

Comprehensive studies of coal tar pitch components

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Abstract. By methods of electron microscopy, adsorption porometry, NMR, IR- EPR spectroscopy, X-ray diffractometry, thermal analysis, chromatography-mass spectrometry the composition, structure and particle morphology of β - and α 2-fraction powders of medium-temperature coal ash were investigated. The morphology and structure of coke residues depending on the heating temperature were investigated. Polyaromatic hydrocarbons in the composition of volatile products of coal ash thermolysis were found to be formed mainly by the decomposition of components of β -fraction. The results obtained are of interest from the point of view of the feasibility of using the isolated fractions of coal ash as precursors for the production of functional carbon materials.

1 Introduction

With the growing global demand for new functional materials based on carbon, the task of increasingly efficient and deep processing of coal into products with high added value is in vogue [1]. One of the valuable products of coal processing is coal tar pitch. It is used as a binder in the production of anodes, for the synthesis of carbon fibres and nanofibers, and as an adsorbent, and for the production of a wide range of different composite materials, in connection with which the need for the production of coal tar pitch is increasing annually [2, 3]. Important properties of coal ash, which determine the direction of its use, are the proportion of fractions in the composition of the coal ash group and the softening point [4]. However, it is known [5-7] that in the process of obtaining and processing coal ash a lot of pollutants are formed. Therefore, the problem of development of new, technological and environmentally safe methods of processing in this industry is acute [8]. At the same time, most of such developments are related to the introduction of modifying additives into the composition of the pitch [9-11], or to the use of different methods of treatment of the pitch prior to carbonization [12, 13]. Such developments require more and more detailed knowledge of the chemical composition and molecular structure of the pitch.

Coal pitch is a complex heterogeneous system of highly condensed carbo- and heterocyclic compounds, as well as products of their compaction, differing in the degree of aromaticity, composition, properties, and molecular structure. Due to the complexity of chemical composition coal pitch is usually characterized by group composition, for the study

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of which the pitch is divided into fractions - groups of substances united by the same ratio to certain solvents. For this purpose, both sequential extraction with several solvents, each of which is added after thorough removal of the previous one, and sequential precipitation are used. The components of the pitch are usually divided into three main fractions: maltene, or γ -substances, soluble in hexane; asphaltenes, or β -substances, soluble in toluene and insoluble in quinoline; the residue insoluble in toluene, or α -substances. The α -fraction is divided into two: α_1 , insoluble in quinoline and in toluene, and α_2 , soluble in quinoline and insoluble in toluene. By changing the composition of the solvents and their number, the number of fractions can be changed, and their composition can be influenced.

The present work is focused on the study of physicochemical properties of individual fractions of coal ash in order to find a group of substances with unique properties, the use of which as precursors will make it possible to develop environmentally friendly technologies for obtaining functional materials for various purposes and, at the same time, to expand the understanding of the role of various components of coal ash in the processes of its structuring during carbonization.

2 Experimental section

Medium-temperature coal pitch, softening point $\approx 87^\circ\text{C}$, was used in the present work. Asphaltenes (β -substances) and maltene (γ -substances) were isolated from the toluene extract of the pitch by dilution of the extract with n-hexane. The extract was obtained at a ratio of 1g of pitch / 40 ml of toluene. Precipitation of asphaltenes from the toluene extract was carried out by adding 200 ml of n-hexane. After flocculation, the precipitate was kept in the mother liquor for 24 hours, then filtered and washed from adsorbed maltene molecules with n-hexane. The asphaltenes were dried at 80°C to remove the residual precipitant. The asphaltenes were isolated as a fine brown colored loose powder with a melting point between $150\text{--}300^\circ\text{C}$. From the toluene insoluble residue, after removing toluene, the α_2 -fraction substances were extracted with 40 mL of quinoline. Then, to obtain a powder, the extract was mixed with the solvents extracted after extraction of γ - and β -substances, the precipitate was filtered, washed with a mixture of solvents, and dried for 1 h at $T=240^\circ\text{C}$ to remove the residue of all solvents. The α_2 -fraction substances were black powder, whose particles were partially sintered at the drying temperature. The yield of α_2 fraction was about 45%, β fraction 5% and γ fraction 43%. Since no coke residue is formed when γ -substances are heated, we studied only β - and α_2 -fractions as the most promising, in our opinion, precursors for obtaining functional carbon materials.

The particle morphology of β - and α_2 -fractions powders was investigated using a scanning electron microscope JEOL JSM6390. Textural characteristics of the studied powders - values of specific surface area, volumes and average pore diameter were carried out by low-temperature nitrogen adsorption method on the ASAP-2020 "Micromeritics" unit.

The content of elements C, H, N, S, O in the powder particles was investigated using elemental analyzer "Flash 2000".

Data on the distribution of hydrogen and carbon atoms on different hydrocarbon structures in β - and α_2 -fractions of coal ash were obtained by ^1H and ^{13}C NMR spectra. NMR spectra of asphaltene macromolecules were recorded on a Bruker Avance III 300 WB spectrometer. High-resolution ^{13}C spectra in solid state were recorded using standard cross-polarization technique with magic angle rotation and proton decoupling (CPMAS) at 75 MHz. Chemical shifts were determined relative to tetramethylsilane. Quantitative calculations from NMR spectra were performed according to the methods described in [15, 16].

Paramagnetic properties were investigated on a Bruker EMX6/1 Micro EPR spectrometer in X-band (9.5 GHz) under normal conditions in air atmosphere, with magnetic field sweep $\Delta N=1300-5700\text{Gs}$ and $\Delta N=3420-3620\text{Gs}$ (microwave attenuator attenuation value 20Db).

Thermal transformations were investigated using a NETZSCH 409 PG Luxx synchronous thermal analyzer.

The composition of volatile components formed during thermal transformations of β - and $\alpha 2$ -fractions was analyzed on an Agilent 6890N chromatograph (HP-5ms capillary column was used) with an Agilent 5973 mass-selective detector; evaporator temperature 250°C; programmable column temperature increase from 50°C to 290°C. Identification of separated components was performed by mass spectra using NIST11 database.

The phase composition and structure of the obtained initial powders and their coke residues were analyzed according to the method [17-19] on a Bruker D8 ADVANCE A25 diffractometer. The diffractograms were interpreted using the ICDD PDF-2 database.

3 Results and discussion

Components of the β -fraction form a loose powder of brown color, the particles of which have spherical or polyhedral shape. The particles are homogeneous in size, and the particle boundaries are clearly distinguishable (Fig. 1.a). Under controlled deposition conditions [20], monodisperse particle systems with a size coefficient of variation of less than 15% can be obtained. The obtained $\alpha 2$ -fraction powders are black in color and consist of agglomerates of structureless particles with sizes ranging from a fraction of a micrometer to 1 μm or more (Fig. 1.b).

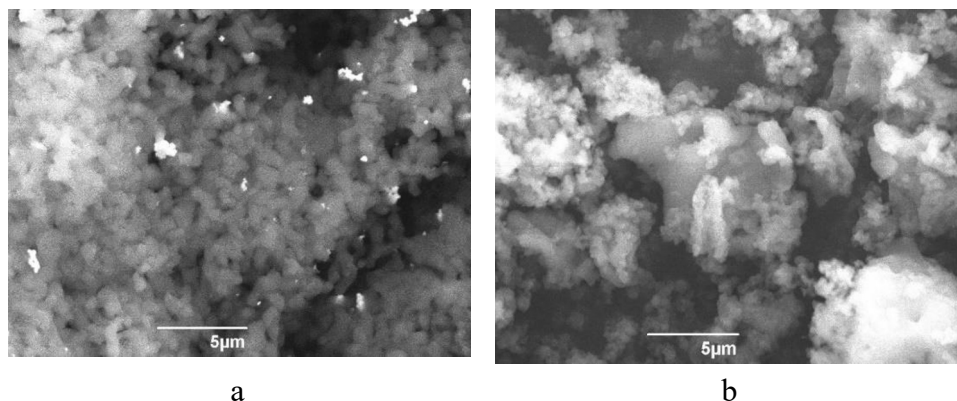


Fig. 1. SEM images of powder particles of β - (a) and $\alpha 2$ - (b) fractions

Textural characteristics were measured for the β -fraction powder. The value of specific surface area of asphaltene powder was 5.4 m^2/g , and the total pore volume was 0.0136 cm^3/g . The porous structure of the particles was mainly formed by slit-shaped mesopores with diameters ranging from 20Å to 500Å, with the maximum on the pore size distribution curve located at $\sim 25\text{Å}$. The volume of mesopores amounted to 0.0124 cm^3/g .

According to the elemental analysis data (Table 1), it can be seen that β - and $\alpha 2$ -fractions are characterized by high carbon content. At the same time, the relative C content of $\alpha 2$ -fraction is higher than that of β -fraction. Also, $\alpha 2$ contains a higher amount of O than the β -fraction. According to [14] the β and $\alpha 2$ fractions differ in their activity towards oxygen. According to the authors of this work, oxygen is attached to the substances of the fractions in the process of extraction from the furnace. The nitrogen content in these fractions is

practically the same, and the sulfur content in the α_2 -fraction is lower than in the β -fraction. When α_2 - and β -fractions are heated in an inert atmosphere up to the temperature of 1200°C the N content decreases, and the ratio of sulfur to carbon practically does not change, from which it can be concluded that sulfur is in the form of heat-resistant thiophene compounds and passes to the coke residue.

Table 1. Elemental composition of β - and α_2 - fractions of coal ash according to C, H, N, S, O analysis data

Sample*	Elemental composition, wt. %					Relative element content			
	C	H	S	N	O	H/C	S/C	N/C	O/C
ASC	92.0	4.2	0.5	1.7	1.6	0.6	0.002	0.02	0.01
β (T ₁₁₀)	92.0	4.4	0.5	2.2	0.8	0.6	0.002	0.02	0.007
β (T ₆₀₀)	92.4	3.0	0.5	1.6	2.5	0.4	0.002	0.01	0.02
α_2 (T ₃₀₀)	90.1	3.4	0.3	2.1	4.1	0.5	0.001	0.02	0.03
α_2 (T ₆₀₀)	92.9	2.5	0.2	1.8	2.6	0.3	0.001	0.02	0.02
α_2 (T ₁₂₀₀)	96.9	0.2	0.2	1.5	1.1	0.03	0.001	0.01	0.01

Note. * The temperature in parentheses is the temperature to which the sample was preheated in an inert atmosphere.

Application of a comprehensive approach to the study of coal tar pitch by physical and chemical methods of analysis (e.g., X-ray diffraction analysis, electron paramagnetic resonance, chromatography, mass spectroscopy, etc.) gives more complete information about the structural features of pitch and its components [21, 23].

According to the X-ray diffractometry data, two maxima (002) and (100) are formed on the X-ray diffractogram, associated with diffuse scattering, which is characteristic of amorphous substances with some degree of ordering of the structure, which is characteristic of compounds based on the structure of which are planes of condensed aromatic rings united in "graphite-like" packages.

X-ray diffraction analysis of the powders showed that the systems are non-monophasic and two phases can be distinguished, which differ in the thickness of the packages containing 4-5 and 10-11 layers in phase 1 and phase 2, respectively, with an interplanar distance (d_{002}) of 3.58 and 3.44 Å, respectively. Upon heating to 1200°C, a decrease in the amount of the 1st phase 80 to 60% and an increase in the second phase from 20 to 40% is observed, while the number of layers in the package does not change.

Coal pitch is characterized by the presence of a large number of paramagnetic centers (PMC). It is known that the concentration of PMCs in different fractions of pitch is different [14]. We obtained the value of $8.44 \cdot 10^{18}$ for β -fraction (Table 2), while for α_2 -fraction - $5.01 \cdot 10^{19}$, the obtained values agree with the data of other authors [24, 25]. When heated in an inert atmosphere up to 300°C, the concentration of PMC in the α_2 -fraction increases approximately 2-fold with decreasing g-factor. When the processing temperature of the α_2 fraction is increased, further increase of the PMC concentration and decrease of the g-factor value are observed.

Table 2. Characteristics of electron paramagnetic resonance spectra

Sample	PMC, n/gr	ΔH , Gs	I, relative unit	g-factor	CAMW
α_2	$5.0144 \cdot 10^{19}$	5.332	$2.1 \cdot 10^6$	2.00307	12005
α_2 (T ₃₀₀)	$1.075 \cdot 10^{20}$	5.332	$7.0 \cdot 10^6$	2.00311	5600
α_2 (T ₆₀₀)	$2.575 \cdot 10^{20}$	6.665	$1.3 \cdot 10^6$	2.00286	2338
β (T ₁₁₀)	$8.44 \cdot 10^{18}$	5.360	$0.4 \cdot 10^6$	2.00295	71327

The calculation of the conditional average molecular weight (CAMW) from the amount of PMC [24] and the data on the increase in PMC concentration show that during heating the bonds between the structural fragments of macromolecules are broken to form stable radicals. The EPR spectra differ in signal intensity, which can be attributed to the presence of more condensed aromatic radicals in the α fraction. Upon heating up to 300 °C, an increase and then a sharp decrease is observed, and already at 1200 °C the EPR signal is not registered. This is due to changes in the internal structure of the sample, accompanied by the formation of chemical bonds between aromatic structural fragments and leading to the appearance of electrical conductivity.

Analysis of the g-factor value shows that the free radicals of alpha and beta fractions are of the same nature and most likely belong to aryl-type radicals, while they are surrounded by radicals of similar structure.

To further detail the structure of the asphaltene macromolecule, NMR spectra were obtained and analyzed ^{13}C . The spectra contain broad bands corresponding to the resonance absorption of carbon atoms in aromatic and saturated aliphatic ($\delta=0-70$ m. d.) and ($\delta=100-170$ m. d.) structures. By the ratio of integral intensities of peaks related to carbon in the aromatic ring and in saturated aliphatic structures, the degree of aromaticity (F_{ar}) was calculated, and by the ratio of integral intensities of peaks corresponding to the values of chemical shifts $\delta=29.7$ and $\delta=14.1$ m. d. NMR ^{13}C signals, the average chain length of the alkyl substituent (n) was calculated; for β - and $\alpha 2$ -fractions n was 2.00 and 1.85, respectively. Based on the results of analyzing the NMR ^{13}C spectra, the main functional groups and structure indices of the hypothetical average macromolecule were established for the β - and $\alpha 2$ -fractions. The data on the carbon distribution among the structural fragments are presented in Table 3.

The table shows that the $\alpha 2$ -fraction has a higher degree of aromaticity and an increased content of carbon atoms bound to oxygen, which is consistent with the results of elemental analysis. Data on the distribution of C by functional groups containing heteroatoms have a large degree of uncertainty, so often in the construction of hypothetical structural units of organic mass, the account of heteroatoms is reduced to the assumption that they are represented mainly by oxygen atoms [26]. Thus, additional studies are required to clarify the functional-group composition associated with heteroatoms.

Table 2. Distribution of carbon atoms by structural fragments. Data NMR ^{13}C

Fragment	%	%	Range δ ^{13}C (m. d.)	Signal attribution (according to [25])
	$\beta(T_{110})$	$\alpha 2(T_{300})$		
CH ₃	2.64	0.97	0–25	C atoms of aliphatic fragments
CH ₂	2.42	0.97	25–51	C atoms of aliphatic fragments
OCH ₃	0.34	0	51–67	C atoms of methyl esters
C–O–C	0	0	67–93	C atoms of bridge fragments
Ar–H	40.70	43.01	93–125	Tertiary C atoms of aromatic rings
Ar–C	52.34	49.88	125–148	Quaternary atoms C of aromatic rings
Ar–O	0.23	4.74	148–171	C atoms of aromatic rings bonded to oxygen atoms
COOH	1.33	0.42	171–187	C atoms of carbonyl groups
C=O	0	0	187–235	C atoms of ketones, aldehydes, quinonmethides
F_{ar}	0.93	0.98	Degree of aromaticity, where $F_{ar} = (C_{Ar-H} + C_{Ar-C} + C_{Ar-O}) / 100$	

Based on NMR ^{13}C spectroscopic data, using the approach described in [27], the average number of carbon atoms included in the hypothetical aromatic core of the molecule was

determined. According to the calculation results, the average macromolecule fragment of both β - and α_2 - fractions consists of 25-30 carbon atoms, which are combined into a peri-condensed type structure of about seven aromatic rings.

According to the data of TG- and DTG analysis of ASC, α_2 - and β -fractions (Fig. 2), the character of thermal decomposition of pitch and its separate fractions differs. The mass loss of the studied ASC sample starts at about 200°C, increases with increasing temperature, reaching a maximum at 340°C, then decreases and decreases slightly at temperatures above 560°C. It is generally believed that the initial section of the DTA curve is associated with the processes in which mainly dehydropolycondensation and association reactions of the components of pitch. The degradation processes above 340°C are accompanied by the formation of polycondensation products based on active radicals of multi-ring aromatic compounds and their compaction products with the formation of solid residue. The coke residue of the pitch sample is 41%. During thermolysis of the β -fraction, three maxima are observed on the DTG curve. The first maximum at 104°C corresponds to the evaporation of toluene trapped by the flocculating precipitate in hexane, while the other two maxima reflect the asphaltene conversion process in the range from 260°C to 550°C. Intense coke formation and outgassing starts at 500°C. The coke residue is 60%. From the DTG curves of α_2 fraction, three stages of mass loss can be distinguished. The first stage with a peak at 340°C, then the mass loss associated with the degradation process occurs at 580°C and 750°C. The solid residue yield of α_2 fraction is 86%.

Chromatographic analysis of volatile decomposition products of coal ash shows the presence of a large content of polycyclic compounds consisting of four or more nuclei [23]. Our comparison of the composition of volatile products of thermal decomposition of separate fractions of coal ash showed that the main part of polycyclic aromatic hydrocarbons (PAHs) is formed during thermal decomposition of substances of β -fraction. Benz(a)pyrene and its isomers account for up to 30% of the volatile products released during thermolysis [28]. The volatile products of the α_2 -fraction contain an order of magnitude smaller content of PAH.

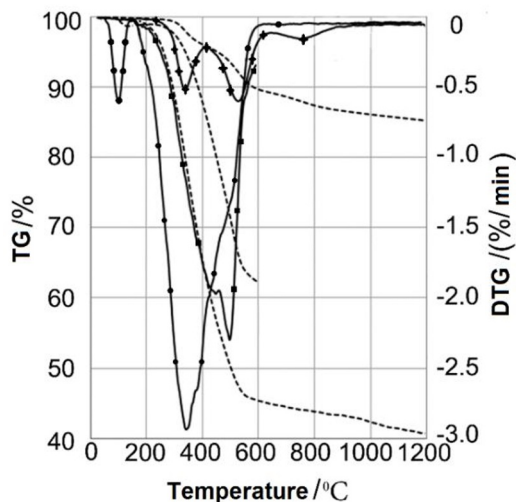


Fig. 2. TG-(-----) and DTG-curves (—) ASC decomposition (•) and its α_2 -fractions and (\times) and β -fractions (■)

Electron microscopic analysis of coke residues of α_2 -fraction showed that in the process of thermolysis, starting from the temperature of 300°C, particles are formed in the form of hollow spherical particles mainly with a smooth surface on which craters are observed,

formed in the process of evaporation of solvent and volatile decomposition products. The surface fracture analysis of the crushed particles, (Fig. 3), shows that the fracture structure has the appearance characteristic of a vitreous amorphous body. From about 900°C, the formation of a layered structure similar to the microstructure of needle coke [29] is observed, which becomes pronounced when heated to a temperature of 1200°C. The coke residue of coal ash obtained at 1200°C in general had a similar structure formed by hollow sphere-like particles, but differed in the presence of many different structured elements, which may be due to the complex composition of the coal tar and the nature of the ongoing reactions in the process of thermolysis, leading to the formation of different structures.

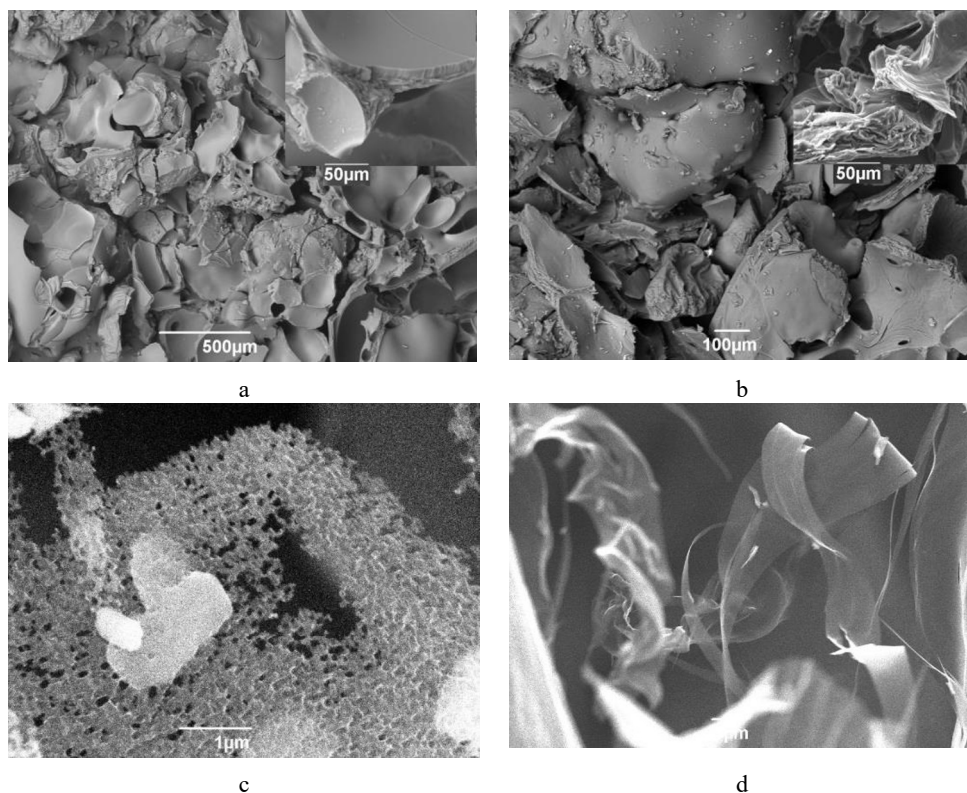


Fig. 3. SEM images of α_2 -fraction coke residues obtained at different temperatures: a - 600°C, b - 1200°C and fragments of ASC coke residues obtained at 1200°C.

4 Conclusions

Thus, studies have shown that qualitative differences in the composition of the elemental and functional groups of β - and α_2 -fractions are not significant. However, the fractions differ significantly in the morphology of particles formed during precipitation and their behavior during thermal decomposition. Thus β -fraction can be isolated from ASC in the form of a finely dispersed loose powder with high homogeneity of particles having mesoporous structure.

The process of thermal decomposition of substances of each fraction is unique and differs from the decomposition in the composition of coal ash. It was found that the main source of PAH during thermolysis is the components of β -fraction. In the coking process of coking of

α 2-fraction powders, a layered microstructure is formed similar to that of needle coke is formed.

In our opinion, the division of pitch into separate narrower fractions will allow us to find new directions of application of components of separate fractions and to obtain precursors for the synthesis of functional carbonaceous materials for various applications, as well as to study in more detail the influence of various components of pitch on the processes of its structurization in the process of carbonization.

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