Study of the molecular structure of hexane-insoluble asphaltenes in coal tar pitch

S A Sozinov, L V Sotnikova, A N Popova and Z R Ismagilov

Federal Research Center of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Sciences, 18 Sovetskiy Ave., 650000, Kemerovo, Russia

E-mail: sozinov71@mail.ru

Abstract. A comprehensive study of the functional-group composition and structure of hexane-insoluble asphaltenes of coal tar pitch was carried out by methods of chemical analysis, nuclear magnetic resonance (NMR), IR spectroscopy, scanning electron microscopy, X-ray diffraction (XRD), thermal analysis in combination with chromatography-mass spectrometry. It is shown that a hypothetical macromolecule of asphaltenes can be considered as a set of condensed aromatic nuclei of the peri-condensed type of 7 rings, which have alkyl substituents and connecting bridges consisting on average of 2 carbon atoms. The ratio of various structural units in the asphaltene powder is as follows: for one S-containing structure there are 4-5 N- and 1.3-1.7 O-containing structures. Sulfur atoms are contained in thiophene-like, thermally stable fragments of the structure and pass into the coke residue without decomposition. Oxygen is contained in thermally unstable carboxyl and phenolic groups, which decompose with the release of CO₂, as well as in the composition of aromatic ethers that pass into the coke residue. The crystallographic characteristics of ordered structures formed by macromolecules of asphaltenes are studied. The average diameter of the packets is La of about 0.66 nm, with a thickness of Lc ≈ 1.30 nm, the distance between individual layers is d002 ≈ 0.34 nm, the average number of layers in the packages is n ≈ 5 - 7 pieces. In this case, the crystallinity of asphaltene powders does not exceed 30%. The data obtained by different methods are in good agreement and more fully characterize the structure of macromolecules of asphaltenes of coal tar pitch.

1. Introduction

When studying the processes occurring during the production of carbon-graphite materials from heavy products of processing of natural sources of hydrocarbons, it was found that the asphaltene fraction can serve as a promising economically viable source for obtaining practically important products. The composition of asphaltenes includes high-molecular components of hydrocarbon raw materials, distinguished by their solubility as substances soluble in toluene and insoluble in alkanes. Asphaltenes have a layered-block supramolecular organization of macromolecules with a crystal-like proturbostrate structure. They do not have a strictly defined composition and are characterized by a set of structural and functional groups included in macromolecules with molecular weights of a wide distribution [1-4]. The literature describes many different models of the structure of a hypothetical asphaltene molecule, which satisfactorily describe the main properties of asphaltenes [5]. Previously, asphaltenes from various initial products of coal and petrochemicals were studied [6]. At the same time, the main part of publications concerns the characterization of oil asphaltenes and is aimed at finding ways to prevent their self-organization into aggregates that impede oil...
production and transportation [7]. However, the study of the process of self-organization of asphaltene macromolecules may be useful for solving some issues of nanotechnology, in particular, it promotes the search for new ways to obtain ordered layers of precursors of carbon-graphite materials [8-13].

Despite the fact that it is not possible to determine the composition and structure of individual macromolecules of asphaltenes, information on the functional group composition is necessary to understand the processes of self-organization of macromolecules during the formation of ordered forms of carbon-graphite materials. In addition, the functional group composition of asphaltenes, depending on their source of origin, is different, therefore, at the first stage of the search for ways to create new functional materials based on heavy coal chemistry products (pitches, bitumens, coal tar), it is necessary to study the functional group composition and structure of all components, including asphaltenes. According to the literature data, the complexity of the task is that, when characterizing the composition and structure of asphaltene macromolecules, there are not enough data from individual research methods, because almost all data on the structure of asphaltenes obtained by traditional methods have limitations for various reasons. So, according to the data of IR spectroscopy, it is impossible to determine the quantitative ratios of functional groups, the limitation of the method is associated with the effect of particle dispersion on the processes of scattering and absorption of working radiation [14]. The presence of associates in solutions additionally complicates their study by the NMR method [14]. Isolation of asphaltenes from multicomponent products leads to the fact that after flocculation of the sediment, which mainly contains the asphaltene fraction, it is difficult to qualitatively separate their molecules from the accompanying maltenes molecules, which ensure the colloidal stability of asphaltenes in solution, as well as from solvent molecules. Depending on the content of maltenes and solvent, the data of elemental, thermal and other methods of analysis can be interpreted in different ways.

Therefore, in this work, to characterize the functional-group composition and structure of hexane-insoluble asphaltenes in coal tar pitch, an integrated research approach was applied by combining various physicochemical research methods: chemical elemental analysis, nuclear magnetic resonance (NMR) and IR spectroscopy, scanning electron microscopy. X-ray diffraction (XRD), differential thermal analysis in combination with gas chromatography-mass spectrometry. The data obtained by a set of methods make it possible to refine both the structure of macromolecules of asphaltenes in coal tar pitch and to check the reliability of the data obtained by separate methods.

2. Experimental

Asphaltenes were isolated from the toluene extract of medium-temperature coal tar pitch (CTP) (softening temperature ≈ 87 °C) by dilution with n-hexane. The extract was obtained from the components at a ratio of 1 g pitch/40 mL of toluene. The precipitation of asphaltenes was carried out by adding 200 mL of n-hexane. After flocculation, the precipitate was kept in solution for a day, then it was filtered and washed from the adsorbed maltenes with n-hexane. Then to remove the residues of the precipitant the precipitate was dried at a temperature of 80 °C.

The morphology of asphaltene powder particles and their elemental composition were investigated using a JEOL JSM6390 SEM scanning electron microscope with an attachment for elemental analysis JED 2300. The content of C, H, N, S, O in the powder particles was investigated using an automatic elemental analyzer Flash 2000.

Data on the distribution of hydrogen and carbon atoms over various hydrocarbon structures in asphaltenes of coal tar pitch were obtained from 1H and 13C NMR spectra. NMR spectra of asphaltene macromolecules were recorded on a Bruker Avance II + 300 WB spectrometer (300 MHz). Chemical shifts are indicated relative to tetramethylsilane. The quantitative NMR spectra were calculated according to the procedures described in [15, 16].

The composition of the functional groups of macromolecules was investigated by FTIR spectroscopy on an Infralum FT-801 spectrometer. IR spectra were recorded in the range 550–5500
cm$^{-1}$. To record IR spectra in the solid phase, tablets were prepared by pressing the powder of the studied asphaltene powders with KBr.

Thermal conversion reactions of asphaltenes were studied using a NETZSCH 449 F3 Jupiter synchronous thermal analyzer. The analysis was carried out in an inert atmosphere under conditions of dynamic heating at a rate of 10 g / min in the temperature range from 25 °C to 650 °C and a sample weight of 5 mg.

The composition of solid and volatile thermolysis products was studied by X-ray diffraction and chromatography-mass spectrometric analysis, respectively.

Determination of the phase composition and structure of the initial powders and coke residues of asphaltenes was carried out according to the procedure [17-20] using the data obtained on a Bruker D8 ADVANCE A25 powder X-ray diffractometer. Diffraction patterns were analyzed with the Diffrac.Suite.Eva software package for data collection and processing (V3.1). The diffraction patterns were decoded using the ICDD PDF-2 database.

The analysis of the component composition of volatile products of thermal conversion of asphaltenes was studied by gas-liquid chromatography and mass spectrometry on an Agilent 6890N chromatograph with an Agilent 5973 mass-selective detector with an HP-5ms capillary column (phase - 5% -phenyl-95% -methylpolysiloxane, 30 m x 0.25 mm x 0.25 μm); evaporator temperature 250 °С; programmed increase in the column temperature from 50 °C with holding for 3 min to 290 °С at a rate of 8 °C / min, holding at 290 °С for 3 min; solvent removal - 0.5 min, flow division 100:1, helium carrier gas flow rate 1 mL / min, aliquot volume for analysis 0.2 μL. The identification of the component composition of the sample under study by mass spectra was carried out using the NIST11 spectra library.

### 3. Results and discussion

To determine the average empirical formula of the macromolecule of asphaltenes, studies of the elemental composition of asphaltenes were carried out (Table 1). To formulate the asphaltene macromolecule formula, it was assumed that the macromolecule fragment includes one of the heteroatoms, the total content of which in the average hypothetical molecule is about 3% according to elemental analysis data. With this assumption, the molecular weights of the structural units of asphaltene macromolecules can range from 500 to 1000 amu. The ratio of various structural units in asphaltene powder is such that one S-containing structure has 4-5 N- and 1.3-1.7 O-containing structures, while the number of carbon atoms can be from 39 to 77 pieces per one heteroatom. The calculation of the relative content of elements per carbon atom is given in Table 1. On average, there is one hydrogen atom for 2 carbon atoms, and one S, N or O atom for 500, 50 or 167 carbon atoms, respectively.

#### Table 1. Elemental composition of asphaltenes according to C, H, N, S, O analysis

| Sample | C   | H   | S   | N   | O   | H/C | S/C | N/C | O/C |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| A1     | 91.69 | 4.19 | 0.41 | 2.07 | 0.7 | 0.5 | 0.002 | 0.02 | 0.006 |
| A2     | 92.03 | 4.38 | 0.53 | 2.23 | 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 |
For further detailing of the structure of asphaltene macromolecule, their IR spectra were obtained and analyzed (Figure 1).

![Figure 1](image_url)

**Figure 1.** (a) IR spectrum of asphaltenes; (b) TG and DTG curves of decomposition of asphaltenes of CTP superposition of the curves of registration of ion currents (IT) with different values of m / z: 28 (1), 44 (2), 30 (3), 46 (4).

The IR spectra of CTP asphaltenes differ mainly in the presence of absorption bands caused by the vibrations of the C-C and C-H bonds of aromatic condensed systems, cyclic, conjugated and aliphatic fragments. The absorption bands in the range of 2850-3050 cm⁻¹ are caused by stretching vibrations of conjugated bonds of aromatic CH-groups (3049 cm⁻¹), symmetric and asymmetric vibrations of CH bonds in CH₃ (2924 cm⁻¹) and CH₂ (2855 cm⁻¹) aliphatic groups. Bending vibrations of C-H bonds of aromatic condensed systems are observed in the range of 715-900 cm⁻¹, and CH₂ and CH₃ of aliphatic groups in the range of 1300-1450 cm⁻¹. The intensity of the bands due to the absorption of terminal methyl groups (2924, 1445 cm⁻¹) in the IR spectra of asphaltenes indicates the predominance of short alkyl substituents in the structure of their molecules. An intense absorption band in the range 1600-1800 cm⁻¹ is caused by the superposition of absorption bands characterizing the stretching vibrations of carbonyl \( \text{C} = \text{O} \) groups and vibrations of conjugated \(-\text{C} = \text{C}\) bonds of the aromatic nucleus, indicating a high content of such structural fragments in the composition of asphaltene molecules of CTP with the overwhelming predominance of aromatic structures. The absorption bands in the range 900-1400 cm⁻¹ are due to the presence of nitrogen-, sulfur- and oxygen-containing groups in the structure of the studied molecules. Due to the low intensity and multiple superposition of absorption bands in this region, the structure of heteroatomic functional groups could not be identified by IR spectroscopy.

The structural group characteristics of the hypothetical “middle molecule” of asphaltenes were calculated using NMR spectroscopy data. For this, the relative content of protons in various structural fragments was determined from the area of the peaks in the corresponding regions of the \(^1\text{H}\) NMR spectrum. \(^{13}\text{C}\) NMR spectroscopy data were used to establish the distribution of carbon by functional groups. The \(^{13}\text{C}\) NMR spectrum of asphaltenes contains broad absorption bands of carbon atoms in saturated (0–70 ppm) and aromatic (100–170 ppm) structures. The aromatic factor was calculated from the ratio of the integral intensities of the peaks related to the aromatic and saturated structures, and the chain length of the alkyl substituent was calculated from the ratio of the integral intensities of the frequency peaks at 29.7 and 14.1 ppm.

Analysis of the ranges of chemical shifts (δ) characteristic of the corresponding groups of hydrogen atoms in the \(^1\text{H}\) NMR spectra [14] indicates the presence of hydrogen in aromatic rings...
(region from 6.7 to 9.0 ppm) and in aliphatic groups of various lengths (region less than 4.5 ppm) with an insignificant proportion in olefinic compounds (range from 6.7 to 4.5 ppm), the content of which is 58%, 40% and 2%, respectively.

Important structural characteristics were calculated, such as the degree of substitution of aromatic rings (σ), average length of alkyl substituents in aromatic rings (n), degree of aromaticity (Far), 0.12, 2.27, and 0.896, respectively.

Based on the analysis of $^{13}$C NMR spectra, the main functional groups and structural parameters of the average macromolecule of asphaltenes of coal tar pitch were established. The data on the distribution of carbon by structural fragments are presented in Table 2.

**Table 2. Distribution of carbon atoms over structural fragments of asphaltenes according to $^{13}$C NMR data**

| Fragment | %   | XC 13C range (δ, ppm) and signal assignment                                      |
|-----------|-----|----------------------------------------------------------------------------------|
| CH$_3$    | 2.64| 0-25 carbon atoms of aliphatic fragments                                          |
| CH$_2$    | 2.42| 25-51 carbon atoms of aliphatic fragments                                          |
| OCH$_3$   | 0.34| 51-67 carbon atoms of methyl esters                                              |
| C-O-C     | 0   | 67-93 carbon atoms of bridging fragments                                          |
| Ar-H      | 40.70| 93-125 tertiary carbon atoms of aromatic rings                                     |
| Ar-C      | 52.34| 125-148 quaternary carbon atoms of aromatic rings                                 |
| Ar-O      | 0.23| 148-171 carbon atoms of aromatic rings bonded to oxygen atoms                    |
| COOH      | 1.33| 171-187 carbon atoms of carbonyl groups                                            |
| C=O       | 0   | 187-235 carbon atoms of ketones, aldehydes, quinone methides                        |
| Fa        | 0.93| Degree of aromaticity, $Fa = I_{total} / I_{aromatic carbon atoms}$                |

Based on the data of $^{13}$C NMR spectroscopy, using the approach [16], the average number of carbon atoms included in the hypothetical aromatic nucleus of the molecule was determined. According to the calculation results, the structure of the polyaromatic core of the middle fragment of the asphaltene macromolecule consists of about 30 carbon atoms, which are combined into 7 aromatic rings with a peri-condensed type structure. The degree of aromaticity measured from the $^{13}$C NMR spectra $Fa = 0.92$, the value obtained is in good agreement with the $Fa$ value calculated from the $^1$H NMR spectra in solution ($Fa = 0.90$). Thus, the combination of $^1$H NMR and $^{13}$C NMR spectroscopy data makes it possible to quantitatively measure the content of individual groups, which provides sufficient information to construct the carbon structure of a hypothetical asphaltene molecule.

The greatest difficulty is the study of the distribution in macromolecules of asphaltenes of functional groups containing heteroatoms. It is known [4] that N atoms are found in heteroaromatic fragments of pyridine, pyrrole and porphyrin nature, S atoms - in the form of sulfide, thiol groups and in thiophene rings, O atoms - in the form of hydroxyl, carboxyl, ether, carbonyl groups and furan rings.

Often, when constructing hypothetical structural units of the organic mass of coal, accounting for heteroatoms is reduced to the assumption that they are represented mainly by oxygen atoms [1]. The elemental composition of the CTP asphaltene studied in this work is distinguished by an increased content of N atoms, for the distribution of which over structural groups the IR and NMR data cannot give a clear answer. To clarify the structure of structural fragments containing N and S atoms, thermal analysis of asphaltenes was carried out with the collection and study of the composition of volatile products and coke residues from the destruction of asphaltenes. The results obtained suggest the structure of heteroatomic functional groups based on the data on the behavior of substances of a similar chemical nature under thermolysis conditions [23].

The TG and DTG curves of the decomposition of CTP asphaltene are shown in Figure 2. Three maxima are observed during the thermolysis of asphaltene, the first maximum corresponds to the evaporation of the solvent (toluene) trapped by the asphaltene precipitate flocculating in hexane, the
other two reflect the process of asphaltene conversion in the range from 260 °C to 550 °C. Intensive coke formation and gas evolution begin at 500 °C.

The method of chromatography-mass spectrometry of volatile products of thermal destruction of asphaltenes (Figure 2) reveals a significant amount of polyaromatic and aromatic N-containing compounds. The amount of volatile compounds containing S will vary depending on the quality of the removal of maltenes. The absence of O-containing compounds is explained by the elimination of fragments with oxygen in the form of simple products with low molecular masses (CO, CO₂), the release of ions characteristic of such products with m / z = 28 and m / z = 44 is recorded in the mass spectra during heating in the temperature range 320 °C - 520 °C. The accumulation of oxygen in coke residues indicates the presence of aromatic ethers in the structure, the thermal stability of which is known.

In coke residues (Table 6), there is an accumulation of carbon (92%), sulfur (0.5%) and oxygen (3%) with a decrease in the content of hydrogen (3%) and nitrogen (1.5%).

The dependence of the amount of S-containing products on the admixture of maltenes in the asphaltene powder can be explained by the fact that macromolecules of maltenes contain thioether bonds, which are destroyed upon thermal action. Because sulfur, which is a part of asphaltene molecules, does not split off when heated to 650 °C; it can be argued that sulfur atoms of asphaltenes are localized only in aromatic fragments.

The inclusion of nitrogen atoms stabilizes the structure of aromatic molecules at temperatures below 500 °C and promotes the condensation of polyaromatic compounds [22]. A decrease in the nitrogen content in coke residues and the presence of N-containing compounds in the composition of volatile products indicate several types of nitrogen bonds in the asphaltene macromolecule. According to the thermal analysis data with the registration of mass spectra during the decomposition of asphaltenes, two ranges are recorded that characterize the formation of nitrogen-containing thermolysis products (ions with m / z = 30 (NO) and m / z = 46 (NO₂)) at T = 320 °C - 530 °C and at temperatures above 530 °C.

![Figure 2. Chromatogram for the total ionic current of the hexane extract of the products of thermal destruction of CTP asphaltenes.](image-url)
The study of the structure of asphaltenes by XRD shows that the initial asphaltene powders consist of particles with a turbostratic structure. The crystallographic parameters of turbostratic carbon structures were calculated from the position, intensity, and width of the signal in the 2θ range from 22 to 28 deg. The average diameter of the packages - La is about 0.66 nm, with a thickness of Lc ≈ 1.30 nm, the distance between individual layers is d002 ≈ 0.34 nm, the average number of layers in the packages is n ≈ 5 - 7 pieces. In this case, the crystallinity of the samples does not exceed 30%. Calculation of the number of aromatic rings in a packet suggests that, on average, the arene layer contains 6 - 7 aromatic rings.

4. Conclusion
As a result of a complex of methods for studying the composition and structure of asphaltenes in coal tar pitch, it was established that the hydrocarbon skeleton of an average hypothetical macromolecule of asphaltenes can be considered as a set of condensed aromatic nuclei of the overcondensed type of 7 rings, which have alkyl substituents and connecting bridges consisting on average of 2 carbon atoms. In this case, on average, there is one hydrogen atom per 2 carbon atoms.

Of greatest interest is the study of the distribution of heteroatoms in the structure of asphaltenes: S, N, O. On average, one S, N, or O atom is contained in a structure of 500, 50, or 167 carbon atoms, respectively. The ratio of various structural units in the asphaltene powder is as follows: for one S-containing structure there are 4-5 N- and 1.3-1.7 O-containing structures. Sulfur atoms are contained in thiophene-like, thermally stable fragments of the structure and pass into the coke residue without decomposition. Oxygen is contained in thermally unstable carboxyl and phenolic groups, which decompose with the release of CO2 and in the composition of aromatic ethers that pass into the coke residue. Nitrogen-containing structures undergo thermal decomposition in two temperature ranges; additional studies are required to determine the structures corresponding to this behavior.

The research results obtained by various methods are in good agreement with each other and complement the general picture of the structure of asphaltene macromolecules.

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

References
[1] Patrakov Yu F, Fedyaeva O N and Kamyanov V F 2005 Fuel 84 (2) 189-99
[2] Fedyaeva O N, Patrakov Yu F 2004 Solid Fuel Chem. 5, 24-31.
[3] Dolomatov M Yu, Shutkova S A and Dezortsev S V 2012 Journal of Structural Chemistry 53 (3) 569-73
[4] Shutkova S A, Dolomatov M Yu 2016 Bashkir Chemical Journal 23 (3) 15–9
[5] Galimova G A et al 2015 Bulletin of Technological University 18 (20) 60–4
[6] Sozinov S A et al 2018 Coke and Chem. 61(11) 447–452
[7] Akbarzade K. et al 2007 Oil and Gas Review 3 28–53
[8] Sozinov S A et al 2018 Coke and Chem. 61(2) 72-7
[9] Anikeeva I V et al 2012 Chemistry of Solid Fuel 4 70-3
[10] Qu W –H et al 2016 J. Phys. Chem. 6 1–28.
[11] Kuzeev I R et al. 2011 Formation of fullerenes in the structure of iron-carbon alloys during crystallization, phase transitions and deformation Oil and Gas Business 6 411-419.
[12] Dickakian Gh, Greenville S C Aromatic pitch from asphaltene fractions. USA Patent No. 4518483. May 21. 1985.
[13] Berveno V P et al. 2005 *Chemistry for Sustainable Development* **13** (3) 423-6
[14] Beiko O A et al. 1988 *Chemical Composition of Oils in Western Siberia. (Novosibirsk: Science. Siberian Branch)* p 288
[15] Kalabin G A 2000 Quantitative NMR Spectroscopy of Natural Organic Raw Materials and Products of its Processing (Moscow: Chemistry) p. 408
[16] Solum M S, Pugmire R J and Grant D.M. 1989 *Energy & Fuels* **No. 3.** P. 187-193.
[17] Popva A N 2017 *Coke and Chem.* **60**(9) 32-6
[18] Khokhlova G P, Barnakov Ch N and Popova A N 2016 *Coke and Chem.* **59**(1) 32-39.
[19] Barnakov Ch N et al 2015 *Chemistry of Solid Fuel.* **1.** 28-32
[20] Popova A N 2017 *Butlerov communications* **51**(7) 86-90
[21] Barnakov Ch N et al 2015 *Eurasian Chemico-Technological Journal* **17**(2) 87-93
[22] Barnakov Ch N et al 2015 *Chemistry of Solid Fuel.* **1** 28-32