

# Study of the Stage Determining the Emission of Carcinogenic Polycyclic Aromatic Hydrocarbons during the Carbonization of the Medium-Softening-Point Pitch

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(Received October 24, 2001)

## Abstract

Composition and properties of the main products of slow heating carbonization (1 °C/min) of the medium-softening-point pitch – tar and solid carbon residue – are studied at different final temperatures. Temperature ranges are determined in which the major amount of tar (640–750 °C) and carcinogenic PAH (700–800 °C) is evolved. It is demonstrated, by determining and comparing the specific surface of carbon residue before and after extraction with benzene, PAH content of the pyrolysis tar and in the extract of carbon residue within the range 700–750 °C, that the emission of carcinogenic PAH within this temperature range is determined by their desorption from the porous structure of the carbon residue at the stage of finishing the formation of pitch coke. At 750–800 °C, the formation of carcinogenic PAH is determined mainly by gas-phase transformation of hydrocarbon fragments that appear during the formation of graphite-like structure.

## INTRODUCTION

Carbonization of hydrocarbon raw material is accompanied by the release of tarry matters containing carcinogenic polycyclic aromatic hydrocarbons (PAH). In the recent years an increasing attention is attracted to problems connected with the understanding of the routes by which carcinogenic PAHs are formed. Investigations considering the formation of the structure of solid carbon residue during the carbonization of pitches and compositions based on them [1–13], emission of volatile products [1–9, 11, 12, 14–18], including carcinogenic PAHs [8, 9, 16–18], during the carbonization of pitches and anode masses based on them,

are known. However, random variation of the composition of raw material, intricacy of laboratory modeling of the industrial carbonization processes and analytical monitoring of a wide range of carcinogenic PAHs bring substantial ambiguity into the reliability of the data on the routes of the formation and emission of carcinogenic PAHs at different stages of carbonization.

In our preliminary studies [19, 20] for the example of medium- and high-softening-point coal tar pitches, we studied carbonization process under comparable conditions allowing one to perform the statistical treatment of the necessary amount of experimental data and to take into account random variation of the

raw material. Study of the dynamics of the evolution of individual components of the gas mixture allowed us to connect the evolution of definite gases with the main stages of carbonization of medium-softening-point pitch [19]: 1) 420–520 °C – intensive evolution of C<sub>1</sub>–C<sub>3</sub> hydrocarbons and CO is the evidence of thermal destruction, dealkylation and low-temperature polycondensation; 2) 520–640 °C – a monotonous increase of the amount of methane, hydrogen and CO is the evidence of pyrolysis processes; 3) 640–800 °C – intensive evolution of hydrogen and methane is the evidence of high-softening-point polycondensation and dehydrogenation. It is demonstrated that the major amount of tar and carcinogenic PAHs is released at temperature above 640 °C [19].

The purpose of the present paper is to study the stage that determined the evolution of carcinogenic PAHs during the carbonization of medium-softening-point coal tar pitch. On the basis of literature analysis, we chose benz(a)anthracene, benz(a)pyrene and dibenz(a,h)anthracene as characteristic carcinogenic PAHs [21–23].

## EXPERIMENTAL

The medium-softening-point coal tar pitch from Novokuznetsk was used as the material for study. Technical characteristics of the pitch were determined at the Central Plant Laboratory of the Krasnoyarsk Aluminium Plant according to the standard procedures: softening temperature (ring – rod), 75 °C; the content of benzene-insoluble substances: 34.3 %; quinoline-insoluble: 13.8 %; the yield of volatile substances, 55.0 %; ash content, 0.10 %.

Thermochemical transformation of the pitch was performed in an inert atmosphere (He) under the linear increase of the furnace temperature to 300 °C at a rate of 10 °C/min, above 300 °C at a rate of 1 °C/min to the final carbonization temperatures of 400, 520, 640, 700, 750 and 800 °C. The set-up and procedure are described in detail in [19]. The content of substances insoluble in benzene ( $\alpha$  fraction), in the initial pitch and in the carbon residue was determined using the standard procedure

(GOST 28357–89). The determination was performed as follows: 100 ml of benzene was added to the ground sample of 1 g (for the initial pitch, the fraction <0.5 mm; for carbon residue, the fraction <0.2 mm). The resulting suspension was boiled with a backflow condenser for 1 h, filtered; the precipitate on the filter was washed with hot benzene and dried to constant mass. The PAH content in the filtrate (extract of the carbon residue) was determined.

The analysis of PAH by means of GC/MS was performed with a HP 6890A gas chromatograph (capillary column HP-5MC 30 m  $\times$  0.25 mm, phase thickness 0.3  $\mu$ m) with mass-selective detector HP 5972A. The conditions of the GC/MS analysis: initial temperature of the thermostat of column: 70 °C; linear heating of the column at a rate of 10 °C/min; final temperature, 300 °C; evaporator temperature, 280 °C; sampling volume 1  $\mu$ l. The PAHs were identified according to retention time of the known compounds from standard samples and by comparing of the experimental mass spectra with those from the NIST CSD database (62 000 compounds) with the help of the standard system of data treatment Chem Station.

The GC/MS analysis was performed in two regimes:

- recording the total ion current with the identification of PAHs by comparing full experimental mass spectra with the mass spectra from the database (detection limit for individual PAHs: 0.1 %);

- recording individual ions with the identification of fifteen non-substituted PAHs according to characteristic ion and retention times using the standard solution of PAH mixture for the EPA-610 procedure (detection limit for individual PAHs: 0.001 %).

The analysis of PAHs by means of GLC was performed using the procedure similar to EPA-610 as described in [24]. Total PAH content ( $\Sigma$ PAH) was determined as a sum of anthracene and phenanthrene concentrations (A + P) and the concentrations of nine individual PAHs: fluoranthene (Fl), pyrene (Py), benz(a)anthracene (BaA), chrysene (Ch), benz(b)fluoranthene (BbF), benz(e)pyrene (BePy), benz(a)pyrene (BaPy), dibenz(a,h)anthracene (DBA), and benz(g,h,i)perylene (BP). The profiles of

PAHs (fractions of individual PAHs in  $\Sigma$ PAH) were calculated according to the equation:  $HF = C_i/C_{\Sigma PAH}$ , where HF is hydrocarbon fraction,  $C_i$  is mass fraction of an individual PAH, %;  $C_{\Sigma PAH}$  is the total mass fraction of PAHs, %.

The yield of the products of pitch carbonization (solid carbon residue, a fraction, tar,  $\Sigma$ PAH, BaPy, BaA, DBA) was calculated in per cent from the mass of initial pitch using the equation  $B = (m/M) \cdot 100$ , where  $m$  is the mass of product and  $M$  is the mass of initial pitch. Mass fraction of the  $\alpha$  fraction in the carbon residue was determined using the equation  $C_{\alpha} = (m_{\alpha}/M_{c.r.}) \cdot 100$  where  $m_{\alpha}$  is the mass of  $\alpha$  fraction,  $M_{c.r.}$  is the mass of carbon residue.

The specific surface of the carbon residue and  $\alpha$  fraction was calculated using thermal desorption of argon. In order to determine  $S_{c.r.}$ , we used the obtained carbon residue (fraction <0.2 mm). In order to determine  $S_{\alpha-fr.}$ , we used the  $\alpha$  fraction of the solid carbon residue washed with benzene after having determined  $S_{c.r.}$ .

The Figures 1–6 and Tables 1–3 show the results of statistical analysis indicating the amount of sampling.

#### ANALYSIS OF PYROLYSIS TAR AT DIFFERENT TEMPERATURES OF PITCH CARBONIZATION

Tars containing carcinogenic PAHs are released at high-temperature stage of carbonization (640–800 °C) [19]; because of this, it is interesting to study in detail the yield and composition of tar within this temperature range.

GC/MS study of the initial pitch and its carbonization tars within temperature region 640–750 °C allowed us to identify ninety six individual compounds, many of which exhibit carcinogenic and mutagenic activity. The contents of unsubstituted PAHs and their alkyl derivatives, oxygen-, sulphur-, and nitrogen-containing compounds, determined by means of internal normalizing, are shown in Table 1. Fifteen unsubstituted PAHs (Table 2) were determined quantitatively in the initial pitch and in the tars of its pyrolysis with the help of the standard solution of PAH mixture for the EPA-610 procedure.

The analysis of the initial pitch demonstrates that the major part of the identified compounds consists of PAHs and their alkyl derivatives (see Table 1). The obtained quantitative results are compared with the literature data [1, 8] (see Table 2). Pitches from different plants, characterized by close softening points (68–74 °C) are substantially different from each other in the quantitative contents of some components or separate groups [8]. The content of the major part of the identified PAHs in the initial pitch almost coincides with the literature data (naphthalene, acenaphthene, fluorine, benz(a)-anthracene) or differs insignificantly (phenanthrene+anthracene); however, for some hydrocarbons (fluoranthene, pyrene, chrisene, benz(a)pyrene, perylene) the obtained values are 2–5 times lower than those reported in literature (see Table 2).

The qualitative composition of the identified organic compounds in carbonization tars coincides with that of the initial pitch (see Table 1). As the results shown in Table 2 demonstrate, in comparison with the pitch, the carbonization tar exhibits increased content of the compounds having 2–4 benzene rings. For example, the content of phenanthrene and anthracene increases by an order of magnitude. The total PAHs content increases most noticeably within the temperature range 700–750 °C.

It is important to note that the phenanthrene content of pitch and its pyrolysis tar is 2–4 times more than anthracene. It is known that in the high-temperature tar of coal pitch, the PAHs of angular structure prevail over the hydrocarbons of linear structure, which is connected with higher thermal stability of the isomers with angular structure [8].

Thus, the described data show that the content of almost all the PAHs in carbonization tars increases with increasing temperature.

The statistical analysis of PAHs in tar released at different carbonization temperatures, performed by means of GLC, allowed us to determine the yield of tar and PAH in more detail (Table 3, Fig. 1), and to examine the PAH composition of tar (Fig. 2) at different carbonization temperatures.

At 520 °C, the release of the primary tar is observed; it contains mainly low-molecular

TABLE 1

PAH content determined by means of GC/MS with internal normalization in the initial medium-softening-point pitch and tars of its carbonization at different temperatures (heating rate: 1 °C/min), %

Substance	Initial pitch	Carbonization tar		
		640 °C	700 °C	750 °C
Phenol and methylphenols	n/d*	0.1	0.5	0.4
Naphthalene	1.2	0.2	5.2	3.1
Methylnaphthalenes	0.3	1.2	5.7	4.1
Biphenyl	0.1	0.1	0.6	0.4
Methylbiphenyls	0.1	0.8	0.5	0.3
Acenaphthylene	n/d	0.3	1.3	1.7
Acenaphthene	1.3	1.4	2.8	2.1
Fluorene	0.7	4.2	5.7	4.4
Methylfluorenes	0.2	1.4	0.8	0.7
Phenanthrene	4.1	17.0	19.6	19.7
Anthracene	1.2	13.3	7.1	5.7
Methylantracenes and methylphenanthrenes	1.3	5.1	2.9	2.4
Fluoranthene	6.2	8.7	10.1	10.3
Pyrene	6.3	7.3	8.8	11.6
Methylpyrenes	1.1	1.7	0.5	1.1
Benzofluorenes	1.8	2.4	1.6	1.7
Benz(a)anthracene	3.3	0.9	0.6	1.2
Methylbenz(a)anthracene	0.7	0.1	n/d	0.1
Chrysene	3.9	2.6	2.2	4.1
Methylchrysenes	1.0	n/d	n/d	n/d
Binaphthalenes	0.6	»	»	»
Benzfluoranthenes	4.8	1.1	0.3	1.6
Benzpyrenes	7.8	0.5	0.2	1.3
Perylene	1.9	n/d	n/d	n/d
Indeno(1,2,3-cd)pyrene	3.5	»	»	»
Dibenz(a,h)anthracene	0.4	»	»	»
Benz(g,h,i)perylene	3.4	»	»	»
Dibenzochrisene	2.6	»	»	»
<b>S-PAH</b>				
Benz(b)thiophen	0.1	»	»	0.2
Dibenzothiophen	0.2	1.0	0.9	0.9
Benz(b)naphtha(2,1-d)thiophen	0.5	0.4	0.3	0.5
Benz(b)naphtha(2,3-d)thiophen	0.9	0.1	n/d	0.1
<b>N-PAH</b>				
Isoquinoline	n/d	0.1	0.5	0.4
Quinoline	»	n/d	n/d	0.1
Methylquinolines	»	»	0.2	0.2
Acridine	0.4	1.4	n/d	1.3
Benzoquinolines	0.2	0.6	2.6	0.6
Carbazole	1.0	10.3	1.6	4.5
Methylcarbazoles	0.3	1.7	0.8	0.6
Acenaphtho(1,2-b)pyridin	0.8	0.5	n/d	0.7
Benz(a)acridine	0.7	0.2	0.2	0.3
Benzcarbazoles	2.0	1.0	n/d	0.4
<b>O-PAH</b>				
Dibenzofuran	0.4	1.2	3.2	2.8
Methyldibenzofurans	0.2	1.0	1.7	1.1
Benzonaphthofurans	0.3	0.8	1.5	0.7

\*Not detected.

TABLE 2

Fraction of non-substituted PAHs determined by means of GC/MS in the initial medium-softening-point pitch (% of the mass of pitch) and in its carbonization tars (% of tar mass) at different temperatures (heating rate: 1 °C/min)

Substance	Initial pitch		Carbonization tar		
	Our data	[1, 8]	640 °C	700 °C	750 °C
Naphthalene	0.31	0.1–0.79	0.22	2.88	3.43
Acenaphthylene	n/d*		0.46	0.82	2.59
Acenaphthene	0.29	0.14–1.15	1.58	1.29	2.59
Fluorene	0.24	0.17–0.47	7.59	4.91	8.86
Phenanthrene	1.48	2.69–3.97	23.09	16.79	28.50
Anthracene	0.28		16.39	3.80	6.85
Fluoranthene	1.52	2.82–4.26	10.51	6.17	11.97
Pyrene	0.84	2.86–4.49	5.19	3.06	8.73
Benz(a)anthracene	0.90	0.79–1.6	0.92	0.47	1.39
Chrysene	0.84	3.63–5.51	2.17	1.17	3.49
Benz(b)fluoranthene	0.87		0.52	0.22	1.14
Benz(a)pyrene	1.10	4.26–10.29	0.29	0.10	0.53
Perylene	0.27	1.03–1.96	0.08	0.03	0.17
Dibenz(a,h)anthracene	0.16		0.02	0.01	0.04
Benz(g,h,i)perylene	0.69		0.08	0.03	0.14

\*Not detected.

PAHs (mass fraction of anthracene and phenanthrene being more than 70 %) (see Fig. 2). At further increase of temperature, the yields of tar, ΣPAH and individual carcinogenic PAHs increase (see Table 3, Fig. 1). The fraction of ΣPAH in tar increases from  $0.03 \pm 0.02$  to  $0.54 \pm 0.05$  while temperature increases from 520 to 800 °C (see Table 3), first of all due to the increase of the fraction of high-molecular PAHs (Fl, BaA, Ch, BbF, BePy, BaPy, DBA, and BP) with the maxima related to pyrene

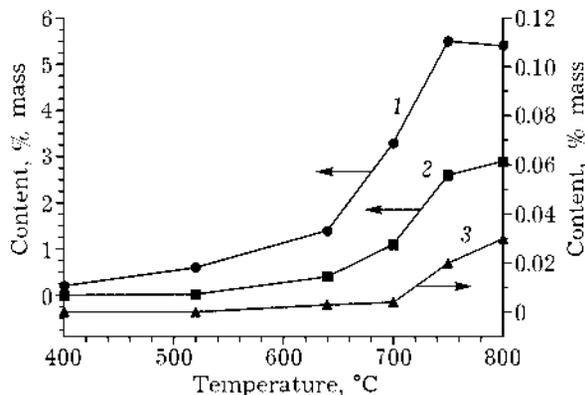


Fig. 1. The yield of tar, PAH sum and benz(a)pyrene (per cent of pitch mass) depending on pitch carbonization temperature (sampling listed in Table 3): 1 - tar, 2 - ΣPAH, 3 - BaPy.

and chrysene (see Fig. 2). The main amount of tar is formed within temperature range 640–750 °C, while the major part of PAHs, including carcinogenic ones, is evolved within temperature range 700–800 °C (see Fig. 1, Table 3). Especially noticeable increase of the yield of ΣPAH (from  $1.1 \pm 0.2$  to  $2.6 \pm 0.3$  %) and carcinogenic PAHs (BaPy yield increasing from  $0.004 \pm 0.001$  to  $0.02 \pm 0.01$  %) is observed within temperature range 700–750 °C (see Table 3). At a temperature above 750 °C, tar is not formed, though the yield of ΣPAH increases due to high-molecular PAHs (see Fig. 2).

Thus, the most intensive formation of PAHs, including carcinogenic ones, occurs within a narrow temperature range (700–750 °C); the increase of their content is connected, on the one hand, with the increase of the tar yield, on the other hand, with the increase of the content of carcinogenic PAHs in the tar. Within the range 750–800 °C, the increase of the content of carcinogenic PAHs in the pyrolysis tar occurs only due to the changes in the composition of PAHs. This may be due to the different routes of PAH formation within temperature ranges 700–750 and 750–800 °C.

TABLE 3  
Content of tarry matter and carcinogenic PAHs in the pyrolysis tar and in the benzene extract of carbon residue at different final carbonization temperatures of the medium-softening-point pitch (heating rate: 1 °C/min), % mass

T, °C/ Sampling (tar, extract)	Tarry matter (gas phase)				Benzene extract of carbon residue				Fraction of ΣPAH		
	Tar	ΣPAH	BaPy	BaA	DBA	ΣPAH	BaPy	BaA	DBA	Tar (gas phase)	Extract of carbon residue
Initial pitch/13						9.8±0.6	0.8±0.1	1.1±0.2	0.41±0.08		0.15±0.01
400/2						6.6±1.4	0.8±0.2	0.7±0.2	0.46±0.08		0.12±0.03
520/3, 2	0.6±0.1	0.02±0.01	< 0.001	< 0.001	< 0.001	3.6±0.3	0.20±0.05	0.30±0.07	0.11±0.03	0.03±0.02	0.27±0.07
640/4, 3	1.4±0.4	0.4±0.1	0.002±0.001	0.02±0.01	0.001±0.001	2.8±0.3	0.08±0.02	0.26±0.08	0.013±0.004	0.29±0.05	0.48±0.04
700/5, 3	3.3±0.7	1.1±0.2	0.004±0.001	0.02±0.01	0.001±0.001	1.5±0.2	0.03±0.01	0.14±0.04	0.003±0.001	0.33±0.07	0.48±0.08
750/4, 3	5.5±0.8	2.6±0.3	0.02±0.01	0.10±0.03	0.004±0.002	0.06±0.04	0.001±0.001	0.002±0.002	<0.001	0.47±0.08	0.15±0.05
800/9, 2	5.4±0.5	2.9±0.4	0.03±0.01	0.17±0.05	0.006±0.002	0.008±0.007	< 0.001	0.001±0.001	< 0.001	0.54±0.05	0.03±0.01
700-750*	2.2±0.8	1.5±0.2	0.02±0.01	0.1±0.03	0.003±0.002	1.5±0.2	0.03±0.01	0.14±0.04	0.003±0.001		

\*The yield of tar and PAHs is determined as a difference of their yield at 750 and 700 °C.

In order to reveal the reasons of a sharp increase of PAH yield within the high-temperature range (640–800 °C), it is interesting to study the carbon residue, including the changes in its specific surface, at different final temperatures of carbonization.

#### STUDY OF THE SOLID CARBON RESIDUE

The following main stages of carbonization are usually observed in the thermal decomposition of pitch: plasticization and the formation of metaphase, semicoke, and formation of coke structure [1, 3]. The formation of meso-phase pitches and semicoke occurs within the temperature range 400–500 °C [6, 10, 11]. At 750 °C, the formation of pitch coke is finished [2, 7]. The results of study (Fig. 3) show that the mass fraction of  $\alpha$  fraction, increasing from (34.3 ± 0.5) % in the initial pitch to (86.9 ± 1.1) % at 700 °C, changes non-monotonically. For example, the yield of  $\alpha$  fraction at 400 °C differs from its fraction in the initial pitch only insignificantly. The heating of pitch to 500–520 °C leads to the 2–3 times increase of the yield of  $\alpha$  fraction, which corresponds to the stage of semicoke formation. At the increase of temperature from 700 to 750 °C, benzene-soluble substances almost disappear from the solid residue (mass fraction being less than 0.3 %); *i. e.* the transition of the system from the two-phase state ( $\alpha$  fraction, or carbon matrix, and the mobile fraction, soluble in benzene) into the single-phase state ( $\alpha$  fraction, or carbon matrix) is observed; the stage of the formation of pitch coke structure is finished.

The transition of the system from one phase state into another is accompanied by structural changes. It is known that the pyrolysis of coal pitch, pitch-coke and other carbon-containing compositions based on it, changes texture characteristics of the formed carbon residue [4, 11, 12, 25]. In particular, it has been stated that a slow increase of the porosity of the carbon residue occurs during the pyrolysis of high-temperature pitch within the temperature range 700–1000 °C; in the opinion of the authors of [4], this occurs due to the formation of gas channels and realization of closed pores.

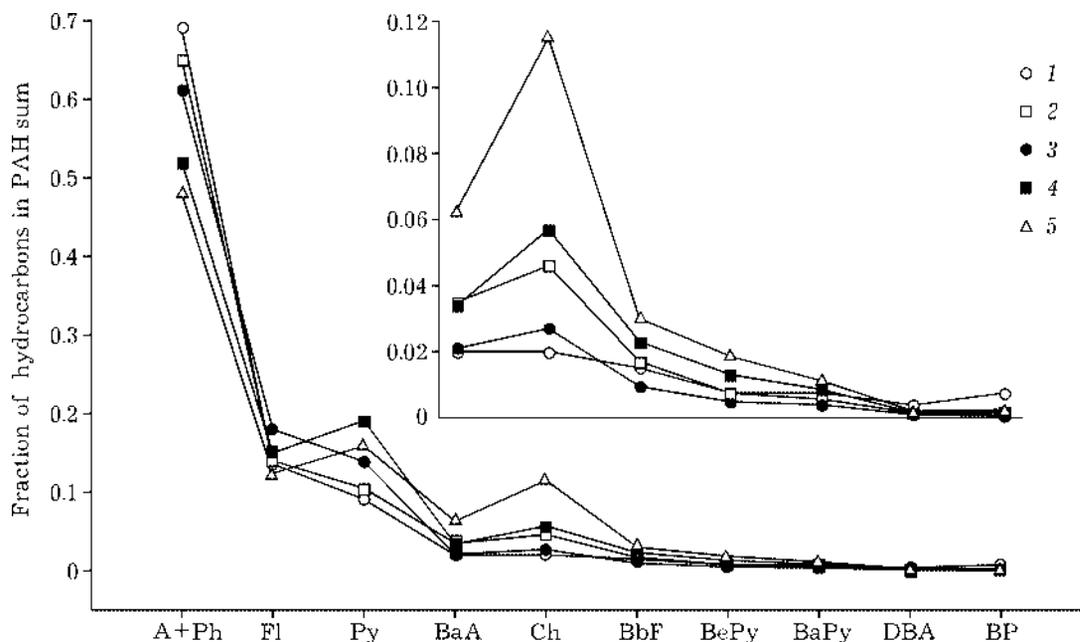


Fig. 2. PAH profiles in tarry matter at different pitch carbonization temperature, °C: 520 (1), 640 (2), 700 (3), 750 (4), 800 (5) (sampling is listed in Table 3). Insertion: profiles of BaA, Ch, BbF, BePy, BaPy, DBA, BP, increased scale.

The general regularities of the pyrolysis of hydrocarbon materials [26, 27] allow us to assume that the high-temperature release of PAHs occurs as a result of one of the following processes:

- 1) accumulation of PAHs in the porous structure of the carbon residue and their desorption at high temperature;
- 2) formation of PAHs during the formation of the structure of carbon residue, due to the

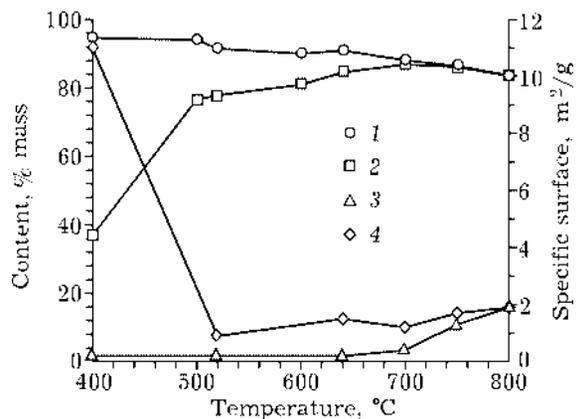


Fig. 3. Dependence of the yield of carbon residue (1),  $\alpha$  fraction of carbon residue (2) (per cent of pitch mass, sampling is listed in Table 3) and their specific surface (3, 4) during sampling 3 (400 and 520 °C), 4 (640, 700 and 750 °C) and 5 (800 °C) on pitch carbonization temperature.

rupture of C-C bond, followed by gas-phase transformation of the hydrocarbon fragments.

To confirm one of the indicated routes of PAH formation, we extracted the carbon residue with benzene at different carbonization temperatures. The very possibility of the extraction of PAHs from the carbon residue is the evidence of the accumulation of PAHs in the porous structure of the carbon residue and their desorption. Extraction with benzene may isolate PAH molecules with bonding energy 5–10 kcal/mol (Van der Waals forces, physical adsorption, weak chemical adsorption). Fragments of molecules cannot be extracted with benzene by breaking the C-C bond, because it is strong (80–100 kcal/mol). To confirm this proposal, we determined the specific surface of the carbon residue before and after extraction with benzene at different final carbonization temperatures, as well as the composition of PAHs in the extracts of the carbon residue and in carbonization tars at the corresponding temperatures.

Study of the samples obtained at different final pitch carbonization temperatures before and after extraction with benzene (see Fig. 3) demonstrates that the specific surface of the  $\alpha$  fraction of initial pitch (30.5 m<sup>2</sup>/g) decreases

sharply at first to  $(0.9 \pm 0.1) \text{ m}^2/\text{g}$  at heating to  $520^\circ\text{C}$ , then increases to  $(1.5 \pm 0.2) \text{ m}^2/\text{g}$  within the temperature range  $520\text{--}640^\circ\text{C}$  and remains almost constant at further increase of temperature. The specific surface of the solid carbon residue does not change within temperature range  $400\text{--}700^\circ\text{C}$ ; it is equal to  $0.2 \text{ m}^2/\text{g}$ . It substantially increases at the further increase of temperature; within temperature range  $750\text{--}800^\circ\text{C}$ , specific surface of the carbon residue and that of the a fraction coincide within the determination error (see Fig. 3). This is the evidence of the increase of porosity of the carbon residue due to the liberation of pores during the desorption of PAHs from the porous structure. Taking this consideration into account, we may assume that the composition of PAHs in the extract of the carbon residue and that in the tar released at this temperature into the gas phase may be close to each other.

#### PAH COMPOSITION AND CONTENT IN THE PYROLYSIS TAR AND IN THE EXTRACT OF THE CARBON RESIDUE

The study of PAH content in the extract of the solid residue depending on pitch pyro-

lysis temperature demonstrates that the yield of PAHs, including carcinogenic ones, decreases with increasing temperature (see Table 3). This increase from  $(9.8 \pm 0.6) \%$  in the initial pitch to  $(6.6 \pm 1.4) \%$  at  $400^\circ\text{C}$  (see Table 3) can be connected with their involvement in thermal polymerization reactions with the formation of polycondensates of aromatic structures, the future nuclei of the mesophase [1, 2, 6, 25]. The increase of temperature to  $700^\circ\text{C}$  leads to the decrease of PAH yield to  $(1.5 \pm 0.2) \%$ , which is the evidence of the participation of PAH molecules in processes accompanying the formation of semicoke and coke. At the increase of carbonization temperature, the fraction of PAHs in the extract of carbon residue increases from  $(0.15 \pm 0.01) \%$  in the initial pitch to  $(0.48 \pm 0.04) \%$  at  $640^\circ\text{C}$  and remains unchanged  $(0.48 \pm 0.08) \%$  while temperature increases to  $700^\circ\text{C}$ . The PAH composition does not change within this temperature range. This is evidenced by a similar character of PAH profiles at  $640$  and  $700^\circ\text{C}$  (Fig. 4). Thus, PAHs are accumulated in the liquid phase concentrated in the porous structure of the carbon residue.

Within temperature range  $700\text{--}750^\circ\text{C}$ , we observe the transformation of the system from

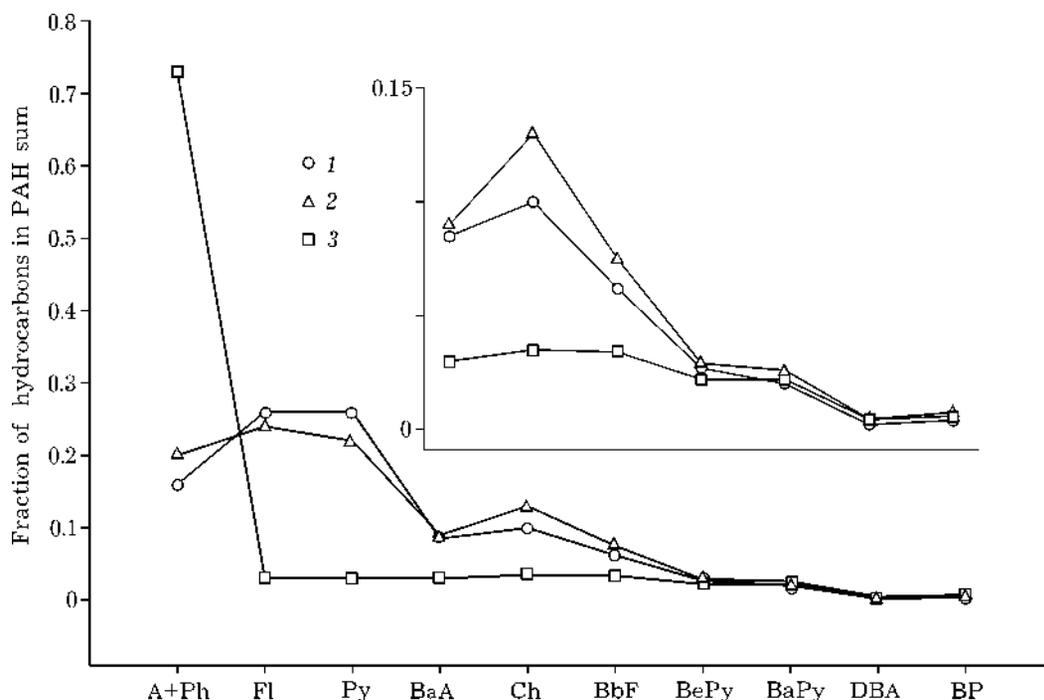


Fig. 4. PAH profiles in the extract of carbon residue at different carbonization temperatures,  $^\circ\text{C}$ : 640 (1), 700 (2), 750 (3) (sampling is listed in Table 3). Insertion: the profiles of BaA, Ch, BbF, BePy, BaPy, DBA, BP, increased scale.

the two-phase state into the single-phase one. This is the stage at which the coke structure is formed; this stage is accompanied by almost complete disappearance of PAHs from the extract of the carbon residue (see Table 3). This process is accompanied by a sharp change of the PAH composition; at 750 °C, all the PAHs are absent from the extract of the carbon residue except anthracene and phenanthrene (see Fig. 4), which concentration in the extract does not decrease. Structural changes are accompanied by the increase of the specific surface of the carbon residue (see Fig. 3) and by the increase of the concentration of carcinogenic PAHs in the pyrolysis tar, which is due both to the increase of the tar yield and to the increase of the concentration of carcinogenic PAHs in it (see Fig. 1, Table 3).

Within this temperature range, the fraction of  $\Sigma$ PAH in the extract of the carbon residue and in the tar released into the gas phase is similar and equal to  $(1.5 \pm 0.2) \%$  (see Table 3). The yield of individual carcinogenic PAHs is similar within the determination error; in particular, the yield of BaP is  $(0.03 \pm 0.01) \%$  (see Table 3). The fractions of  $\Sigma$ PAH in tar at 750 °C ( $0.47 \pm 0.08) \%$  and in the extract of the carbon residue at 700 °C also coincide within the determination error.

The comparison between PAH profiles in tar and in the extract of carbon residue demonstrates their similar character; in particular, this is true for all the carcinogenic PAHs (Fig. 5). In other words, we observe the coincidence

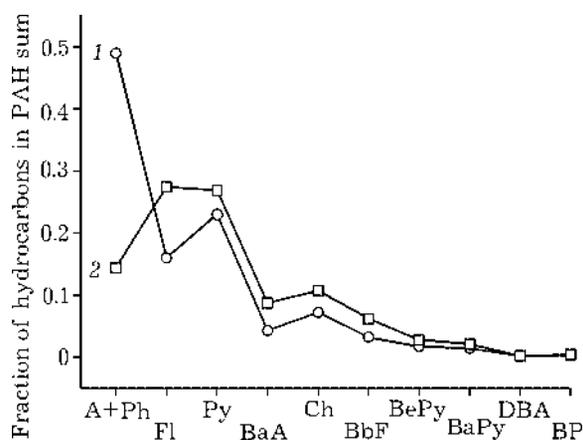


Fig. 5. PAH profiles in the pyrolysis tar (1) and in the extract of the carbon residue (2) within temperature range 700–750 °C (sampling indicated in Table 3).

between the composition of PAHs in the carbon residue and that in tar released into the gas phase. Higher A + Ph content of the tar in comparison with their content in the extract of the carbon residue is the evidence of the possible contribution from both the gas-phase synthesis processes [28] and the secondary processes of pyrolysis in the solid residue. Attention should be paid to the fact that, on the one hand, within the temperature range 640–750 °C, the A + Ph concentration remained unchanged in the extract of the carbon residue and was equal to 7.9–10.8 %; on the other hand, the equilibrium concentration of the isomers of anthracene and phenanthrene in tar changed with the increased carbonization temperature (see Table 2). For example, while temperature increases from 640 to 700 °C, the fraction of phenanthrene (the most thermodynamically stable isomer with angular structure) increases; correspondingly, the ratio of phenanthrene to anthracene increases from 1.4 to 4.4. Within the temperature range 700–750 °C, the content of anthracene and phenanthrene in carbonization tar increases, but their ratio remains practically unchanged (see Table 2).

Thus, within the temperature range 700–750 °C, the facts stated experimentally are: 1) the increase of the specific surface of carbon residue, which is the evidence of the increase of porosity as a result of PAH desorption; 2) coincidence between the PAH composition in tar and in the extract of carbon residue; 3) coincidence between the PAH composition in the extract of carbon residue and in the tar released into the gas phase. This allows us to conclude that the release of the major part of carcinogenic PAHs during carbonization is determined by their desorption from the porous structure of the carbon residue within the temperature range 700–750 °C at the stage when the structure of pitch coke finishes its formation. The evidence of this fact is the transitions of the system from two-phase state into single-phase one.

Within temperature range 750–800 °C, the release of tar into the gas phase finishes (see Fig. 1); the fraction of carcinogenic PAHs (BaPy, BaA, DBA) in tar goes on increasing (see Table 3) only due to the change of the PAH composition (see Fig. 2). This may be due to the

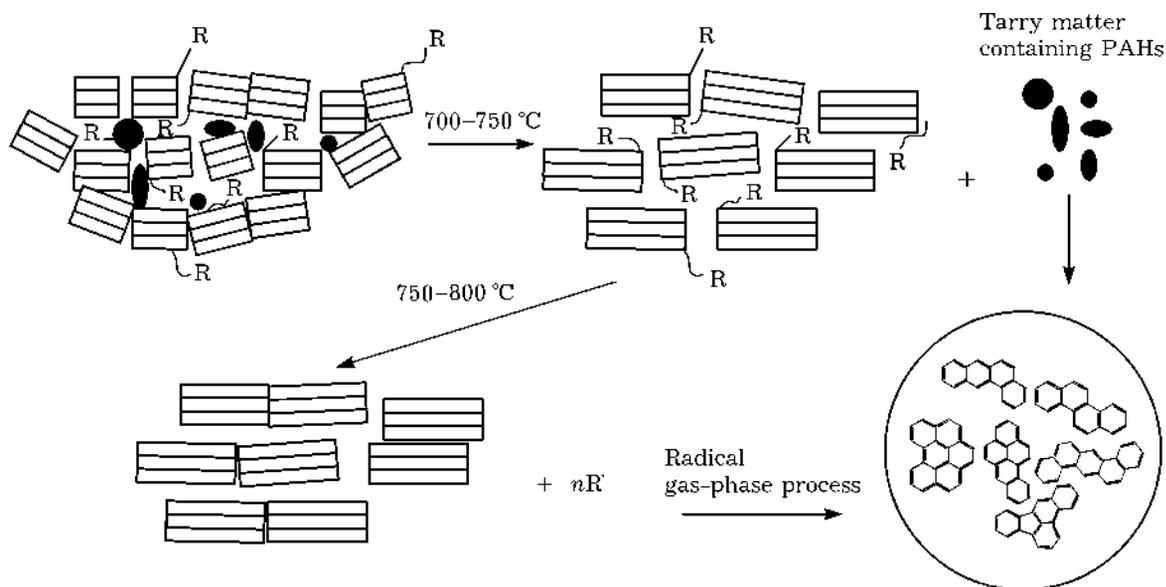


Fig. 6. A scheme of PAH evolution within temperature range 700–800 °C.

change of the route of PAH formation. The formation of carcinogenic PAHs at these temperatures is most likely connected with the rupture of C–C bond followed by the transformation of the hydrocarbon fragments in the gas phase and possibly on the surface of the solid phase. It is known that the pyrolysis of aromatic hydrocarbons in the gas phase is observed within temperature range 700–800 °C [8, 28]. For example, benzene starts to form biphenyl intermediate in the gas phase at 700 °C, anthracene and phenanthrene at 750 and 800 °C form bianthryl and biphenanthryl intermediates, respectively [28]. Recombination of low-molecular and most reactive aromatic radicals leads to the formation of high-molecular PAHs.

The scheme of PAH evolution within temperature range 700–800 °C is shown in Fig. 6. When temperature increases to 640–700 °C, tarry substances that contain  $(48 \pm 8)\%$  PAHs and can be extracted with benzene are accumulated in the porous structure of the carbon residue. Within temperature range 700–750 °C, tars containing  $(48 \pm 8)\%$  PAHs get desorbed into the gas phase; the contents and compositions of PAHs in the tar and in the benzene extract of the carbon residue are identical. Desorption is accompanied by the increase of the specific surface of the carbon residue, which is the evidence of the liberation of pores, and by the transition of the carbon residue into

the single-phase state. Within the range 750–800 °C, the formation of PAHs occurs due to the gas-phase process of sequential transformation of hydrocarbon fragments formed as a result of the rupture of C–C bonds when forming the structure of carbon residue.

## CONCLUSIONS

The dynamics of formation and the composition of the main products of medium-softening-point pitch carbonization, *i. e.*, tar and carbon residue, are investigated.

It is stated that at the high-temperature carbonization stage (649–750 °C) the major amount of tar is released; the carcinogenic PAHs are evolved within temperature range 700–800 °C.

It is demonstrated that the main yield of carcinogenic PAHs in carbonization processes is determined by their desorption from the porous structure of the carbon residue within a narrow range 700–750 °C at the stage when the structure of pitch coke finishes its formation. The formation of carcinogenic PAHs at temperatures above 750 °C is determined mainly by gas-phase transformations of the hydrocarbon fragments that appear during the formation of the graphite-like structure of carbon residue.

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