

RESEARCH PAPER

Activation of carbon sorbents used in the hydrocracking process of vacuum oil distillation residue

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Abstract

The article is devoted to studying the effect of modification of carbon sorbents, used as a catalyst during hydrocracking of vacuum residue, on their textural characteristics. Methods for modifying the main textural characteristics of the carbon support are shown. They provide a high degree of conversion of residual asphaltene associates during hydrocracking. To determine the optimal pore space in carbon sorbents, the sizes of asphaltene associates in the initial feedstock were determined by laser diffraction. A comparative analysis of the sizes of asphaltene associates with the pore space of a carbon sorbent was carried out for the first time. Using radiograph diffraction, infrared spectroscopy, radiograph fluorescence, and thermogravimetric analysis, the distinctive features of the thermal activation of carbon sorbents were established. Based on radiograph diffraction, a crystalline phase of calcite was discovered in the composition of carbon sorbents. As a result of thermal activation, according to the radiograph fluorescence method, the sulfur content in carbon sorbents decreases. It has been shown that activation of carbon with water vapor increases the formation of mesopores and macropores, but no direct dependence of the specific surface area on the thermal activation medium was found. It has been shown that within industrially used carbon sorbents, the conversion of asphaltenes does not occur on the internal surface of the pores but on their much smaller outer surface. An increase in the contact area of asphaltene associated with the surface of carbon sorbents (due to an increase in pore diameters) can be achieved by their heat treatment at a temperature of 400 °C in a nitrogen atmosphere or steam-thermal treatment at a temperature of 800 °C. Additional use of the internal surface inside the pores of carbon sorbents during asphaltene cracking increases their conversion degree. The textural characteristics of coals can serve as indicators of their applicability as additives in the reaction media for vacuum residue hydrocracking.

Keywords: Carbon carrier, Carbon sorbents, Hydrocracking, Pore size and pore volume, Specific surface area, Vacuum residues

1. Introduction

Within the decrease in the reserves of conventional light oils, the production of unconventional heavy hydrocarbon resources is increasing, that is, heavy high-viscosity oil containing a large amount of resin–asphaltene components.^{1–6} The resource potential of heavy high-viscosity oils on the planet is many times greater than the predicted recoverable reserves of traditional hydrocarbons.^{7–11} The

constant improvements in reservoir-producing methods have made their extraction profitable for mining companies, which in turn resulted in an increase in the density and viscosity of hydrocarbon feedstock entering the processing refineries due to the increased content of polyaromatic and heteroatomic compounds, resins, and asphaltenes.^{12–15} At oil refineries, the following processes are often used to process these residues: multistage deasphalting with propane or other solvents; light thermal

Received 29 August 2023; revised 27 April 2024; accepted 29 April 2024.
Available online 21 June 2024

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<https://doi.org/10.62593/2090-2468.1029>

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cracking (visbreaking); delayed coking.^{16–22} Refining processes based on deasphalting do not lead to converting resin–asphaltene components of heavy oil residue (HOR). The profitable utilization of the resulting asphalt residue requires the presence of bitumen production units. The purpose of visbreaking is to reduce the viscosity of HOR. The main disadvantage of the process is a rather low degree of conversion, which cannot be further increased due to changes in instrumentation or technological parameters. A limiting factor for the use of delayed coking for processing residual fractions of heavy, high-viscosity oils is the high content of metals and sulfur in the feedstock, which inevitably leads to the production of coke of poorer quality and deterioration of environmental performance. The technologies developed based on the hydrocracking process should also be noted: H-Oil with an ebullioscopic catalyst layer; LC-Fining, where catalysts based on carbon carriers modified with metals of groups VI and VIII can be used; the Uniflex process with iron-containing ultrafine catalyst; Eni-slurry with ultrafine microcrystalline molybdenum sulfide dispersed in the raw material in the form of irregular clusters with an average catalyst diameter of 0.5–2 μm ; CANMET process with an additive based on ferrous sulfate. According to various sources, the conversion of residue into light oil products within these processes, is limited to 70%. In Veba-combi-cracking (VCC), it reaches up to 90–95%. Hydrocracking in a VCC slurry reactor presents a well-known technology for processing heavy hydrocarbon feedstock into valuable low-boiling hydrocarbon fractions.²³ Slurry phase hydrocracking processes are currently being studied throughout the world. Highly efficient cracking processes of heavy residual feedstock, providing conversion of more than 95% while maintaining the maximum yield of the target product – light fractions, are based on the use of hydrogen under high pressure and expensive catalysts, which

leads to an increase in their production cost.^{24–31} Thus, the main problems in the development of catalysts for HOR deep processing are associated with a high content of sulfur and organometallic compounds, resin, and asphaltene molecules in the feedstock, which leads to an increase in energy consumption and, as a result, leads to low profitability of the hydrocracking.

Therefore, one of the most promising and popular technologies for deep processing of heavy hydrocarbons is VCC, which combines cracking and hydrogenation reactions.^{32–34} On the industrial level, the process of hydrocracking of heavy hydrocarbon feedstock proceeds in the temperature range of 440–485 $^{\circ}\text{C}$ at a hydrogen pressure of 19–21 MPa in hollow gas–liquid phase reactors (R-101, R-102, and R-103) operating similarly to bubbling columns with ascending flow (Fig. 1).³⁵

The reaction mass in the reactors (R-101, R-102, and R-103) presents a suspension consisting of heavy hydrocarbon feedstock, solid sorbents (not >2 wt. % for feedstock) and hydrogen (6 wt. % for feedstock).³⁶ In the apparatuses, E-102, E-103, and E-201, heavy hydrocarbon raw materials are separated from the products of conversion in a compartment with a spent solid sorbent predominantly containing coke compounds, substances such as carbene-carboids, metals (Ni and V), sulfur, and representing heavy feedstock from vacuum residue hydrocracking. The batch addition of hydrogen at each stage of the process leads to its point consumption in the ongoing reactions of the transformation of high-molecular compounds of heavy hydrocarbon feedstock. It helps to manipulate the reaction mechanism and leads to significant savings. As a result of the hydrocracking of heavy hydrocarbon feedstock, fuel gas is formed, consisting mainly of methane and, to a lesser extent, ethane, propane, and butane fractions, components of gasoline and diesel fuel, and vacuum gas oil. The conversion of

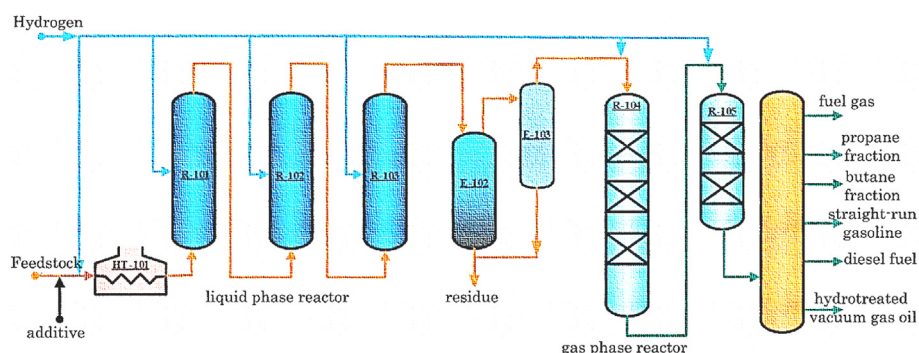


Fig. 1. Scheme of the plant for hydrocracking of heavy hydrocarbon feedstock.

heavy hydrocarbon feedstock during hydrocracking is 90%, asphaltenes is ~80%, and the yield of target fractions is more than 80%.³⁶ However, in slurry hydrocracking processes, the catalyst can only be used once due to its deactivation. Therefore, this requires a low cost of the catalyst used.

Solid sorbents in liquid-phase hydrocracking reactors ensure uniform passage of the reaction mass over the reactor volume and uniform distribution of hydrogen and adsorption of asphaltenes, sulfur, and metals. Currently, carbon carriers are used as sorbents. They are characterized by high porosity and large specific surfaces and distinguished by different dispersity and textural characteristics. The efficiency of carbon sorbents in the hydrocracking process can be achieved by changing their textural characteristics. In Purón et al.³⁷ the catalytic activity of Ni–Mo catalysts with supports made of mesoporous aluminum oxide and clayey silica with different textural properties was investigated. The presence of mesopores in the support (mineral matrix) is necessary for increasing the catalyst's efficiency when cracking large molecules present in heavy residual fractions. The textural properties of the catalysts greatly influenced the products' conversion and composition: a large number of large-diameter pores led to higher conversion of resins and asphaltenes, which provided better diffusion of asphaltene molecules. For the hydrocracking of residues in the suspension phase, multimetallic catalysts were proposed.³⁸ Research showed that using mineral additives modified with Mo and Ni metals made it possible to reduce the residue hydrocracking temperature and increase the conversion degree due to the synergistic effect between Mo–Ni sulfides and mineral components. Other researchers²³ pointed out the need for macropores and mesopores in catalysts for hydrocracking reactions. Residual feedstocks with high asphaltene content required supports with large pores that allowed large molecules to penetrate the pores to the active sites. The catalyst support with small pores promoted the external deposition of metal and carbon, which led to pore clogging.³⁹ The use of carbon sorbents as carriers for hydrocracking catalysts, in contrast to γ -alumina, mixed oxides, silicas, and mineral aluminosilicates, lead not only to high conversion of resin–asphaltene components but also to a high degree of desulfurization, denitrification, and demetallization to low coke formation.^{40,41} The paper⁴² investigated active carbons prepared by steam activation of coal in vacuum residue hydrocracking. Activated carbon with mesopores showed greater selectivity regarding the adsorption of asphaltenes and suppressed coke

formation even at high hydrocracking temperatures. The researchers found that activated carbon prevented the conversion of asphaltenes to coke.

Since the heavy hydrocarbon feedstock has a large number of large molecules of polyaromatic hydrocarbons, resins, and asphaltenes^{43,44} for their adsorption on the surface of the carbon sorbent, the latter must have a significant volume of pores with a large diameter and a certain surface composition, which is achieved via activation. The use of highly efficient carbon sorbents in the process of vacuum residue hydrocracking would reduce their consumption, significantly reduce the heavy residue volume, and the amount of metals and sulfur in the final products, as well.

The present work is devoted to studying the influence of the activation conditions of carbon sorbents used in the process of vacuum residue hydrocracking on their textural properties.

2. Materials and methods

The following products were chosen as the objects of study:

- (1) Carbon carrier 1 with an average particle size of ~496.46 μm .
- (2) Carbon carrier 2 with a particle size of ~345.82 μm , obtained by carbonization of carbon carrier 1 with water vapor at 800 °C.
- (3) Carbon carrier 3 obtained by grinding particles of carbon carrier 2 in a ball mill to ~168.1 μm .
- (4) Carbon carrier 4 with a particle size of ~288.91 μm , obtained by heat treatment of carbon carrier 2 in a stream of nitrogen at 400 °C.
- (5) Carbon carrier 5 with a particle size of ~274.36 μm , obtained by heat treatment of carbon carrier 2 in a stream of nitrogen at 500 °C.

The purpose of the activation of carbon sorbents is to improve their textural properties to the level of analogs. At present, similar carbon sorbents produced are widely used for cracking processes of heavy oil feedstock:

- (1) Coarse carbon carrier 6 with a particle size of ~910.17 μm .
- (2) Medium-dispersed carbon carrier 7 with a particle size of ~264.19 μm .
- (3) Finely dispersed carbon carrier 8 with a particle size of ~83.27 μm .

The particle sizes of carbon carriers were determined using the laser light scattering method on a Horiba Laser Scattering Particle Size Distribution Analyzer LA-950 (Kyoto, Japan). The elemental

composition of carbon carriers was studied by radiograph fluorescence analysis on a Rigaku ZSX Primus II radiograph fluorescence spectrometer (Tokyo, Japan). The phase composition was studied using radiograph diffraction analysis on a multifunctional diffractometer Rigaku SmartLab (Tokyo, Japan), shooting parameters: angular interval 2θ : from 3° to 65° with a scanning step of 0.02 and exposure of 1 s at a point. Thermal analysis was carried out on a thermal analyzer STA 6000 (PerkinElmer, Waltham, Massachusetts USA). To establish the characteristics of the composition of the sorbents, an analysis of the infrared spectra was carried out. Infrared spectra were recorded on a Frontier (“PerkinElmer”, Waltham, Massachusetts USA) Fourier-transform infrared spectroscopy spectrometer in the range of $450\text{--}4000\text{ cm}^{-1}$. The baseline was corrected using the software. The specific surface area of carbon carriers was determined by the BET method from low-temperature nitrogen adsorption and desorption isotherms on a Nova 1200e (“Quantachrome Instruments”, Boyton Beach, Florida, USA) surface area and pore size analyzer. Also, based on the data of low-temperature adsorption and desorption of nitrogen of carbon carriers, the volume of mesopores (from 2 to 50 nm) and their size distribution were determined using the BJH method, and the volume and area of micropores (up to 2 nm) were found using the de Boer t-plot method. The external specific surface area of carbon carrier particles was determined according to basic standards ASTM 6556 ‘Standard Test Method for Carbon Black – Total and External Surface Area by Nitrogen Adsorption.’ For a comparative analysis of the pore sizes of carbon carriers with the sizes of asphaltene associates in heavy vacuum residue, being feedstock of a VCC unit, the sizes of asphaltene associates were preliminarily determined. Using a laser particle size analyzer, the sizes of asphaltene associates in a toluene solution were determined, previously isolated from residue according to the standard method described in Petrov et al.⁴⁵ The size of 90% of asphaltene associates in the residue was in the range from 50 to 100 nm, and 10% was less than 50 nm. The surface morphology of carbon carriers was studied using an EVO LS10 scanning electron microscope (“Carl Zeiss NTS”, Jena, Germany).

3. Results and discussion

The results of radiograph diffraction analysis of carbon carriers are presented in Fig. 2. From Fig. 2, it can be seen that all the studied carbon sorbents have a well-defined radiograph amorphous phase (indicated by a red line on the diffraction patterns)

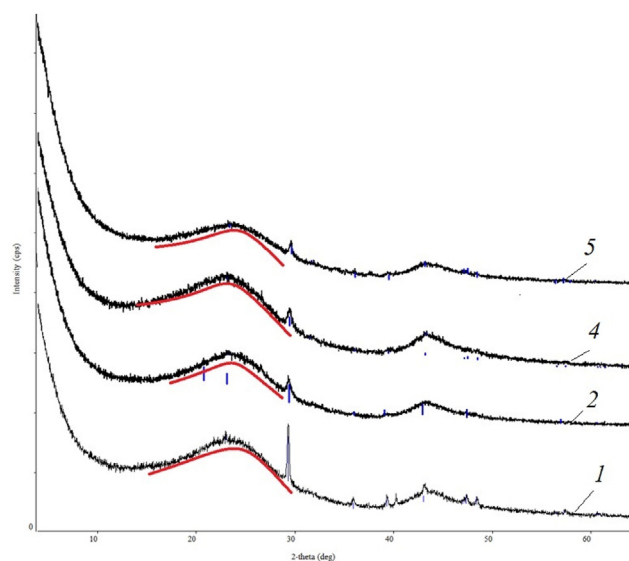


Fig. 2. Diffraction pattern of carbon carriers 1–5.

and a crystallized calcite phase (indicated by a blue line on the diffraction patterns).

The sorbent samples revealed the presence of calcite in all samples due to its high stability. In the activation of carbon carrier 2 in a stream of nitrogen at 500°C (carbon carrier 5), a decrease in the proportion of the amorphous phase is observed. As a result of the activation of the carbon carrier with water vapor, the calcite content decreases.

The results of radiograph fluorescence analysis of carbon carriers are presented in Table 1. It can be seen that carbon sorbents present almost pure carbon. The dominant metals in sorbents are calcium, iron, silicon, and magnesium. Carbon sorbents are characterized by low sulfur content (up to 0.7%).

Carbon sorbents, obtained from activation with water vapor and nitrogen stream, are characterized by increased carbon content. After heat treatment of sorbents in a stream of nitrogen, the hydrogen content in their composition is significantly reduced; to a lesser extent, there was a decrease in silicon and aluminum content.

The results of the infrared spectral analysis of carbon sorbents are shown in Fig. 3.

The infrared spectra of carbon sorbents differ, especially the spectra of sorbents after heat

Table 1. Elemental composition of carbon sorbents.

Carbon carrier	Elemental composition, % wt								
	C	H	Ca	S	Mg	Fe	Si	Al	K
1	90.44	8.66	0.20	0.25	0.15	0.13	0.05	0.02	0.1
2	93.16	5.93	0.11	0.32	0.14	0.20	0.02	0.02	0.1
4	94.09	5.05	0.14	0.42	0.05	0.12	0.02	0.01	0.1
5	95.76	2.92	0.37	0.48	0.04	0.29	0.03	0.01	0.1

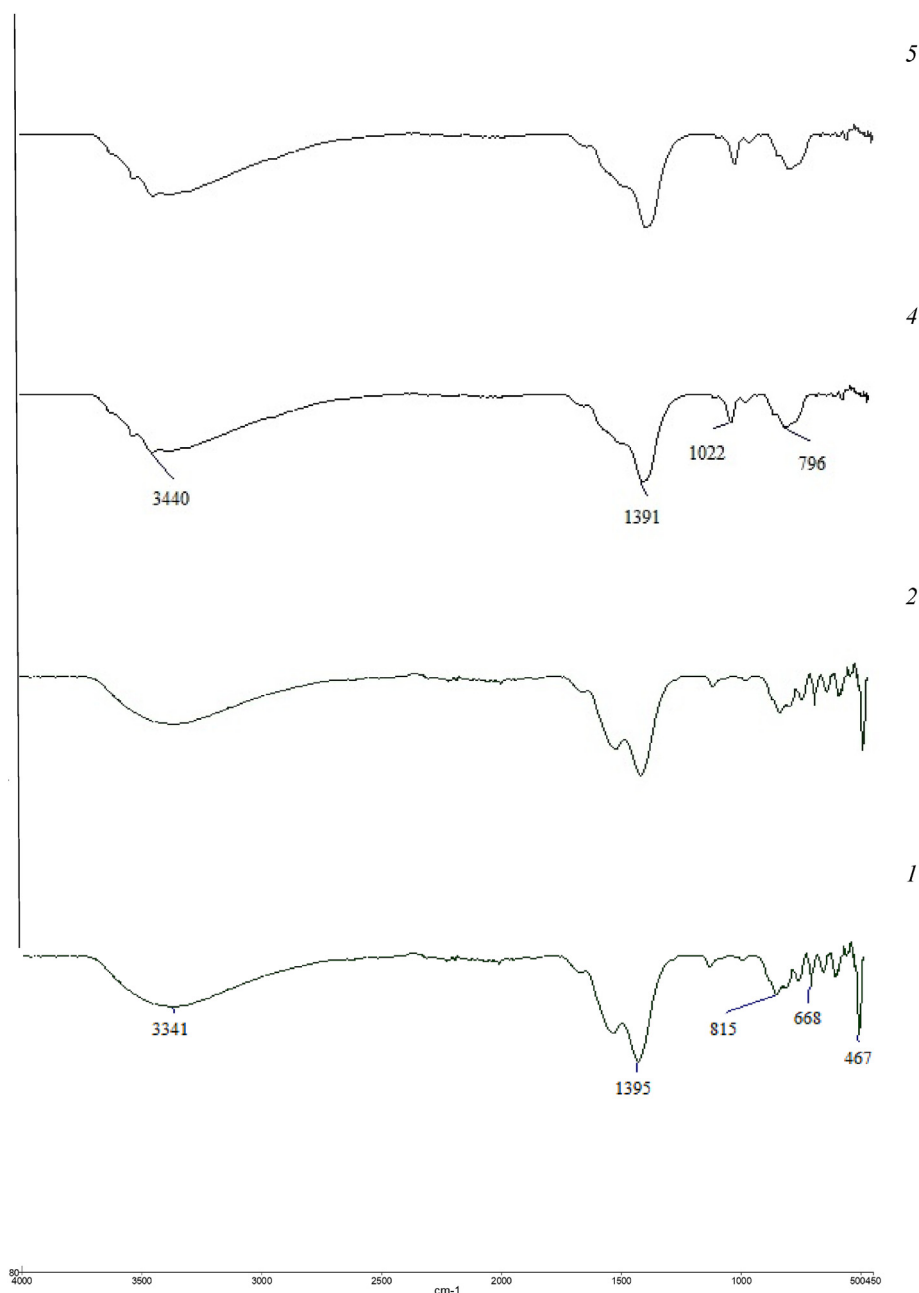


Fig. 3. Fourier-transform infrared spectroscopy spectra of carbon carriers.

treatment in a nitrogen stream, with obvious external similarity. The spectra in the region from 720 to 900 cm^{-1} contain sorption bands of vibrations of C–H bonds in naphthenic, aliphatic, and aromatic structures. Intense peaks of bending vibrations are observed in various aliphatic structures at 1380 and 1450 cm^{-1} (CH_3 and CH_2 groups). Out-of-plane deformation vibrations of the $\text{C}_{\text{arom}}\text{-H}$ bonds of aromatic rings are characterized by a triplet in the region of 740–890 cm^{-1} , which is manifested in the initial carbon sorbent (1) and the

carbon sorbent after activation with steam (2). A sorption band at 815 cm^{-1} in the spectra indicates bending vibrations of para-disubstituted aromatic rings. For carbon sorbents (4 and 5), the triplet in this region becomes less pronounced due to activation in a nitrogen stream, which indicates ongoing carbonization processes. However, one should remember the partial overlap of the bands of the $\text{C}_{\text{ar}}\text{-H}$ group due to vibrations of the structural elements of mineral impurities present in carbon sorbents.

Thus, the sorption bands present in all spectra are the characteristic bands for calcite (712 , 870 , and 1435 cm^{-1}) and the sorption band at 1022 cm^{-1} , characteristic for stretching vibrations of the Si–O bond (960 – 1030 cm^{-1}). The absorption band at 1610 cm^{-1} is formed by vibrations of C–C bonds in aromatic structures. The broad sorption band region of 3100 – 3500 cm^{-1} includes stretching vibrations of the OH hydrogen bond (3440 cm^{-1}) with a peak at 3340 cm^{-1} , characteristic of stretching vibrations of N–H bonds. The absorption peak at 1500 cm^{-1} indicates the presence of stretching of the C–C bonds of the aromatic ring. A low-intensity sorption band in the 1030 cm^{-1} region may indicate the presence of

sulfoxide groups (S=O) and siliceous minerals in the carbon sorbent samples. A low-intensity peak in the spectra of carbon sorbents in the region of 1730 cm^{-1} indicates stretching vibrations of the carbonyl group C=O.

Data from thermogravimetric analysis (TGA) of carbon sorbent 1 in air indicate the presence of predominantly five temperature regions (Fig. 4). TGA curves obtained in air and nitrogen show the same trend, which is connected by the same chemical bonds that form the molecular structure of the carbon sorbent.

The first endothermic effects occur at 30 – $170\text{ }^{\circ}\text{C}$ (Table 2), associated with the evaporation of

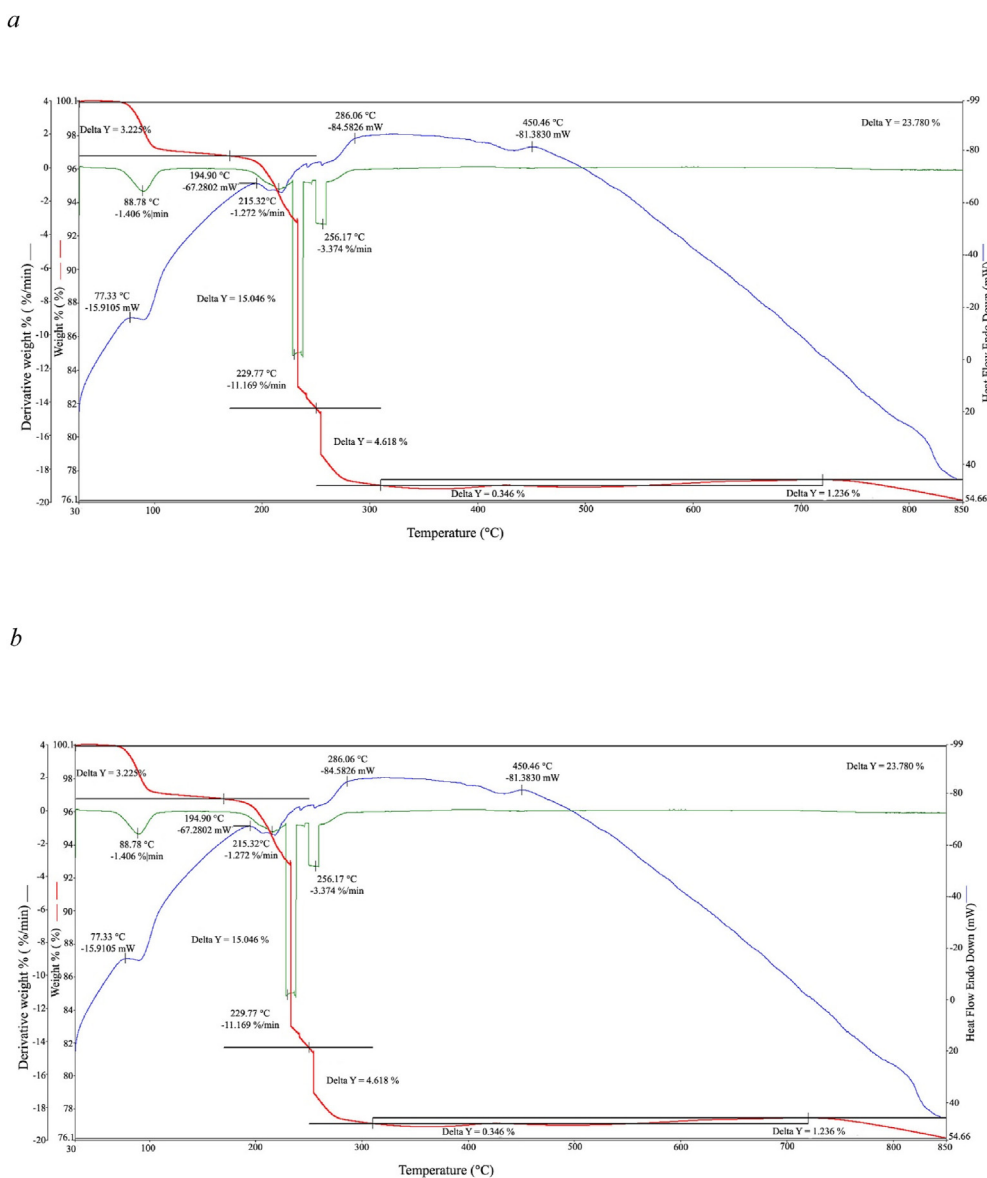


Fig. 4. Differential and gravimetric thermal analysis (DTA/TGA) of the carbon carrier 1 (a) in air and (b) in nitrogen. TGA, thermogravimetric analysis.

Table 2. Weight loss of carbon carrier 1 during thermogravimetric analysis.

Gas environment	Temperature range (maximum effect), °C weight loss, % wt.							Total weight loss in 30–850°C range, %wt
Air	30–170 –3.22	170–250 –15.05	250–310 –4.62	310–720 +0.35	720–850 –1.24			23.78
Nitrogen	30–170 –3.86	170–230 –3.37	230–310 –5.44	310–520 –0.75	520–850 –0.06			13.42

hygroscopic moisture from the sorbent and the loss of volatile components. At temperatures above 170 °C in air, a large loss of mass occurs (15.05% wt.) with a maximum at 229 °C, which is due to the thermal decomposition of fragments of its molecular structure with the detachment of low-molecular compounds from the carbon matrix, passing into the gas phase. This is accompanied by a decrease in the mass of the sample, which sharply increases at temperatures above 220 °C. In this temperature range in a nitrogen environment on the TGA curve, the weight loss is insignificant (3.37% wt.) and is associated with the destruction of C–H bonds, accompanied by an endothermic effect. Thermal decomposition curves of samples of the studied coals obtained in an atmosphere of nitrogen (inert

gas) change significantly, which is associated with the absence of oxygen participating in the oxidation reactions of the carbon sorbent. Thus, during the thermal analysis of a carbon sorbent in a nitrogen stream, the total weight loss was 13.42%; in the air, it amounted to 23.78%.

Weight loss in the range of 250–310 °C corresponds to the destruction and combustion of aliphatic and alicyclic fragments of the carbon sorbent. With further heating to 720 °C, the destruction of aromatic structures, decomposition, and oxidation of the organic mass of coal occurs with an exothermic effect. In the temperature range of 720–850 °C, decomposition and oxidation of inorganic compounds of the mineral part of the carbon sorbent occurs. At temperatures above 310 °C in the

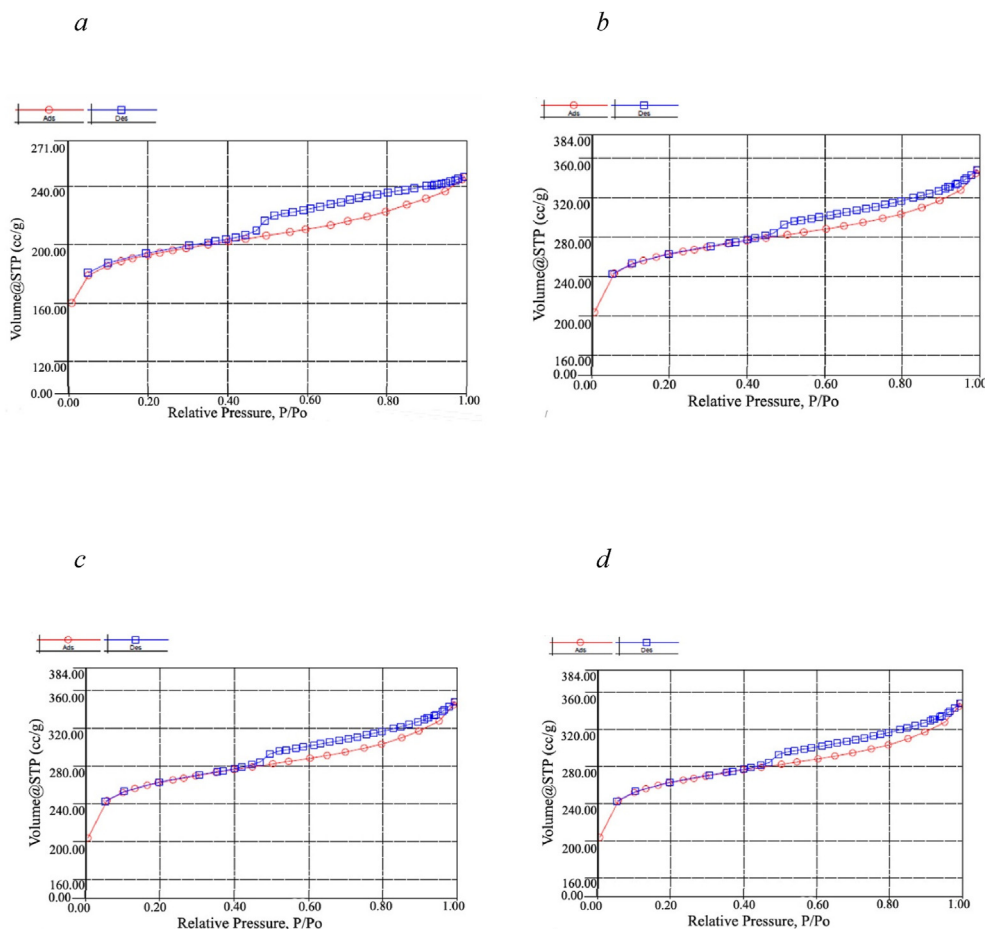


Fig. 5. Nitrogen sorption isotherms of carbon carriers: (a) 2; (b) 3; (c) 4; (d) 5.

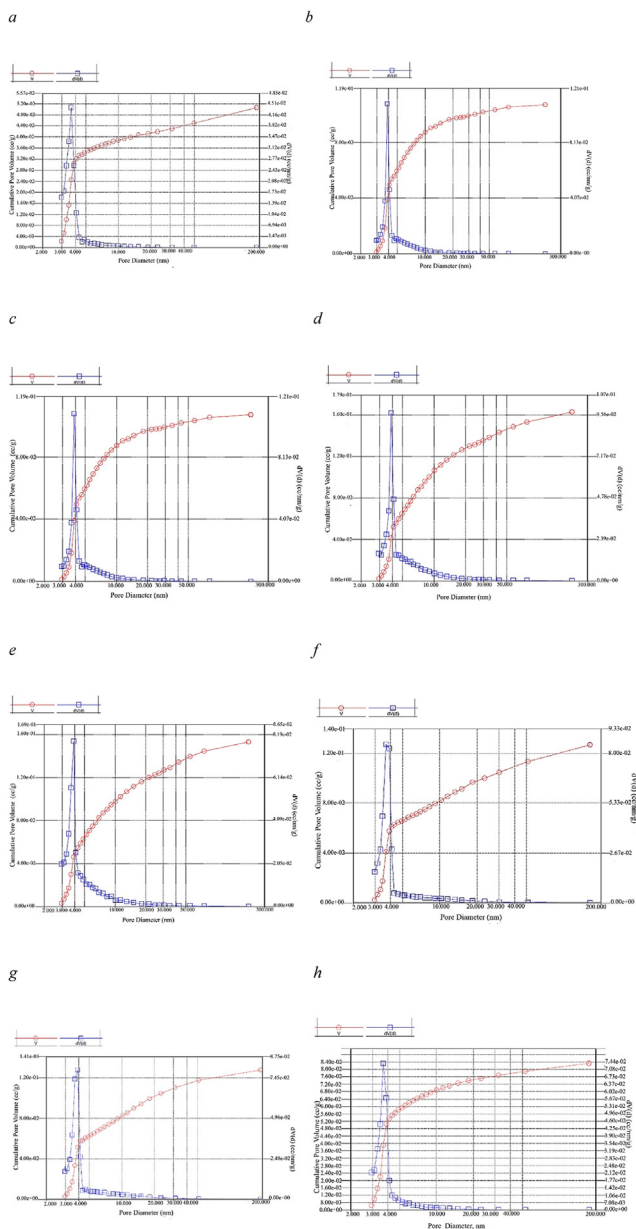


Fig. 6. Integral (red line) and differential (blue line) curves of pore volume distribution by size of carbon carriers: (a) 1; (b) 2; (c) 3; (d) 4; (e) 5; (f) 6; (g) 7; (h) 8.

air, a slight increase in mass is observed, associated with introducing oxygen from the air into the molecular structure of the carbon sorbent.⁴⁶ At temperatures above 450 °C, the intensity of exothermic effects begins to decrease.

The porous structure of sorbent samples has been studied. Significant differences have been established in the characteristics of the porous structure of carbon sorbents obtained by low-temperature nitrogen adsorption/desorption methods (Fig. 5). The isotherms have a similar appearance and are predominantly of the ‘Langmuir type,’ which is typical for microporous adsorbents. Thus, in the initial section of the isotherms, there is a sharp increase in adsorption in the region of low relative pressures, which indicates adsorption in micropores. In addition, the isotherms have a ‘hysteresis loop,’ indicating the presence of irreversible capillary condensation in the mesopores. The presence of macropores in carbon sorbents is indicated by the S-shaped curve due to the occurrence of poly-molecular adsorption (first, a filled monolayer is formed on the surface, and then subsequent layers are formed, which leads to the appearance of an S-shaped adsorption isotherm), which is characteristic of dispersed macroporous samples.

Thus, analysis of nitrogen sorption isotherms on carbon sorbents showed that they contain pores of various sizes. The convex nature of the isotherms indicates the presence of small pores (micropores) in the sorbents. The shape of the isotherm hysteresis loop indicates a nonuniform distribution of mesopore sizes throughout the volume and their shapes. The mesopore volume distribution by size of carbon sorbents is presented in Fig. 6. As can be seen, the analyzed sorbents have a narrow pore volume distribution by size with a predominant diameter of 3.4–4.0 nm. The parameters of the porous structure of the initial (1) and activated carbon sorbents, determined based on nitrogen sorption isotherms, are presented in Tables 3 and 4.

Table 3. Textural characteristics of carbon sorbents.

Carbon carrier	Average particle size, μm	Specific surface area according to BET, m^2/g	External specific surface, m^2/g
1	496.46	398.2	136.1
2	345.82	712.3	96.7
3	168.1	968.8	142.3
4	288.91	714.9	140.1
5	274.36	768.6	172.1
6	910.17	282.4	165.9
7	264.19	267.9	148.3
8	83.27	428.1	167.5

Table 4. Data on the adsorption characteristics of carbon carriers.

Carbon carrier	Mesopore volume based on BJH, cm ³ /g	Micropore volume by de Boer t-plot method, cm ³ /g	Micropore area de Boer t-plot method, m ² /g
1	0.050	0.11	263.7
2	0.11	0.25	618.5
3	0.16	0.33	829.5
4	0.16	0.24	577.8
5	0.15	0.25	600.3
6	0.127	0.050	116.5
7	0.123	0.052	119.6
8	0.07	0.11	262.8

Carbon carrier 3, after grinding to particle sizes from 10 to 500 μm with an average particle size of 168.1 μm, has a larger total and external specific surface area of 968.8 and 142.3 m²/g, respectively. The carbon sorbent before grinding (sample 2) was presented in the form of particles having sizes from 10 to 1000 μm, having a high specific surface area according to BET – 712.3 m²/g and a small external surface area –96.7 m²/g (Table 3). The high values of the BET-specific surface area of carbon carriers against the background of low values of the outer surface area indicate the presence of many mesopores and micropores in them.

The studied carbon carriers show a high linear dependence of the specific surface area values according to BET and the volume (area) of micropores according to the de Boer t-plot method (Fig. 7).

The linear dependence of the values of the specific surface area of carbon carriers on the volume of micropores indicates a high proportion of the surface of micropores in the specific surface area value according to BET. It should be noted that the sizes of

micropores are inferior to those of asphaltene associates, and their surface becomes inaccessible for asphaltene adsorption. Thus, to choose an effective carbon carrier for further cracking of asphaltene associates in residue, the BET-specific surface area is of little use and is not fully sufficient.

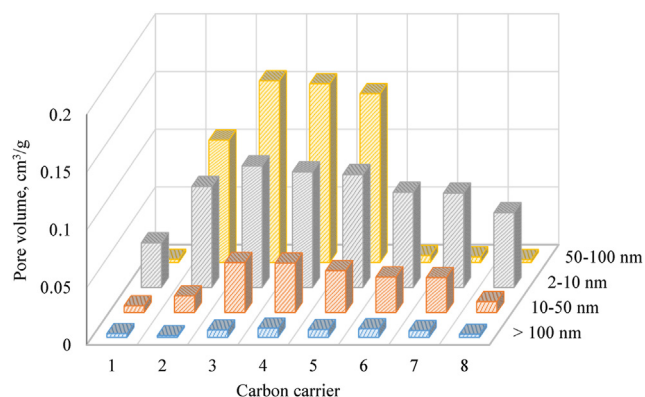


Fig. 8. Distribution of pore diameters (nm) by volume cm³/g in carbon carriers 1–8.

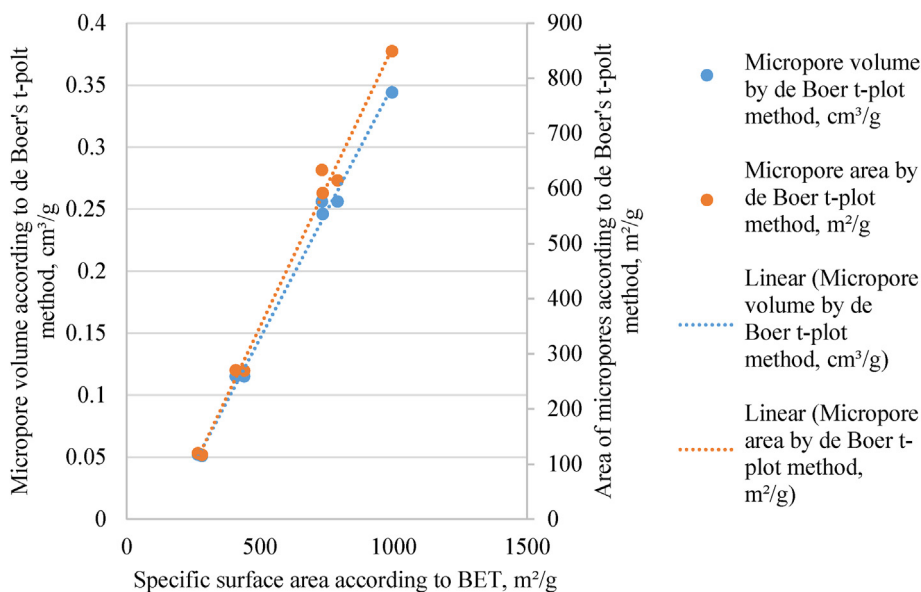
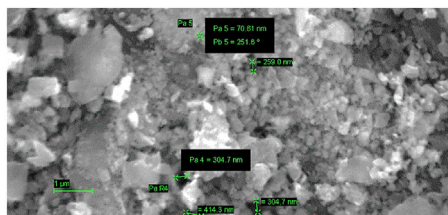


Fig. 7. Correlation dependence of the specific surface area of carbon carriers 1–8 on the volume and area of micropores.

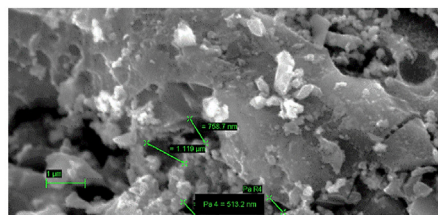
Calcinating the sorbents in a nitrogen atmosphere at 500 °C increases the external and total surface area of the carbon sorbent to 768.6 and 172.1 m²/g (sample 5). Carbon carriers 6 and 7 have the

smallest values of the specific surface area –282.4 and 267.9 m²/g, respectively (Table 3).

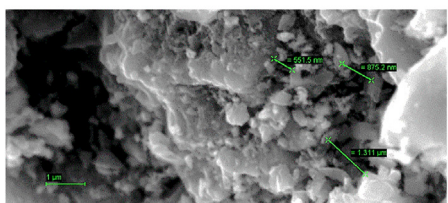
The largest volume of mesopores, comparable in size to those of asphaltene associates, is



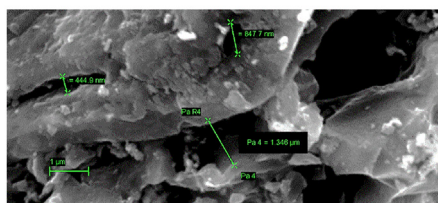
Carbon sorbent 1



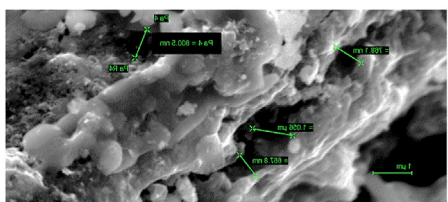
Carbon sorbent 2



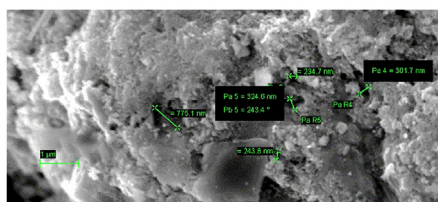
Carbon sorbent 4



Carbon sorbent 5



Carbon sorbent 6



Carbon sorbent 7



Carbon sorbent 8

Fig. 9. Surface morphology of carbon carriers.

characteristic for carbon sorbents 4 and 5, past the stage of calcination at a temperature of 400 and 500°C –0.16 and 0.15 cm³/g, respectively – third carbon sorbent –0.16 cm³/g. The minimum mesopore volumes of 0.07 and 0.050 cm³/g are characteristic of samples 1 and 8 (Table 4).

All presented carbon sorbents are distinguished by a high content of pores with a diameter of up to 2 nm. The maximum content of pores with a diameter of less than 2 nm is characterized by the third carbon sorbent sample – 0.33 cm³/g. The volume of micropores of carbon carriers 2, 4, and 5 lies in a narrow range of 0.24–0.25 cm³/g. According to the de Boer t-plot method, carbon carriers 6 and 7 have the smallest volume of micropores –0.050 and 0.052 m²/g, respectively. As known, catalysts for processing light fuel fractions are characterized by a pore diameter of up to 2 nm. Catalysts with a sufficient amount of mesopores are required to process distillate vacuum fractions with larger molecules. Catalysts with both mesopores and macropores are suitable for processing HORs. The presence of micropores in carbon sorbent samples leads to the adsorption of molecules smaller than resins and asphaltenes in their pore space, the cracking of which under VCC of residue presents a desirable process. It is interesting to observe an increase in the total surface area of carbon sorbent samples with an increase in the volume of micropores. According to the de Boer t-plot method, carbon carriers 6 and 7 have the smallest area of micropores –116.5 and 119.6 m²/g, respectively. Carbon carrier 3 has particle sizes from 10 to 500 μm, and is characterized by the largest area of micropores according to the de Boer t-plot method –829.5 m²/g (Table 4). The number of pores of different diameters in carbon sorbent samples is shown in Fig. 8.

The content of mesopores and macropores in samples of carbon sorbents from the minimum amount to the maximum amount is arranged in the following sequence: 1<8<7<6<2<5<4<3. Among them, the third carbon sorbent sample is characterized by a maximum pore volume of 0.157 cm³/g, suitable for adsorption asphaltene associates from vacuum residue. After heat treatment of carbon sorbent samples 4 and 5, the content of mesopores with a diameter of 50–100 nm increases from 0.11 to 0.15 cm³/g at 500°C and up to 0.15 cm³/g at 400°C, respectively. The lowest number of mesopores is characterized by carbon carriers 8 and 1 –0.0023 and 0.0026 cm³/g. Since in the first and eighth samples of the carbon sorbent, the main number of pores belongs to micropores comparable or smaller in size with asphaltene associates; their hydrocracking occurs mainly on the outer surface (Table 3).

Images of pores obtained using electron scanning microscopy are presented in Fig. 9. As can be seen from the morphology of the surface of the carbon sorbent, as a result of activation, the size of macropores increases, which present microcavities and depressions of a predominantly round shape with a diameter from 513 nm to 1.3 μm. A pronounced topography characterizes the outer surface of the sorbents.

In addition, the composition of carbon sorbents, obtained by activation in a nitrogen stream, contains macropores larger than 1 μm; these formations are similar in shape and structure to the capillary structure. Increasing the activation temperature from 400 to 500°C in a nitrogen stream does not lead to a significant change in the morphology of the carbon sorbent but promotes the formation of more macropores in the form of slits, cavities, and channels.

4. Conclusions

The possibility of increasing mesopores and macropores in a carbon carrier by sequential thermal activation with water vapor and a nitrogen environment has been demonstrated for the first time. Using radiograph diffraction analysis, it was established that in the sorbents, the carbon matrix is formed by an amorphous phase and is of a significant amount with a small share of the crystalline phase of calcite. Radiograph fluorescence analysis showed that the main nonhydrocarbon elements in the sorbents are calcium, iron, magnesium, and sulfur, with an admixture of potassium. According to infrared-Fourier spectroscopy data, the carbon matrix of sorbents, composed of systems of aromatic rings, contained sulfo, hydroxo, and amino groups, and a carboxyl functional group corresponding to aromatic acids. Carbon sorbents have a large cation exchange capacity, which determines their high adsorption properties relative to heteroatomic and metal-containing compounds of heavy vacuum residues. It has been established that during thermal activation of carbon sorbents, there are no significant changes in the phase and chemical composition, but there is a significant increase in its specific surface area and pore space.

As a result of studying the textural characteristics of carbon carriers for thermal cracking of residues, differences in specific surface area, pore sizes, and pore space volumes depending on manufacturers and activation methods are shown. The main pore volume in carbon carriers 1 and 8 occupy micropores with a diameter of 2–10 nm, the size of which is insufficient for diffusion and adsorption of asphaltene associates in them. Thus, the cracking of

asphaltene molecules, and resins occurs not on the developed surface inside the porous carbon carriers but on the outer surface of the particles, which is 136.1 and 167.5 m²/g, respectively. An increase in the degree of conversion of asphaltenes during hydrocracking of residue can be achieved by increasing the volume of mesopores and macropores in carbon carriers comparable in size with adsorbed molecules of resins and asphaltene associates. The carbonization of a carbon carrier at 800 °C in the presence of water vapor leads to an increase in its specific surface area from 398.2 m²/g (1) to 712.3 m²/g (2), as well as an increase in the volumes of micropores, mesopores, and macropores by almost two times. Grinding in a ball mill of a carbon carrier after carbonization leads to the greatest increase in the specific surface area up to 968.8 m²/g (3) and the volume of micropores, the surface area of which reaches 829.5 m²/g. Heat treatment of the carbon carrier at 400 °C in a stream of nitrogen that has passed the carbonization stage (4) leads to an increase in the volumes of mesopores and macropores. An increase in the heat treatment temperature of the carbon carrier from 400 to 500 °C (5) leads to a rise in the area of micropores in it from 577.8 to 600.3 m²/g. Thus, the maximum adsorption and the degree of conversion of asphaltene associates in the residue will most effectively take place on the developed surface of carbon carriers 3 and 4, with the largest number of mesopores and macropores, as well as high values of the specific surface area of 968.8 and 734.8 m²/g, respectively.

Based on scanning electron microscopy, distinctive features were established in the macrostructure of carbon sorbents; after activation, the mouths of micropores are located on the outer surface having microheterogeneity, in which cavities in the form of channels with a diameter of up to 1 μm or more are visible. Developing mesopores and macropores in carbon sorbents is valuable since the degree of processing of vacuum residues in suspension-phase hydrocracking reactors depends on their quantity and forms. The method of thermal analysis has shown that the optimal carbonization temperature is 800°C, and at temperatures from 400 to 500°C in a nitrogen stream, a carbon sorbent with a highly developed pore surface can be obtained.

The results obtained from studying carbon carriers at different stages of activation indicate that it is possible to control the technological processes of activation of carbon carriers, considering their chemical composition and structure. The results obtained can be used to develop catalytic systems for hydrocracking processes of vacuum residues from oil distillation units. We believe that the study

results will serve as an incentive to search for ways to activate and modify carbon sorbents to expand their use in processes of advanced processing of heavy hydrocarbon raw materials.

Ethics information

The manuscript doesn't involve any human or animal subjects and meets all the Research Ethics.

Funding

Financial support of the Ministry of Science and Higher Education of the Russian Federation under agreement no. 075-15-2021-699.

Author contribution

Elizaveta G. Zaitseva: Formal analysis, Investigation; Aliya G. Safiulina: Writing - Original draft; Sergey M. Petrov: Conceptualization, Data Curation, Project administration.

Conflicts of interest

The author(s) of this study disclosed no potential conflicts of interest with regard to the research, authorship, and/or publication of this work.

Acknowledgements

This study was carried out using the equipment of the Center for Collective Use 'Nanomaterials and Nanotechnology' of the Kazan National Research Technological University with the financial support of the Ministry of Science and Higher Education of the Russian Federation under agreement no. 075-15-2021-699.

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