Complex research of the components of the coal tar pitch

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Abstract. The composition, structure and morphology of particles of β- and α2-fraction powders of medium-temperature coal tar pitch were studied using the methods of electron microscopy, adsorption porosimetry, NMR, IR-EPR spectroscopy, X-ray diffraction microscopy, thermal analysis, and chromatography-mass spectrometry. The morphology and structure of coke residues were investigated depending on the heating temperature. It has been established that polyaromatic hydrocarbons in the composition of volatile products of thermolysis of coal tar pitch are formed mainly during the decomposition of the β-fraction components. The results obtained are of interest from the point of view of the directions of using the isolated fractions of coal tar pitch as precursors for obtaining functional carbon materials.

1. Introduction

With the growing global demand for new functional materials based on carbon, the urgent task is to develop increasingly efficient and deep processes for transformation of coal into products with high added value [1]. Coal tar pitch is one of the valuable products of coal processing. Pitch is used as a binder in the production of anodes, for the synthesis of carbon fibers and nanofibers, adsorbents and for the production of a wide range of various composite materials, and therefore the demand for pitch production is growing every year [2, 3]. Important properties of pitch that determine the direction of its use are the ratio of fractions in the group composition of the pitch and the softening temperature [4]. However, it is known [5-7] that in the process of obtaining and processing coal tar pitch, many pollutants are formed. Therefore, there is an acute problem of developing new, technologically advanced and environmentally safe processing methods in this industry [8]. At the same time, most of these developments are associated either with the introduction of modifying additives into the pitch composition [9-11], or with the use of different methods of pitch processing before carbonization [12, 13]. Such developments require more and more detailed knowledge of the chemical composition and molecular structure of pitch.

Coal tar pitch is a complex heterogeneous system of highly condensed carbo- and heterocyclic compounds, as well as their condensation products, differing in the degree of aromaticity, composition, properties, and molecular structure [14]. Due to the complexity of the chemical composition, coal tar pitch is usually characterized by a group composition, for the study of which the pitch is divided into fractions - groups of substances united by the same ratio to certain solvents. For this, both sequential extraction with several solvents, each of which is added after carefully removing the previous one, and sequential precipitation are used. Pitch components are usually divided into three main fractions: maltenes, or γ-substances soluble in hexane, asphaltenes, or β-substances soluble in toluene and insoluble in quinoline, a residue insoluble in toluene, or α-substances. The α-fraction is divided into two:
α1, insoluble in quinoline and toluene, and α2, soluble in quinoline and insoluble in toluene. By changing the composition of solvents and their number, one can change the number of fractions, as well as influence their composition.

This work is devoted to the study of the physicochemical properties of individual fractions of coal tar pitch in order to find a group of substances with unique properties, the use of which as precursors will allow the development of environmentally friendly technologies for the production of functional materials for various purposes and at the same time expand the understanding of the role of various components of pitch in the processes of its structuring during carbonization.

2. Experimental

In this work, we used medium-temperature coal tar pitch with softening temperature ≈ 87 °C. Asphaltenes (β-substances) and maltenes (γ-substances) were isolated from the toluene extract of pitch by diluting the extract with n-hexane. The extract was obtained at a ratio of 1 g pitch/40 mL of toluene. The 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 a day, then filtered and washed with n-hexane to remove adsorbed maltenes. To remove residues of the precipitant, the asphaltenes were dried at a temperature of 80 °C. Asphaltenes were isolated in the form of a finely dispersed free-flowing brown powder with a melting point in the range of 150-300 °C. From the toluene-insoluble residue, the substances of the α2-fraction were extracted with 40 ml of quinoline. Further, to obtain a powder, the extract was mixed with the solvents recovered after the isolation of γ- and β-substances, the precipitate was filtered off, washed with a mixture of solvents and dried for 1 hour at T = 240 °C to remove residues of all solvents. The α2-fraction substances were black powder, the particles of which were partially sintered at the drying temperature. The yield of the α2-fraction was about 45%, the β-fraction 5% and the γ-fraction 43%. Because when γ-substances are heated, no coke residue is formed, the study was carried out only for β- and α2-factions, as the most promising, in our opinion, precursors for obtaining functional carbon materials.

The morphology of β- and α2-faction powder particles was investigated using a JEOL JSM6390 scanning electron microscope. The texture characteristics of the studied powders - the values of the specific surface area, volumes and average pore diameter were carried out by the method of low-temperature nitrogen adsorption on an ASAP-2020 Micromeritics instrument.

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

Data on the distribution of hydrogen and carbon atoms over various hydrocarbon structures in the β- and α2-fraction of coal tar pitch were obtained from the 1H and 13C NMR spectra. NMR spectra of asphaltene macromolecules were recorded on a Bruker Avance III 300 WB spectrometer. High-resolution solid-state 13C spectra were recorded using standard proton decoupling magic angle spinning cross polarization (CPMAS) at 75 MHz. Chemical shifts were determined relative to tetramethylsilane. Quantitative calculations from the NMR spectra were performed according to the methods described in [15, 16].

The study of paramagnetic properties was carried out on a Bruker EMX6 / 1 Micro EPR spectrometer in the X-region (9.5 GHz) under normal conditions in an air atmosphere, with a magnetic field sweep ΔH = 1300-5700 G and ΔH = 3420-3620 G (the value of the microwave attenuation 20 dB).

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

The analysis of the composition of volatile components formed in the course of thermal transformations of β- and α2-fractions was carried out on an Agilent 6890N chromatograph (an HP-5ms capillary column was used) with an Agilent 5973 mass-selective detector; evaporator temperature 250 °C; programmable increase in column temperature from 50 °C to 290 °C. The separated components were identified by mass spectra using the NIST11 library.
Analysis of the phase composition and structure of the obtained initial powders and their coke residues was carried out according to the method [17-19] on a Bruker D8 ADVANCE A25 diffractometer. Diffraction patterns were decoded using the ICDD PDF-2 database.

3. Results and discussion
The components of the β-fraction form a free-flowing brown powder, the particles of which are spherical or polyhedral in shape. The particles are uniform in size, the boundaries of the particles are well distinguishable (Fig. 1.a). Under controlled deposition conditions [20], monodisperse systems of particles with a coefficient of variation in size less than 15% can be obtained. The obtained powders of the α2-fraction are black and consist of agglomerates of structureless particles with sizes from fractions of a micrometer to 1 μm or more (Fig. 1 b).

![SEM images of powder particles of β- (a) and α2- (b) fractions.](image)

For the β-fraction powder, the texture characteristics were measured. The specific surface area of the asphaltene powder was 5.4 m²/g, the total pore volume was 0.0136 cm³/g. The porous structure of particles is mainly formed by slit-shaped mesopores with a diameter of 20 Å to 500 Å, with the maximum on the pore size distribution curve located at ~ 25 Å. The mesopore volume was 0.0124 cm³/g.

According to the elemental analysis data (Table 1), it can be seen that the β- and α2-fractions are characterized by high carbon content. The relative content of C in the α2-fraction is higher than in the β-fraction. Also α2 contains more O than β-fraction. According to [14], the β and α2 fractions differ in their activity towards oxygen. According to the authors of this work, oxygen is bound to the substances of the fractions in the process of separation from the pitch. The nitrogen content in these fractions is practically the same, and the sulfur content in the α2-fraction is lower than in the β-fraction. When α2- and β-fractions are heated in an inert atmosphere up to a temperature of 1200°C, the N content decreases, and the sulfur-to-carbon ratio practically does not change, from which we can conclude that sulfur is in the form of refractory thiophene compounds and passes into the coke residue.

The use of an integrated approach in the study of pitch by physicochemical methods of analysis (for example, methods of X-ray structural analysis, electron paramagnetic resonance, chromatography, mass spectroscopy, etc.) provides more complete information about the structural features of pitch and its components [21, 23].

According to X-ray diffractometry data, two maxima (002) and (100) are formed on the X-ray diffraction pattern, which are associated with diffuse scattering characteristic of amorphous substances with a certain degree of structural order, which is characteristic of compounds whose structure is based on planes of condensed aromatic rings, combined into "Graphite-like" packages.
Table 1. Elemental composition of β- and α2- fractions of coal tar pitch according to C, H, N, S, O - analysis

| Sample* | Elemental composition, wt. % | Relative content of elements |
|---------|-----------------------------|-----------------------------|
|         | C   | H   | S   | N   | O   | H/C | S/C | N/C | O/C |
| CTP     | 92.0 | 4.2 | 0.5 | 1.7 | 1.6 | 0.6 | 0.002 | 0.02 | 0.01 |
| β (T110) | 92.0 | 4.4 | 0.5 | 2.2 | 0.8 | 0.6 | 0.002 | 0.02 | 0.00 |
| β (T600) | 92.4 | 3.0 | 0.5 | 1.6 | 2.5 | 0.4 | 0.002 | 0.01 | 0.02 |
| α2 (T300) | 90.1 | 3.4 | 0.3 | 2.1 | 4.1 | 0.5 | 0.001 | 0.02 | 0.03 |
| α2 (T600) | 92.9 | 2.5 | 0.2 | 1.8 | 2.6 | 0.3 | 0.001 | 0.02 | 0.02 |
| α2 (T1200) | 96.9 | 0.2 | 0.2 | 1.5 | 1.1 | 0.03 | 0.001 | 0.01 | 0.01 |

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

X-ray diffraction analysis of the powders showed that the systems are non-monophase and two phases can be distinguished, which differ in the thickness of packets containing 4-5 and 10-11 layers in the 1st and 2nd phases, respectively, with an interplanar spacing (d002) of 3.58 and 3.44 Å, respectively. When heated to 1200 °C, there is a decrease in the amount of the first phase from 80 to 60% and an increase in the second from 20 to 40%, while the number of layers in the package does not change.

Coal tar pitch is characterized by the presence of a large number of paramagnetic centers (PMCs). It is known that the concentration of PMCs in different fractions of pitch is different [14]. We obtained a value of 8.44 * 10¹⁸ for the β-fraction (Table 2), while for the α2-fraction - 5.01 * 10¹⁹, the obtained values are consistent with the data of other authors [24]. When heated in an inert atmosphere to 300 °C, the concentration of PMCs in the α2-fraction increases approximately twofold with a decrease in the g-factor. With an increase in the processing temperature of the α2-fraction, a further increase in the PMC concentration and a decrease in the value of the g-factor are observed.

Table 2. Characteristics of the electron paramagnetic resonance spectra

| Sample | PMC, n/g | ΔH, G | I, rel. units | g-factor | CAMW |
|--------|----------|-------|--------------|----------|------|
| α2     | 5.0144·10¹⁹ | 5,332 | 2.1·10⁶ | 2.00307 | 12005 |
| α2 (T300) | 1.075·10²⁰ | 5,332 | 7.0·10⁶ | 2.00311 | 5600 |
| α2 (T600) | 2.575·10²⁰ | 6,665 | 1.3·10⁶ | 2.00286 | 2338 |
| β (T110) | 8.44·10¹⁸ | 5,360 | 0.4·10⁶ | 2.00295 | 71327 |

Calculation of the conditional average molecular weight (CAMW) based on the number of PMCs [24] and data on an increase in the concentration of PMCs show that during heating, the bonds between the structural fragments of macromolecules are broken with the formation of stable radicals. The EPR spectra differ in the signal intensity, which can be associated with the presence of a larger amount of condensed aromatic radicals in the α-fraction. Upon heating to 300 °C, an increase is observed, and then a sharp decrease, and already at 1200 °C, the EPR signal is not recorded. 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 shows that free radicals of the alpha and beta fractions are of the same nature and, most likely, belong to the aryl type radicals, while they are surrounded by radicals of similar structure.

To further refine the structure of the asphaltene macromolecule, the 13C NMR spectra were obtained and analyzed. The spectra contain broad bands corresponding to the resonant absorption of carbon atoms in the composition of aromatic and saturated aliphatic (δ = 0–70 ppm) and (δ = 100–170 ppm) structures. The degree of aromaticity (Fα) was calculated from the ratio of the integral intensities of peaks related...
to carbon in the aromatic ring and in saturated aliphatic structures, and from the ratio of the integral intensities of the peaks corresponding to the values of chemical shifts $\delta = 29.7$ and $\delta = 14.1$ ppm of $^{13}$C NMR signals the average chain length of the alkyl substituent ($n$) was calculated, for the $\beta$- and $\alpha_2$-fraction $n$ was 2.00 and 1.85, respectively. Based on the analysis of $^{13}$C NMR spectra, the main functional groups and structural parameters of the hypothetical average macromolecule for $\beta$- and $\alpha_2$-fractions were established. Data on the distribution of carbon by structural fragments are presented in Table 3.

### Table 3. Distribution of carbon atoms over structural fragments. $^{13}$C NMR data

| Fragment | $\%_{\beta(110)}$ | $\%_{\alpha(100)}$ | Range of $\delta^{13}$C (ppm.) | Signal assignment (according to [25]) |
|----------|-------------------|-------------------|-------------------------------|-------------------------------------|
| CH$_3$   | 2.64              | 0.97              | 0–25                          | Atoms C of aliphatic fragments       |
| CH$_2$   | 2.42              | 0.97              | 25–51                         | Atoms C of aliphatic fragments       |
| OCH$_3$  | 0.34              | 0                 | 51–67                         | C atoms of methyl esters             |
| C–O–C    | 0                 | 0                 | 67–93                         | Atoms C 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 C atoms 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 and quinone methides |

$F_{ar}$ 0.93 0.98 The degree of aromaticity, where $F_{ar} = (CAr–H + CAr–C + CAr–O) / 100$

From the data in the Table, it can be seen that the $\alpha_2$-fraction has a higher degree of aromaticity and an increased content of carbon atoms associated with oxygen, which is consistent with the results of elemental analysis. The data on the distribution of C over functional groups containing heteroatoms have a large degree of uncertainty; therefore, when constructing hypothetical structural units of organic matter, accounting for heteroatoms is often reduced to the assumption that they are mainly represented by oxygen atoms [25]. Thus, to clarify the functional-group composition associated with heteroatoms, additional studies are required.

Based on the $^{13}$C NMR spectroscopy data, using the approach described in [16], the average number of carbon atoms that make up the hypothetical aromatic nucleus of the molecule was determined. According to the calculation results, the averaged fragment of the macromolecule of both $\beta$- and $\alpha_2$-fractions consists of 25-30 carbon atoms, which are combined into a peri-condensed structure of about seven aromatic rings.

According to the data of TG and DTG analysis of CTP, $\alpha_2$- and $\beta$-fractions (Fig. 2), the nature of the thermal decomposition of pitch and its individual fractions is different. The weight loss of the test sample of the CTP begins at about 200 °C, with an increase in temperature, it increases, reaching a maximum at 340 °C, then it decreases and at temperatures above 560°C decreases slightly. It is generally accepted that the initial portion of the DTA curve is associated with processes in which the reactions of dehydropolycondensation and the association of pitch components mainly occur. Degradation processes above 340 °C are accompanied by the formation of polycondensation products based on active radicals of multi-ring aromatic compounds and products of their condensation with the formation of a solid residue. The coke residue of the pitch sample is 41%. During thermolysis of the $\beta$-fraction, three maxima are observed on the DTG curve. The first maximum at 104 °C corresponds to the evaporation of toluene trapped in a precipitate flocculating in hexane, the other two reflect the conversion of asphaltenes in the range from 260 °C to 550 °C. Intensive coke formation and gas evolution starts at 500 °C. Coke residue amounts to 60%. Three stages of weight loss can be distinguished from the DTG curves of the $\alpha_2$-fraction. The first stage with a peak at 340 °C, then the weight loss associated with the destruction process occurs at 580 °C and 750 °C. The yield of the solid residue $\alpha_2$-fraction is 86%.
Chromatographic analysis of volatile decomposition products of coal tar pitch shows the presence of a high content of polycyclic compounds in their composition, consisting of four or more nuclei [14, 23]. Our comparison of the composition of the volatile products of thermal decomposition of individual fractions of pitch showed that the bulk of polycyclic aromatic hydrocarbons (PAHs) is formed during the thermal decomposition of substances in the β-fraction. Benzo(a)pyrene and its isomers account for up to 30% of the volatile products released during thermolysis [26]. The volatile products of the α2-fraction contain an order of magnitude less PAH.

Electron microscopic analysis of coke residues of the α2-fraction showed that in the process of thermolysis, starting from a temperature of 300 °C, particles are formed in the form of hollow spherical particles, predominantly with a smooth surface, on which craters are observed, which are formed during the evaporation of the solvent and volatile decomposition products. Analysis of the fractures of the surface of crushed particles (Fig. 3) shows that the structure of the cleavage has the form characteristic of a vitreous amorphous body. Approximately from a temperature of 900 °C, a process of formation of a layered structure similar to the microstructure of needle cookes [27] is observed, which becomes pronounced when heated to a temperature of 1200 °C. The coke residue of coal tar pitch obtained at 1200 °C generally had a similar structure formed by hollow spherical particles, but differed in the presence of many different structured elements, which may be associated with the complex composition of the pitch and the nature of the reactions occurring during the thermolysis process, leading to the formation of various structures.

Figure 2. TG (-----) and DTG-curves (—) of decomposition of CTP (•) and its α2-fractions and (+) and β-fractions (■).
Figure 3. SEM images of coke residues of the α2 fraction obtained at different temperatures: (a) - 600 °C, (b) - 1200 °C and fragments of coke residues of CTP (c) and (d) obtained at 1200 °C.

4. Conclusion
Thus, the conducted studies have shown that the qualitative differences in the elemental and functional group composition of the β- and α2-fractions are not significant. However, the fractions differ significantly in the morphology of particles formed during deposition and their behavior during thermal decomposition. Thus, the β-fraction can be isolated from the CTP in the form of a finely dispersed free-flowing powder with a high uniformity of particles with a mesoporous structure.

The process of thermal decomposition of substances of each fraction is unique and differs from decomposition in the composition of coal tar pitch. It was found that the main source of PAHs during thermolysis are the components of the β-fraction. In the process of coking of powders of the α2-fraction, a layered microstructure is formed, similar to that of needle cokes.

In our opinion, the separation of pitch into individual, narrower fractions will allow finding new directions for using the components of individual fractions and obtaining precursors for the synthesis of functional carbon materials for various applications, as well as studying in more detail the influence of various pitch components on the processes of its structuring during carbonization.

Acknowledgments
The work was carried out within the framework of the state assignment for the Institute of Coal Chemistry and Material Science of FRC of Coal and Coal Chemistry SB RAS (project AAAA-A17-117041910151-9). The study was carried out using the equipment of the Kemerovo Center of Equipment Shared Use (KemCESU) of FRC of Coal and Coal Chemistry SB RAS.

The authors are grateful to O S Efimova for performing C H N S-analysis, L M Khitsova for performing thermal analysis and S A Sozinov for performing the electron microscopic analysis.
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