively.
Figure 1. Isotherm of adsorption - desorption of nitrogen at 77K by carbon sorbent No. 1.

Figure 2. Isotherm of adsorption - desorption of nitrogen at 77K by carbon sorbent No. 2.
Figure 3. Isotherm of adsorption - desorption of nitrogen at 77K by carbon sorbent No. 3.

Figure 4 shows the differential pore size distribution in the samples of the studied carbon sorbents.

Adsorption isotherms characterize the porous structure of a material and make it possible to determine a number of its properties. The highest adsorption capacity for nitrogen in the region of low relative pressures is possessed by carbon sorbent No. 3, which indicates higher values of the specific surface area in comparison with other samples. The appearance of the nitrogen adsorption isotherm by carbon sorbent No. 2 (Figure 2) can be attributed to type IV isotherms according to the IUPAC classification [13, 14], inherent in mesoporous bodies. However, carbon sorbents No. 1 and No. 3 are
characterized by a microporous structure, which is confirmed by the appearance of the type I isotherm (Figure 1 and 3) and the obtained experimental research data (Table 1).

It should be noted that hysteresis is observed on all isotherms, the type of which can be used to judge about the pore shapes and the type of porous structure of the sorbent [15]. Figure 2 shows a pronounced hysteresis relative to other isotherms shown in Figures 1 and 3. For carbon sorbent No. 2, the hysteresis belongs to the H3 type (Figure 2), which indicates the presence of slit-like pores in the structure. For the rest of the samples of carbon sorbents (Figures 1 and 3), hysteresis of the H4 type is observed, which indicates pores consisting of plane-parallel particles. According to the presented pore distributions (Figure 4), for carbon sorbents No. 1 and No. 3, pores with sizes less than 20 nm predominate. However, for carbon sorbent No. 2, pores with a diameter of more than 20 nm predominate, this feature is expressed in a wide hysteresis loop (Figure 2) for this sample.

4. Conclusion
Thus, the described method of measuring the parameters of the porous structure of carbon sorbents obtained from Kuzbass fossil coals using the automatic analyzer of surface area and porosity ASAP 2020 "Micromeritics" makes it possible to determine the main parameters of the porous structure. It is shown that the selected research conditions make it possible to record adsorption isotherms and to obtain textural characteristics of carbon sorbents (specific surface area, total pore volume, micro- and mesopore volume). In addition, by varying the various methods of calculating the texture characteristics of carbon sorbents, implemented by the software of the ASAP 2020 analyzer "Micromeritics" (Table 2), one can obtain more detailed information about the objects of study and determine the scope of their further application.

Acknowledgments
The work was carried out within the framework of the state assignment of the Federal Research Center of Coal and Coal Chemistry SB RAS (project AAAA-A17-117041910151-9).

When performing the work, the equipment of the Center for Collective Use of the Federal Research Center of Coal and Coal Chemistry SB RAS was used.

References
[1] Kolyshkin D A and Mikhailova K K 1972 Activated Coals (Leningrad: Chemistry) 56 p.
[2] Mukhin V M, Tarasov A V and Klushin V N 2000 Active Coals of Russia " A V Tarasova Ed. "(Moscow: Metallurgy) 352 p.
[3] Peredery M A 2005 Solid Fuel Chemistry 1 76-89
[4] Kozlov A P et al 2018 Bulletin of the Kuzbass State Technical University 3 (127) 93-101
[5] Peredery M A 2000 Solid Fuel Chemistry 1 35-44
[6] Geoffrey S S et al 2016 Journal of Environmental Chemical Engineering 4(2) 2291-312
[7] Zvekov A A et al 2019 Coke and Chemistry 62(6) 240-4
[8] Zykov I Yu et al 2019 Bulletin of the Kuzbass State Technical University 15 20-7
[9] Zvekov A A et al 2019 Coke and Chemistry 62(8) 365-70
[10] Zykov I Yu et al 2019 Bulletin of Kuzbass State Technical University 14 64-9
[11] Fedorova N I et al. 2018 Coke and Chemistry 8 19-23
[12] Zykov I Yu, Dudnikova Yu N and Tsvetkov V E 2019 Chemistry for Sustainable Development 27 592-6
[13] IUPAC Reporting physisorption data for gas/solid system 1985 Pure Appl Chem. 57 603
[14] Brunauer S Deming L S Deming W S and Teller E 1940 J Amer Chem Soc. 62 1723
[15] Fenelonov V B 2002 Introduction to the Physical Chemistry of the Formation of the Supramolecular Structure of Adsorbents and Catalysts (Novosibirsk: Publishing house of the SB RAS) 414 p.