Chemistry for Sustainable Development **27** (2019) 643–649

UDC 665.7.033.28

DOI: 10.15372/CSD2019185

Study of the Molecular Structure of Asphaltenes from Coal-Tar Pitch

S. A. SOZINOV, S. YU. LYRSCHIKOV, V. YU. MALYSHEVA, L. M. HITSOVA, L. V. SOTNIKOVA, O. S. EFIMOVA, A. N. POPOVA, Z. R. ISMAGILOV

Federal Research Center of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia

E-mail: sozinov71@mail.ru

Abstract

A comprehensive study of the functional and group compositions of hexane-insoluble coal-tar pitch asphaltenes was carried out by means of nuclear magnetic resonance (NMR), infrared spectroscopy (IRS), thermal analysis and gas chromatography – mass spectrometry. It was shown that the hydrocarbon skeleton of an average hypothetical asphaltene macromolecule can be considered as a set of condensed aromatic nuclei of re-condensed type containing 7 rings, which have alkyl substituents and connecting bridges, consisting of 2 carbon atoms on average. Moreover, the structure contains one S atom on average per 500 C atoms, N or O – per 50 or 167 carbon atoms, respectively, and one hydrogen atom per 2 carbon atoms. The ratio of various structural units in the powder of asphaltenes is as follows: there are 4–5 N- and 1.3–1.7 O-containing structures per one S-containing structure. Sulphur atoms are present in thiophene-like, thermally stable fragments of the structure and pass into the coke residue. Oxygen is present in thermally unstable carboxyl and phenolic groups decomposing with the evolution of CO_2 when heated above 300 °C, as well as in aromatic esters passing into the coke residue. Results of the investigation of structural groups composition obtained using different methods are in good agreement with each other and will allow modeling of the structural unit of coal tar pitch asphaltene macromolecule.

Keywords: coal-tar pitch, asphaltene, composition, molecular structure

INTRODUCTION

Investigation of the processes taking place during the preparation of graphitized carbon materials from the heavy products of natural hydrocarbon processing showed that asphaltene fraction may become a promising and economically profitable source for obtaining practically important products [1]. Asphaltenes include high-molecular components of hydrocarbon raw materials distinguished as the substances soluble in toluene and insoluble in alkanes. Asphaltenes possess layered block supramolecular arrangement of macromolecules having crystal-like proturbostratic structure; they do not have strictly definite composition and are characterized by a set of structural and functional groups included into macromolecules with a broad distribution of molecular masses [2–5]. Many different models of the structure of a hypothetical asphaltene molecule providing a satisfactory description of the main properties of the substance have been published in the literature [6, 7]. It should be stressed that, as a rule, investigations of asphaltenes are aimed at the search for the routes to prevent their aggregation, which hinders oil mining and transportation [9]. However, investigation of the process of self-arrangement of asphaltene macromolecules may help in solving some problems in nanotechnologies, in particular in search for the new ways to obtain ordered layers of the precursors of graphitized carbon materials [8, 10–15].

Though it does not seem possible to determine the composition and structure of separate asphaltene macromolecules, the information on the functional group composition is important for understanding the regularities of macromolecule self-organization during the formation of ordered forms. In addition, the functional group composition of asphaltenes differs depending on their origin. In this connection, at the first stage of the search for routes to new functional materials based on the heavy products of coal chemistry (pitch, bitumen, coal tar pitch), it is necessary to study the functional group composition and structure of all components including asphaltenes. The complexity of the formulated problem is in the insufficiency of the data obtained by separate research methods to characterize the composition and structure of asphaltene macromolecules [16] because almost all the data on asphaltene structure obtained using traditional methods have limitations due to various reasons. The data of IR spectroscopy do not allow the determination of the quantitative relations between functional groups. The limitation of the method is connected with the effect of the dispersed state of particles on scattering and absorption of the working radiation [16]. The presence of associates in solutions brings complications to their studies by means of NMR [16]. The isolation of asphaltenes from multicomponent products makes it difficult, after flocculation of the precipitate containing mainly asphaltene fraction, to separate their molecules from the accompanying petrolene molecules providing the colloidal stability of asphaltenes in solution, and from the molecules of the solvent. Depending on petrolene and solvent content, the data of elemental, thermal and other methods of analysis may be interpreted in different manners.

In this connection, an integrated approach is applied in the present work to characterize the functional group composition and the structure of asphaltenes from coal tar pitch. This approach combines the use of different physicochemical methods: chemical elemental analysis, nuclear magnetic resonance (NMR) and NMR spectroscopy, differential thermal analysis in combination with gas chromatography – mass spectrometry (GC-MS). Results obtained using this set of methods allow us both to define the structure of asphaltene macromolecules from coal tar pitch more accurately and to test the reliability of the result using separate methods.

EXPERIMENTAL

Asphaltenes were isolated from the toluene extract of medium-temperature coal tar pitch (CTP) (softening temperature was about 87 °C) by dilution with n-hexane. For this purpose, an extract of 4 g of CTP and 50 ml of toluene was obtained. The toluene extract of CTP contains β- and γ-fractions of pitch – asphaltenes and petrolenes, respectively. Asphaltenes were precipitated by adding 200 ml of n-hexane. To intensify mixing, ultrasound was applied during precipitation. After flocculation, the precipitate was kept in solution for 24 h, then it was separated by filtering and washed from petrolenes, and dried at a temperature of 80 °C. Thus prepared samples differed from each other by precipitation conditions: without ultrasound (A1 and A2 samples) and with ultrasonic treatment (samples A3 and A4). In addition, the samples differed from each other in the intensity of asphaltene washing from co-precipitating petrolenes. For samples A2 and A4, the number of stages of washing from petrolenes was increased by a factor of 2.

The content of C, H, N, S, O in asphaltenes was determined with the element analyzer Flash 2000 (Thermo Fisher Scientific, Great Britain).

The data on the distribution of hydrogen and carbon atoms over different hydrocarbon structures in the asphaltenes of CTP were obtained from ^{1}H and ^{13}C NMR spectra. The NMR spectra of asphaltenes were recorded with an Avance III 300 WB spectrometer (Bruker, Germany). Calculations of the quantitative characteristics of NMR spectra were carried out according to procedures described in [17, 18].

The composition of the functional groups of asphaltene macromolecules was studied by means of IR Fourier spectroscopy with the help of an Infralyum FT-801 spectrometer (Russia). IR spectra were recorded within the range 550–5500 cm^{-1}.

Reactions of the thermal transformations of asphaltenes were studied using the STA 449 F3 Jupiter synchrotron thermal analyzer (Netzsch, Germany). The analysis was carried out in the inert atmosphere under the conditions of dynamic heating at a rate of 10 °C/min within temperature range 25–650 °C, the weighted portion was 5 mg.

The composition of volatile products of thermolysis was determined by means of GC-MS us-

TABLE 1

Composition of asphaltenes according to the data of elemental analysis

Sample	Elemental composition, mass %					Relative content of elements			
	C	H	S	N	O	H/C	S/C	N/C	O/C
A1	91.7	4.2	0.4	2.1	0.7	0.5	0.002	0.02	0.006
A2	92.0	4.4	0.5	2.2	0.7	0.6	0.002	0.02	0.006
A3	91.4	4.4	0.6	2.1	0.7	0.6	0.002	0.02	0.006
A4	91.1	4.2	0.6	2.0	0.5	0.5	0.002	0.02	0.004

ing an Agilent 6890N chromatograph (USA) with the mass-selective detector Agilent 5973. Identification of the component composition of the samples under investigation from the mass spectra was performed using the NIST-11 spectral library.

RESULTS AND DISCUSSION

The results of the elemental analysis of asphaltenes are presented in Table 1. Determination of the average empirical formula of asphaltene macromolecule was carried out admitting that the composition of a fragment of the macromolecule includes one of heteroatoms, their total content in an average hypothetical molecule is approximately equal to 3 mass %. With this admission, the molecular masses of the structural units of asphaltene macromolecules may vary from 500 to 1000 Da. The relations between different structural units in an average asphaltene macromolecule are so that there are 4–5 N-containing structures and 1.3–1.7 O-containing ones per one S-containing structure, and there are 39 to 77 carbon atoms per one heteroatom. Calculation of the relative content of elements per one C atom is presented in Table 1. On average, there is one H atom per two C atoms, one S, N or O atom per 500, 50 or 167 C atoms, respectively.

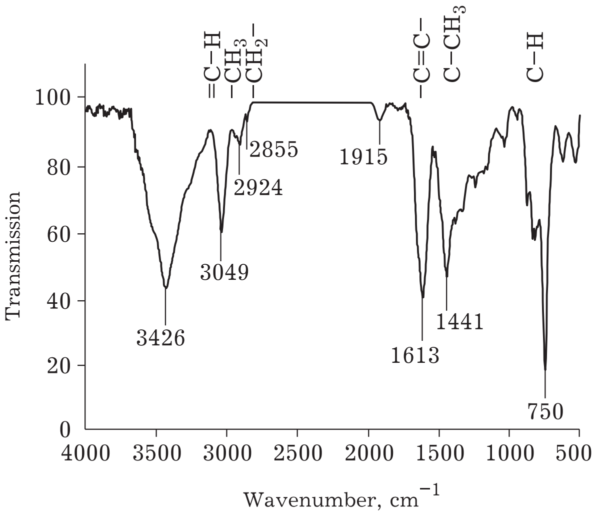


Fig. 1. Example of an IR spectrum of CTP asphaltene sample.

The IR spectra of CTP asphaltenes (Fig. 1) contain mainly absorption bands due to the vibrations of C–C and C–H bonds in aromatic condensed systems, cyclic, conjugated and aliphatic fragments. The intensity of bands related to the absorption by the end methyl groups (2924, 1445 cm^{-1}) points to the prevalence of rather short alkyl substituents in the structure of asphaltene molecules. An intense band in the region of 1600–1800 cm^{-1} may be due to the superposition of absorption bands characterizing the stretching vibrations of carbonyl >C=O groups and –C=C– bonds of the aromatic ring. This is the evidence of the high content of these structural fragments in the molecules of CTP asphaltenes with the overwhelming prevalence of aromatic structures.

The structural group characteristics of a hypothetical average asphaltene molecule were determined with the help of the data of NMR spectroscopy. On the basis of the results of sample studies by means of ^{1}H NMR, proton content in different structural fragments was calculated, while the data of ^{13}C spectra were used to calculate carbon distribution over functional groups. The ^{13}C NMR spectrum of asphaltenes contains broad bands corresponding to the resonance absorption of carbon atoms in saturated structures (the range of chemical shifts 0–70 ppm) and aromatic structures (100–170 ppm). The degree of aromaticity was calculated from the ratio of the integral intensities of the peaks related to carbon in the aromatic ring to saturated aliphatic structured, while the length of the chain of alkyl substituents was calculated from the ratio of the integral intensities of peaks corresponding to the chemical shifts of ^{13}C NMR for chained (29.7 ppm) and end (14.1 ppm) aliphatic fragments [18].

Analysis of the ranges of chemical shifts (δ) characteristic of hydrogen atoms of the corresponding groups in the ^{1}H NMR spectra [17] points to the presence of hydrogen: in aromatic rings (the region of 6.7–9.0 ppm), in aliphatic groups of different lengths (the region below 4.5 ppm), with an insignificant fraction of H (~2 %) in olefin compounds (the region of 6.7–4.5 ppm). The data of the integration of ^{1}H NMR spectra in accordance with the accepted attributions are presented in Table 2.

Results of the determination of the degree of aromatic ring substitution (σ), average length of alkyl substituents in aromatic rings (n) and the degree of aromaticity (F_{ar}) according to the data of ^{1}H NMR spectra are presented in Table 3 [17, 18].

The major functional groups and the parameters of the structure of an average CTP asphaltene molecule were determined from the results of the analysis of ^{13}C NMR spectra. The data on the distribution of carbon over structural fragments are presented in Table 4.

The average amount of carbon atoms incorporated into a hypothetical aromatic core of a mol-

TABLE 2

Distribution of hydrogen atoms over structural fragments in asphaltenes according to the data of ^{1}H NMR spectra

Hydrogen atom	%	Range of δ ^{1}H, ppm	Signal assignment [18]
H_{ar}	57.87	9.0–6.7	Protons of aromatic groups
H_α	15.81	4.5–2.0	Protons in all alkyl groups in α positions at aromatic rings and double bonds
H_β	13.95	2.0–1.0	Protons of methyl, methylene and methyn groups in β position with respect to aromatic ring and double bond, and methylene groups in saturated structures
H_γ	9.27	1.0–0.0	Protons of methyl groups not bound with aromatic rings or occupying γ position with respect to the rings and more remote positions
H_{olef}	2.15	6.7–4.5	Protons of olefin structures

TABLE 3

Structural parameters of asphaltene molecules according to the data of ^{1}H NMR spectroscopy

Parameter	Value	Equation
Degree of aromatic ring substitution (σ)	0.12	$\sigma = (H_\alpha/2) / (H_\alpha/2 + H_{ar})$
Average length of alkyl substituents in aromatic rings (n)	2.27	$n = (H_\alpha/2 + H_\beta/2 + H_\gamma/2) / (H_\alpha/2)$
Degree of aromaticity (F_{ar})	0.90	$F_{ar} = (C/H - H_\alpha/2 - H_\beta/2 - H_\gamma/3) / (C/H)$
Relative content of protons C/H	1.66[a]	–

[a] Data of elemental analysis.

TABLE 4

Distribution of carbon atoms over structural fragments of asphaltenes according to ^{13}C NMR data

Fragment	%	δ ^{13}C range (ppm)	Signal assignment [17]
CH_3	2.64	0–25	C atoms of aliphatic fragments
CH_2	2.42	25–51	C atoms of aliphatic fragments
OCH_3	0.34	51–67	C atoms of methyl ethers
C–O–C	0	67–93	C atoms of bridge fragments
Ar–H	40.70	93–125	Tertiary C atoms of aromatic rings
Ar–C	52.34	125–148	Quaternary C atoms of aromatic rings
Ar–O	0.23	148–171	C atoms of aromatic rings bound with oxygen atoms
COOH	1.33	171–187	C atoms of carbonyl groups
C=O	0	187–235	C atoms of ketones, aldehydes, quinone methides

Note. Degree of aromaticity F_{ar} = 0.93, where $F_{ar} = (C_{Ar-H} + C_{Ar-C} + C_{Ar-O})/100$.

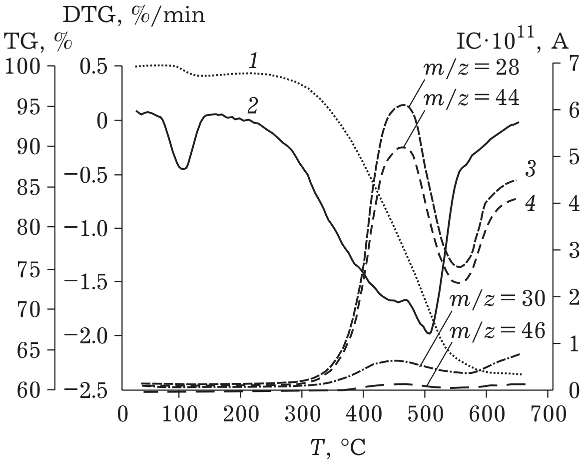


Fig. 2. TG (*1*) and DTG (*2*) curves of the decomposition of CTP asphaltenes with superimposed curves of ion currents (IC) with different values of *m*/*z*.

ecule was determined from the data of ^{13}C NMR spectra using the approach described in [18]. According to calculation results, the structure of the polyaromatic core of an average asphaltene macromolecule is composed of about 30 carbon atoms united in seven aromatic rings with the structure of peri-condensed type. The degree of aromaticity calculated from the integral intensities of absorption bands in the ^{13}C NMR spectrum was F_{ar} = 0.93. This value is in good agreement with the value calculated from ^{1}H spectra (F_{ar} = 0.90).

The most difficult task is to study the distribution of functional groups containing heteroatoms in asphaltene macromolecules. It is known [5] that N atoms occur in heteroaromatic fragments – pyridine, pyrrole and porphyrine, S atoms are in sulphide, thiol groups and in thiophene cycles, O atoms are in hydroxyl, carboxyl, ether, carbonyl groups and furan rings.

It is often admitted in building up hypothetical structural units of the organic mass of coal that heteroatoms are represented mainly by oxygen atoms [2]. The elemental composition of CTP asphaltenes studied in the present work is distinguished by an increased content of N with respect to O. It is impossible to reveal the distribution of nitrogen atoms over structural groups according to the data of IR and NMR spectroscopy, so we investigated the component composition of volatile products formed in thermolysis and the elemental composition of the coke residue to determine the structure of the fragments containing N and S atoms. Comparing the results with the data on the behaviour of the substances of similar chemical nature under the conditions of thermolysis, one may assume the structure of heteroatomic functional groups [19].

Three maximal of mass loss are observed in thermograms during asphaltene thermolysis (Fig. 2). The first maximum corresponds to the evaporation of residual solvent (toluene) captured by asphaltene precipitate flocculating in hexane, while other two maxima depict asphaltene conversion within temperature range from 260 to 550 °C. Intense coke formation and gas evolution start at 500 °C.

GC-MS examination of the volatile products of asphaltene thermal destruction (Table 5) reveal a substantial amount of polyaromatic and aromatic N-containing compounds. The amount of volatile compounds containing S vary depending on the quality of petrolene separation. The absence of O-containing compounds may be explained by the detachment of the fragments in the form of simple products with low molecular masses – CO, CO_2. The formation of ions with m/z = 28 and 44, characteristic of these products, is observed in the mass spectra of gases released during heating within temperature range 320–520 °C. Calculation of the elemental composition of volatile products according to GC-MS data is presented in Table 6.

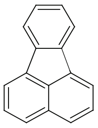
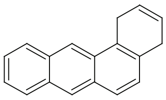
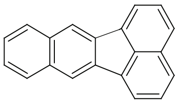
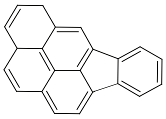
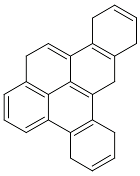
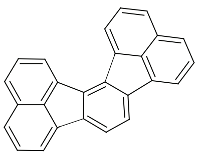
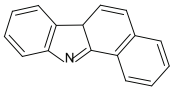
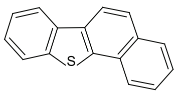
Coke residues (see Table 6) exhibit carbon, sulphur and oxygen concentrating with a decrease in hydrogen and nitrogen content. Accumulation of oxygen in coke residues is the evidence of the presence of aromatic ethers in the structure, since the high thermal stability of these compounds is well known [19].

The dependence of the amount of sulphur-containing products on the content of petrolene admixture in asphaltene samples may be explained by the fact that petrolene macromolecules contain thioether bonds destroyed under thermal action [7]. Sulphur incorporated in asphaltene molecules is not detached under heating to 650 °C, so it may be stated that sulphur atoms are localized only in the aromatic fragments of asphaltenes.

Inclusions of N atoms stabilize the structure of aromatic molecules up to the temperature of 500 °C and promote condensation of polyaromatic compounds [19]. A decrease in nitrogen content in coke residues and the presence of N-containing compounds in volatile products point to the presence of N-containing fragments of different structures in asphaltene macromolecule. According to the data of mass spectrometry of released gases, thermal decomposition of asphaltenes is

TABLE 5

Composition of the volatile products of thermolysis of asphaltenes according to the data of GC-MS

Ion, *m/z*	Formula	Number of rings		Number of isomers	Content, %
		aromatic	naphthene		
202	 $C_{16}H_{10}$	3	1	2	8.4
228	 $C_{18}H_{12}$	4	0	2	6.8
252	 $C_{20}H_{12}$	4	1	6	30.0
276	 $C_{22}H_{12}$	5	1	4	22.6
302	 $C_{24}H_{14}$	6	0	4	13.6
326	 $C_{26}H_{16}$	5	2	8	6.6
217	 $C_{12}H_{9}N$	3	1[a]	3	11.1
234	 $C_{16}H_{10}S$	3	1[a]	3	1.0

[a] Contains heteroatom.

TABLE 6

Average elemental composition in the volatile products and coke residues of asphaltenes

Sample	Elemental composition, mass %					Relative content of elements			
	C	H	S	N	O	H/C	S/C	N/C	O/C
C1	92.4	3.0	0.5	1.6	2.5	0.4	0.002	0.01	0.02
C2	91.4	2.9	0.5	1.8	3.4	0.4	0.002	0.02	0.03
L	94.1	5.2	0.1	0.6	–	0.7	0.0005	0.006	–

Notes. 1. C1 is coke residue of sample A1, C2 is coke residue of sample A3 (according to the data of elemental analysis); L means the volatile products of sample A1 (according to the data of GC-MS). 2. Dash means that O-containing compounds were not detected in the volatile products of thermolysis.

accompanied by the evolution of NO and NO_2 (recorded as ions with $m/z = 30$ and 46, respectively) within the temperature range of 320–530 °C and above.

CONCLUSION

It was established in the integrated studies of the composition and molecular structure of coal tar pitch asphaltenes that the hydrocarbon skeleton of an average hypothetical asphaltene macromolecule may be considered as a set of condensed aromatic cores of re-condensed type composed of seven rings, which hold alkyl substituents and connecting bridges composed of two carbon atoms on average. There is one hydrogen atom per two carbon atoms on average.

The most interesting aspect is the investigation of the distribution of heteroatoms S, N, O in asphaltene structure. There is one S, N or O atom in a structure of 500, 50 or 167 carbon atoms, respectively. The ratio of different structural units in asphaltene macromolecule is: 4–5 N- and 1.3–1.7 O-containing structures per one S-containing structure on average. Sulphur atoms are present in thiophen-like, thermally stable structural fragments and pass into coke residue without decomposition. Oxygen is incorporated into thermally unstable carboxyl and phenol groups decomposing with the evolution of CO_2, and into aromatic ethers passing into coke residue. Nitrogen-containing structures undergo thermal decomposition within two temperature range. Additional investigation is required to determine the type of the structures corresponding to this behaviour.

Results of the studies of the structural group composition obtained using different methods are in good agreement with each other and serve as the basis to model the structural unit of the molecule.

Acknowledgements

The work was carried out within the State Assignment to ICCMS FRC CCC SB RAS (Project No. AAAA-A17-117041910151-9).

Investigation was carried out using the equipment of the Kemerovo Shared Equipment Centre of FRC CCC SB RAS.

REFERENCES

1 Posadov I. A., Pokonova Yu. V. Structure of oil asphaltenes. A manual. Leningrad: LTI, 1977. 75 p.

2 Patrakov Yu. F., Fedyaeva O. N., Kamyanov V. F. A structural model of the organic matter of barzas liptobiolith coal, *Fuel*. 2005. Vol. 84, No. 2–3. P. 189–199.

3 Fedyaeva O. N., Patrakov Yu. F. Structure and properties of macromolecular fragments of the organic substance of coal, *Khimiya Tverdogo Topliva*. 2004. No. 5. P. 24–31.

4 Dolomatov M. Yu., Shutkova S. A., Dezortsev S. V. Structure of molecular nanoparticles of oil asphaltenes, *Zhurn. Struktur. Khimii*. 2012. Vol. 53, No. 3. P. 569–573.

5 Shutkova S. A., Dolomatov M. Yu. Investigation of the structural characteristics of oil saphaltenes of archipelagic type, *Bashkir. Khim. Zhurn*. 2016. Vol. 23, No. 3. P. 15–19.

6 Galimova G. A., Yusupova T. N., Ibragimova D. A., Yakupov I. R. Composition, properties and fractions of asphaltenes of oil dusperse systems, *Vestn. Tekhnolog. Un-ta*. 2015. Vol. 18, No. 20. P. 60–64.

7 Privalov V. E., Stepanenko M. A. Coal tar pitch. Moscow: Metallurgiya, 1981. 208 p.

8 Sozinov S. A., Sotnikova L. V., Popova A. N., Khitsova L. M. Investigation of the products of thermal destruction of hexane-insoluble asphaltenes of coal tar pitch, *Koks i Khimiya*. 2018. No. 11. P. 29–35.

9 Akbarzade K., Khammani A., Khart A., Chzhan D., Allenson S., Krik J., Kabir Sh., Dzhamaluddin A. J., Marshal R., Rogers P., Mallins O. K., Solbakken T. Asphaltenes: problems and outlooks, *Neftegazovoe Obozrenie*. 2007. No. 3. P. 28–53.

10 Sozinov S. A., Sotnikova L. V., Popova A. N., Kolmykov R. P., Russakov D. M. Preparation of the films of hexane-insoluble asphaltenes from coal tar pitch, *Koks i Khimiya*. 2018. No 2. P. 47–52.

11 Anikeeva I. V., Kryazhev Yu. G., Solodovnichenko V. S., Drozdov V. A. Obtaining composites with nanoparticles of globular carbon distributed in amorphous carbon matrix, *Khimiya Tverdogo Topliva*. 2012. No. 4. P. 70–73.

12 Qu W.-H., Guo Yu-B., Shen W., Li W.-C. Using asphaltene supermolecules derived from coal for the preparation of efficient carbon electrodes for supercapacitors, *J. Phys. Chem*. 2016. No. 6. P. 1–28.

13 Kuzeev I.R., Zakirnichnaya M. M., Popova S. V., Gimalova M. R. Formation of fullerenes in the structure of iron-carbon alloys during crystallization, phase transitions and deformation, *Neftegazovoe Delo*. 2011. No. 6. P. 411–419.

14 USA Pat. No. 4518483, 1985.

15 Berveno V. P., Bryukhovetskaya L. V., Naymushina T. M., Sozinov S. A., Dodonov V. G., Pugachev V. M., Shchukin L. I. Nanotexture of carbon fibre from pitch, *Chemistry for Sustainable Development*. 2005. Vol. 13, No. 3. P. 421–424.

16 Beyko O. A., Golovko A. K., Gorbunova L. V., Kamyanov V. F., Lebedev A. K., Plyusnin A. N., Savinykh Yu. V., Sivirilov P. P., Filimonova T. A. Chemical composition of oil of West Siberia. Novosibirsk: Nauka, 1988. 288 p.

17 Kalabin G. A., Kanitskaya L. V., Kushnarev D. F. Quantitative NMR spectroscopy of natural organic raw material and the products of its processing. Moscow: Khimiya, 2000. 408 p.

18 Solum M. S., Pugmire R. J., Grant D. M. 13C Solid-state NMR of Argonne premium coals, *Energy & Fuels*. 1989. No. 3. P. 187–193.

19 Chistyakov A. N. Chemistry and processing of tar pitch. A manual. Chelyabinsk: Metallurgiya, 1990. 160 p.