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## Study of the Liquid Products of Pre-Boring of Middle-Metamorphized Coals for Enhanced Environmental Safety of Thermal Technologies

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### Abstract

Data on the yield and composition of liquid products formed in the process of semi-coking of coals of the middle stages of metamorphism were obtained using a complex of analytical methods. It was demonstrated that the yield of semi-coking resins decreases with an increase in the genetic maturity of coal, but the aromaticity of liquid products increases, as indicated by a decrease in the H/C atomic ratio, as well as the presence of high-molecular-weight hydrocarbons in the form of asphaltenes and resinous substances. It was revealed by means of chromatography-mass spectrometry that during low-temperature pyrolysis, liquid products are formed, which are represented by a complex mixture of saturated and aromatic hydrocarbons. In all the resins, normal and branched *n*-alkanes and *n*-alkenes are identified. The aromatic hydrocarbons of the studied resins contain one to five benzene rings per molecule. Different amounts of these components in the composition of liquid products are due to differences in the chemical structure of the organic mass of coal samples studied. The obtained results expand the understanding of the composition of liquid products formed from the organic mass of coal during its low-temperature heat treatment in the semi-coking mode and open the ways to improve the environmental safety of basic technologies taking into account the number, individual composition and toxicity indicators of all the products formed.

**Keywords:** coals, low-temperature pyrolysis, semi-coking resin, asphaltenes, hydrocarbons

### INTRODUCTION

Modern technologies of the use and thermal treatment of solid fuels (combustion, gasification, coking, power chemical processing) include pyrolysis of the organic matter of fuel as one of the most important stages of the process. Thermal decomposition of separate classes of compounds incorporated in the organic mass of coal proceeds with the highest intensity within temperature range 300–600 °C, after which the prevailing

processes are structuring in the solid residues of carbonization [1, 2]. During thermal destruction of the solid fuels within the indicated temperature range, a part of their organic matter is transformed into rather low-molecular compounds that can be analyzed using physicochemical methods. Investigation of the composition of liquid products obtained from solid fuels is reasonably considered as a key to the revelation of the structure of their organic matter. The most informative approach is the investigation of the

composition of liquid products formed at relatively low destruction temperature (in the processes of semi-coking, thermal dissolution, *etc.*) [3–6] because they contain the fragments of the macromolecules of initial material. Detailed data on the chemical composition of resins obtained under the conditions maximally excluding high-temperature pyrolysis point to the native structure of the fragments of the organic mass of coal, their genetic connection with the initial biomaterial, the routes of its biogeochemical transformation in the course of coalification [7]. Knowledge of this kind is of great practical importance because it allows solving the problem of optimal ecologically safe use of the power chemical potential of the entire series of natural coal.

In the present work, we report the results of the studies of the yield and composition of liquid products of low-temperature destruction of coal depending on the stage of its metamorphism.

## EXPERIMENTAL

The objects of the investigation were four samples of coal of different grades collected at coal-mining enterprises of the Kuznetsk Basin: G (the mine named after Kirov), Zh (Karagaylinskoe mine administration), K (Berezovskaya mine), KS (Bachatskiy open-pit mine).

The technical analysis of the extracted fractions was carried out using standard methods. The composition of the organic mass was determined by means of elemental analysis.

Petrographic analysis was carried out with an automatic complex for the evaluation of the grade composition of coal, the SIAMS-620 system (Russia), in oil immersion. Microcomponents were calculated automatically with the 300 times magnification in reflected light. Attribution of the coal samples to the grade composition was carried out in agreement with the unified classification of coal with respect to genetic and technological parameters on the basis of vitrinite reflectance ( $R_{o,r}$ ), the sum of fusinized components ( $\Sigma LC$ ) and the yield of volatiles ( $V^{daf}$ , %).

High-resolution NMR  $^{13}C$  spectra in the solid state were recorded with a Bruker Avance III 300 WB instrument (Germany) using the standard procedure of cross-polarization with rotation at the magic angle and uncoupling from protons (CPMAS) at the frequency of 75 MHz, contact time 1500  $\mu s$ , accumulation 4096 scans, delay between scans 2 s, the frequency of sample rotation

5 kHz. To obtain the quantitative data, spectrum modeling was carried out with the help of Dmfit software. The ranges of chemical shifts of NMR  $^{13}C$  samples corresponding to the resonance absorption of the following groups of carbon atoms were determined, ppm: 170–148 – carbon atoms of aromatic systems bound with oxygen atoms ( $C_{ar}O$ ); 148–93 – carbon atoms of aromatic systems with substituted and unsubstituted hydrogen atom ( $C_{ar} + CH_{ar}$ ); 65–0 – carbon atoms of alkyl fragments ( $C_{alk}$ ). Degree of aromaticity  $f_a = (C_{ar} + CH_{ar}) / (C_{ar} + CH_{ar} + C_{alk})$  [8].

Determination of the yield of products of semi-coking from coal was carried out using the gravimetric method according to GOST 3168–93 (ISO 647:1974). The essence of the standard method is in heating a weighted portion of the fuel under study to 600 °C in a glass retort 100 cm<sup>3</sup> in volume and determination of the yield of primary resin ( $T_{sK}$ ) and pyrogenetic water ( $W_{sK}$ ) followed by their separation, and the yield of semi-coke (sK) and gaseous products ( $G_{sK}$ ).

Before analytical studies, carbon-containing inclusions of coal dust, soot and other suspended matter insoluble in toluene were separated from the resin of semi-coking according to the procedure described in [9].

The products of low-temperature pyrolysis of coal, similarly to natural liquid hydrocarbon raw material, are composed of many components, so their composition was studied using the same approaches as those used to study oil composition. The group analysis of the resin of semi-coking included its separation into asphaltenes (high-molecular high-boiling polycyclic heteroatomic compounds), neutral hydrocarbons in the form of oil, and oxygen-containing resins [10]. At the first stage, the resin of semi-coking was poured with a 20-fold (by mass) amount of hexane and kept for 24 h. Precipitated asphaltenes were separated by filtering, washed with hexane, then dried to the constant mass. The accuracy of the determination of asphaltene content was 1.5 %.

The part of liquid products of semi-coking soluble in hexane (resins and oils) were separated by means of liquid chromatography on silica gel. The adsorption column was filled with silica gel of ASK grade (in 15-fold excess with respect to the weighted portion of the substance under investigation). Then the weighted portion of sample ~2 g in mass was introduced into the column. Elution was carried out sequentially by hexane and a mixture of ethanol and benzene (1 : 1 by volume). The content of oil (eluated with hexane) and res-

ins (eluated with the mixture of ethanol and benzene) was determined using the gravimetric method after the evaporation of the solvent. The deviation of the yields of fractions in parallel measurements did not exceed 5 %.

The IR spectra of the resins of semi-coking were recorded with the IR Fourier spectrometer Infracum FT-801 (Russia) within the range 400–4000  $\text{cm}^{-1}$ . For the determination of the optical density of bands ( $D$ ), the base line was the straight line drawn between the transmission maxima in the region of 650 and 1800  $\text{cm}^{-1}$ . Then the optical density was normalized to the optical density of the band in the region of 1458  $\text{cm}^{-1}$ . Spectral coefficients were calculated from the IR spectra:

$C_1 = D_{1597}/D_{1458}$ ;  $C_2 = D_{1710}/D_{1458}$ ;  $C_3 = D_{1377}/D_{1458}$ ;  $C_4 = D_{1377}/D_{1597}$  [11–13], which is the ratio of the optical densities of absorption bands at the frequencies of 1710, 1597, 1458 and 1377  $\text{cm}^{-1}$ .

Gas chromatographic-mass spectrometric analysis of the resins of semi-coking was carried out using the Agilent 7000 Triple Quad instrument (the USA) within the region of 15–500 Da in the mode of temperature programming from 50 to 300 °C with the rate of 7 °C/min; evaporator temperature was 300 °C; capillary column VF-5MS (5 % diphenyl and 95 % dimethylsiloxane) 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ; helium as the carrier gas. Individual compounds were identified

with the help of the NIST02 computer library of mass spectra.

## RESULTS AND DISCUSSION

The characteristics of the studied samples of coal are presented in Tables 1 and 2. The results of petrographic analysis (see Table 1) show that these are the coals of the medium stage of metamorphism of technological grades G, Zh, K, KS, with the vitrinite reflectance ( $R_{o,r}$ ) varied from 0.75 to 1.25 %. Coal samples of G and Zh grades contain significant amounts of vitrinite components (Vt), with the highest amount characteristic of the coal sample of Zh grade (up to 86 %). The maximal amount of inertinite (I) and leaning components ( $\Sigma\text{LC} = 64$  %) was established in the sample of K grade.

The ash content varies from 3.1 % for the coal sample of KS grade to 8.9 % for the sample of Zh grade. With an increase in the genetic maturity of samples, the yield of volatiles ( $V^{\text{daf}}$ ) and the atomic ratios H/C and O/C decrease. The largest amount of oxygen and heteroatoms is present in the organic mass of the coal sample of G grade (see Table 2).

The data on the relative distribution of carbon atoms over structural fragments in the coal sam-

TABLE 1

Characteristics of the petrographic composition of coal samples under investigation

Coal sample code	Petrographic parameters %				Vitrinite reflectance		Coal grade according to GOST 25543–88
	Vt	Sv	I	$\Sigma\text{LC}$	$R_{o,r}$ , %	$\sigma_R$	
40	72	4	24	26	0.75	0.06	G
39	86	2	12	13	0.81	0.06	Zh
50	31	13	56	64	1.01	0.04	K
45	45	19	36	49	1.25	0.07	KS

Note.  $W^a$  – analytical moisture,  $A^d$  – ash content,  $V^{\text{daf}}$  – yield of volatiles,  $S_t^d$  – total sulphur, daf – dry ash-free state of the sample.

TABLE 2

Characteristics of the studied coal samples

Coal grade	Technical analysis, %				Elemental composition, % by daf			Atomic ratio	
	$W^a$	$A^d$	$V^{\text{daf}}$	$S_t^d$	C	H	(O + N + S)	H/C	O/C
G	1.1	4.5	42.2	0.4	83.7	5.6	10.7	0.80	0.10
Zh	1.1	8.9	33.5	0.3	87.8	5.9	6.3	0.81	0.05
K	1.0	8.1	22.8	0.5	88.9	4.9	6.2	0.66	0.05
KS	1.8	3.1	19.5	0.6	88.5	4.5	7.0	0.61	0.06

Note.  $W^a$  – analytical moisture,  $A^d$  – ash content,  $V^{\text{daf}}$  – yield of volatiles,  $S_t^d$  – total sulphur, daf – dry ash-free state of the sample.

TABLE 3

Parameters of the fragmentary composition of coal samples (the data of NMR  $^{13}\text{C}$  spectra)

Coal grade	Distribution of carbon atoms over structural groups, rel. %							$f_a$
	$\text{CH}_3$	$\text{CH}_2$	$\text{CH}_3\text{O}$	$\text{C}_{\text{alk}}\text{O}$	$\text{C}_{\text{ar}}\text{H} + \text{C}_{\text{ar}}$	$\text{C}_{\text{ar}}\text{O}$	$\text{COOH}$	
	Диапазон значений химических сдвигов резонансного поглощения, м. д.							
	0–25	25–51	51–67	67–93	93–148	148–171	171–187	
G	4.66	26.01	2.09	–	63.48	3.65	0.11	0.67
Zh	5.72	20.52	1.53	0.37	66.60	4.54	0.72	0.72
K	3.24	13.77	1.22	0.29	79.09	2.11	0.28	0.82
KS	4.08	9.10	1.07	0.44	82.76	2.13	0.42	0.86

Note.  $f_a = \text{C}_{\text{ar}} + \text{CH}_{\text{ar}} / (\text{C}_{\text{ar}} + \text{CH}_{\text{ar}} + \text{C}_{\text{alk}})$ .

ples under investigation determined from NMR  $^{13}\text{C}$  spectra are presented in Table 3. One can see that with the growth of the metamorphism stage the parameter of aromaticity  $f_a$  of the studied samples increases from 0.67 (G grade) to 0.86 (KS grade). It may be stressed that with an increase in  $f_a$  the total amount of aliphatic carbon in the structural fragments decreases (from 30.67 to 13.18 %), as determined from the chemical shifts of the signals in NMR spectra within the range 0–51 ppm. In this situation, a decrease (from 26.01 % in coal samples of Zh grade) to 9.10 % in the sample of KS grade) proceeds mainly due to the fragments with chemical shifts located in the region 25–51 ppm (see Table 3). At the background of a decrease in the amount of carbon in aliphatic structures, the content of aromatic fragments increases (the range 93–148 ppm) in the organic mass of the studied coal from 63.48 to 82.76 %.

TABLE 4

Yield of the products of semi-coking of coal samples

Coal grade	Yield of the products of semi-coking, % by daf			
	sK	T <sub>sK</sub>	W <sub>sK</sub>	G <sub>sK</sub>
G	70.3	13.4	7.0	9.3
Zh	73.5	11.3	2.2	13.0
K	84.3	5.6	1.5	8.6
KS	88.7	2.7	0.6	8.0

TABLE 5

Characteristics of the resins of semi-coking from the studied coal samples

Coal grade	Elemental composition of resin, %			Atomic ratio		Component composition of resin, %		
	C	H	(O + N + S)	H/C	O/C	Oils	Resins	Asphaltenes
G	84.0	8.8	7.2	1.26	0.06	20.2	67.3	12.5
Zh	82.7	8.3	9.0	1.20	0.08	26.0	66.2	7.8
K	86.6	8.1	5.3	1.12	0.05	29.1	65.3	5.6
KS	87.5	7.6	4.9	1.04	0.04	44.0	52.1	3.9

The data on the yield of the products of semi-coking of the studied samples are shown in Table 4. It was established that with an increase in the stage of metamorphism, the amount of semi-coke increases at the background of a decrease in resin and steam-gas products. The largest amount of resin and steam-gas products is observed for coal of G grade and is due to the presence of a larger amount of aliphatic fragments in its organic mass (see Table 3) and heteroatoms determined as (O + N + S) (see Table 2).

The characteristics of the resins of semi-coking are listed in Table 5. One can see that there are heteroatoms in the elemental composition of the organic mass of resins (O + N + S), and the lowest amount of these atoms was detected in the sample of KS grade. The maximal atomic ratios H/C and O/C are characteristic of the resins obtained from G and Zh coal grades.

The component composition of the resins of semi-coking is represented by high-molecular hydrocarbons in the form of asphaltenes and neutral resins. The highest amount was determined in pyrolyzates obtained from coal of G and Zh grades. It should be noted that the resin from the KS grade coal sample contains the largest amount of the oil fraction (up to 44 %).

Investigation of the resins of semi-coking by means of IR spectroscopy revealed a similar set of characteristic absorption bands in their spec-

TABLE 6

Spectral parameters of the resins of semi-coking obtained from coal grades under investigation (the data of IR spectra)

Coal grade	Spectral parameter of the resins of semi-coking			
	$C_1$	$C_2$	$C_3$	$C_4$
	$D_{1597}/D_{1458}$	$D_{1710}/D_{1458}$	$D_{1377}/D_{1458}$	$D_{1377}/D_{1597}$
G	0.77	0.23	0.64	0.82
Zh	0.70	0.06	0.60	0.85
K	0.69	0.10	0.58	0.83
KS	0.79	0.11	0.61	0.77

tra. Rather intensive absorption bands with the maximal at  $1377$  and  $1458\text{ cm}^{-1}$  and in the high-frequency range  $2877\text{--}3000\text{ cm}^{-1}$  provide evidence of the presence of aliphatic hydrocarbon structures, while in the region with the maximum at  $1597$  and  $3040\text{ cm}^{-1}$  aromatic compounds are present. Judging from the profile of the spectrum in the region  $700\text{--}900\text{ cm}^{-1}$ , a definite degree of substitution in the aromatic rings is characteristic of the aromatic structures. Therefore, we confirm the statement [13, 14] that coal tar pitch is not just a mechanical mixture of the components but a much more complicated system in which along with individual hydrocarbons there are numerous products of their interactions.

Analysis of the spectral coefficients (Table 6) shows that the resin obtained during semi-coking of KS grade coal possesses the highest aromaticity. This is proved by the lower H/C ratio (see Table 5) and the highest spectral coefficient  $C_1$ , depicting the fraction of aromatic structural fragments in the molecules of the organic compounds of resin. With the growth of the stage of coal metamorphism, the spectral coefficient  $C_2$  de-

creases (relative content of carbonyl functional groups) in the resins of semi-coking, *i.e.* their oxidation decreases. A slight decrease in  $C_4$  coefficient may be the evidence of a decrease in the fraction of aliphatic structural fragments in the molecules of the resins of semi-coking. The value of the branching coefficient ( $C_3$ ) remains practically unchanged (see Table 6).

It was discovered by means of gas chromatography – mass spectrometry (Table 7) that the resins obtained by low-temperature pyrolysis include aliphatic hydrocarbons in the form of *n*-alkanes (with chain length  $C_{11}\text{--}C_{25}$ ) and *n*-alkenes (with chain length  $C_{12}\text{--}C_{22}$ ). With an increase in the degree of coal metamorphism, the amount of aliphatic hydrocarbons in the pyrolysates decreases substantially. The resins of semi-coking obtained from coal grades K and KS contain almost no *n*-alkenes.

Aromatic hydrocarbons of all the studied resins contain mono-, bi- and polycyclic compounds. The total content of monoarenes varies from  $15.2\text{--}15.7\%$  (in resin from G and Zh coal grades) to  $12.5\%$  (in the resin from KS coal) of the sum of all identified components. Among monoarenes,

TABLE 7

Gas chromatographic–mass spectrometric analysis of the resins of semi-coking obtained from the coal grades under investigation

Hydrocarbon group	Relative content of the components in the resins of semi-coking obtained from coal grades under investigation, % of the sum of identified compounds			
	G	Zh	K	KS
Aliphatic hydrocarbons, including	27.0	31.9	18.2	8.0
<i>n</i> -alkanes $C_{11}\text{--}C_{25}$	20.6	26.1	17.7	8.0
<i>n</i> -alkenes $C_{12}\text{--}C_{22}$	6.4	5.8	0.5	n/d
Monoaromatic hydrocarbons (alkyl benzenes)	15.2	15.7	13.5	12.5
Biaromatic hydrocarbons (naphthalene and its homologues)	10.2	31.5	36.8	38.6
Polycyclic aromatic hydrocarbons (PAH)	3.7	9.9	29.4	35.0
Aromatic oxygen-containing compounds (phenols, ethers, furans)	43.9	10.9	2.1	5.0

Note. N/d – not detected.



*n*-alkylbenzenes, *n*-alkyltoluenes, *n*-alkylxylenes were detected in all resin samples.

Biarene hydrocarbons are represented in the resins under study by naphthalene, biphenyl and their alkyl-substituted homologues. Among bicyclic compounds, alkyl-substituted naphthalenes containing one to three carbon atoms in the alkyl fragment were identified. Biphenyl homologues include the isomers with one and two methyl substituents.

Polycyclic hydrocarbons in the resins under study contain three to five benzene rings in the molecules. Triarenes are represented by anthracenes, phenanthrenes and fluorenes with methyl substituents. Among tetracyclic aromatic structures, benzanthracenes, fluoranthenes and pyrenes with methyl substituents were identified. Among pentaarenes, benzfluoroanthenes and benzpyrenes were revealed. The largest amount of four- and

five-ringed hydrocarbons was identified in the resins of semi-coking of K and KS coal grades.

Oxygen-containing compounds were determined in all resins of semi-coking of G and Zh coal grades mainly in the form of aromatic phenols with alkyl substituents containing 1–4 carbon atoms. In the resins obtained from coal of K and KS grades, dibenzofurans were identified.

On the basis of the data obtained, a correlation analysis was carried out to reveal the dependence between the degree of coal metamorphism expressed as the parameter  $f_a$  of the organic mass of coal, and the amount of separate components in the resins of semi-coking. Analysis of the data (Fig. 1) shows that with an increase in the genetic maturity of coal, the content of alkyl benzenes in the resins of low-temperature pyrolysis decreases at the background of an increase in the concentrations of biaromatic hydrocarbons in the

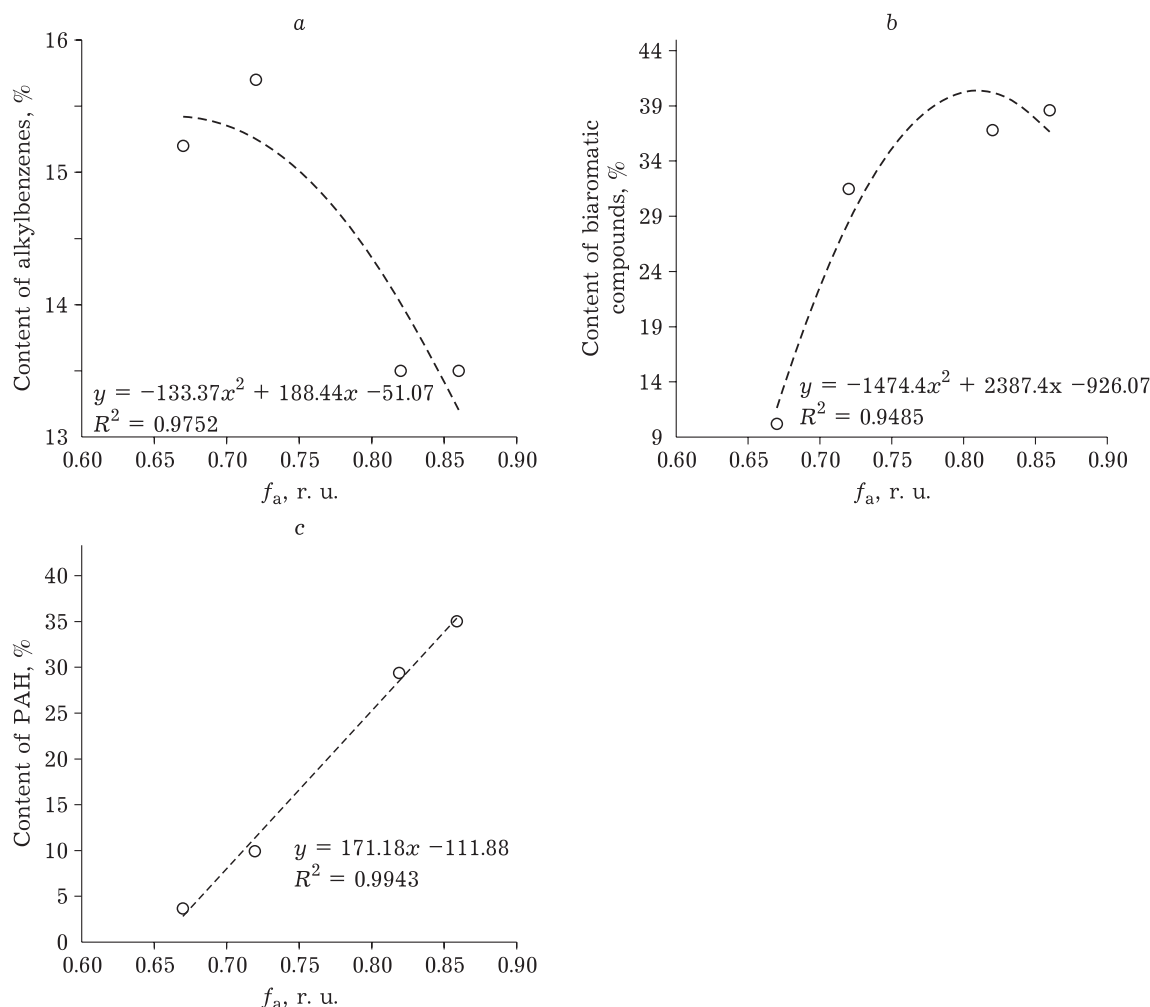


Fig. 1. Dependence between the degree of aromaticity  $f_a$  of the organic mass of coal grades under study and the content of components in resins obtained through low-temperature pyrolysis: alkylated benzenes (a), naphthalene and its derivatives (b), polycyclic aromatic hydrocarbons (PAH) (c).

form of naphthalenes with various alkyl substituents. A close correlation was detected between the degree of aromaticity of the organic mass of coal grades under study and the content of polycyclic aromatic hydrocarbons (PAH) in the resins of semi-coking. Therefore, with an increase in the degree of chemical maturity of coal, the fraction of condensed organic compounds in their resins of semi-coking increases, which depicts the features of the fragmentary structure of the high-molecular organic matter of initial coal. It is known that the main macromolecular structure of the substances in coal is a combination of condensed aromatic carbon layers and the chains of higher or lower complexity binding them to each other, in the form of heterocyclic and aliphatic groups of atoms, as well as oxygen-containing functional groups. With an increase in the genetic maturity of coal, the amount of carbon included into the aromatic cycles of coal substances increases, the number of naphthene cycles and functional groups decreases, and the degree of mutual graphite-like ordering of aromatic cores increases [15–17].

## CONCLUSION

As a result of the studies, the analytical data were obtained on the changes of the composition of liquid products of low-temperature destruction of coal of the medium degrees of metamorphism. It was revealed that with an increase in the genetic maturity of coal grades G, Zh, K and KS, the yield of the resins of semi-coking decreases but the aromaticity of liquid products increases, as indicated by a decrease in the value of H/C atomic ratio and the presence of relatively high (above 50 %) content of high-molecular hydrocarbons in the form of asphaltenes and resins.

It was demonstrated by means of gas chromatography–mass spectrometry that the resins of semi-coking are complicated mixtures of saturated and aromatic hydrocarbons.

Among saturated hydrocarbons, *n*-alkanes and *n*-alkenes were identified. Among aromatic hydrocarbons, mono-, bi- and trisubstituted *n*-alkylbenzenes were identified, along with alkylated naphthalenes and polycyclic hydrocarbons. In the composition of hetero-organic compounds, mainly oxygen-containing compounds in the form of phenols with alkyl substituents were detected, and dibenzofurans in small amounts. Different concentrations of these components in the liquid products are due to differences in the chemical

structure of the organic mass of coal from which they were obtained. It was established that with an increase in the degree of aromaticity of the organic mass of coal samples under study, the fraction of aromatic hydrocarbons in the form of naphthalene and its homologues, as well as polycyclic aromatic hydrocarbons, increases in the liquid products of low-temperature pyrolysis.

The obtained results broaden the notions of the composition of liquid products formed from the organic mass of coal samples during their low-temperature thermal treatment in the mode of semi-coking, and bring a substantial contribution to the scientific foundations of the development of efficient methods of processing and combustion of solid combustible fossils. The ways are thus opened to enhance the ecological safety of basic technologies taking into account the amount, individual composition and the parameters of toxicity of all the formed solid, liquid and gaseous products.

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