

## Thermal Dissolution of Coking Coals in the Anthracene Fraction of Coal Tar

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**Abstract**—The thermal dissolution of two samples of 1GZhR and ZhR coal in the anthracene fraction of coal tar is studied. The yield of quinoline-soluble products increases considerably in the temperature range of coal softening. Optimal thermal-dissolution conditions are determined for selective production of quinoline-soluble pitch-like products. At 350–380°C, the yield of quinoline-soluble products is 70–73% after 1–2 h. The yields of the distillate fraction and the gas are 0.9% and 0.2%, respectively. The ash-free pitch-like product is a plastic mass with a softening temperature of 76–81°C. It consists mainly of polycyclic aromatic hydrocarbons with a few short alkyl substituents in the aromatic rings. The spatial structure mainly includes poorly structured polycyclic aromatic molecules of the  $\gamma$  component. The proportion of relatively ordered graphite-like packets is 31–37%. Each packet contains five stacked polycyclic aromatic molecules of diameter 17 Å. In terms of its composition and plasticity, the product is suitable as a source of alternatives to coal pitch.

**Keywords:** coal, coal tar, anthracene fraction, thermal dissolution, pitch-like product

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### INTRODUCTION

The production of many carbon-based materials employs coal pitch, which is a byproduct of blast-furnace coke production. At room temperature, coal pitch is an externally uniform solid containing a complex mixture of polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds, with four or more rings. Because coal pitch has a useful combination of high coking properties and low viscosity in the molten state, we note excellent physicochemical properties in its products, such as anode mass, electrodes, pitch coke, graphite-based construction materials, carbon fibers, puddled iron, refractories, roofing materials, electrical components, and components for the nuclear and aerospace industries [1–3].

At present, the Russian coke industry is unable to meet the demand for pitch. This shortage is exacerbated by innovations in steel production that reduce coke consumption. We may expect further drop in the demand for coke and hence in pitch production as a result of the broader adoption of pulverized-coal injection in blast furnaces and the adoption of arc furnaces at steel plants. At the same time, industrial demand for pitch – especially in aluminum production – is rising, along with the requirements on coke

quality [3, 4]. These trends, which may be observed in many countries, call for the development of alternatives to coal pitch that do not rely on coking.

Coal pitch is also an environmental hazard, on account of the copious generation of carcinogens such as benz(a)pyrene in high-temperature coking.

A key factor determining the utility of coal pitch in producing high-quality carbon materials is its content of polycyclic aromatic hydrocarbons, which give rise to coking properties. In this respect, the thermal dissolution of coal seems a promising source of replacements for coal pitch. This process is attractive because the coal's organic mass includes fragments that contain polycyclic aromatic hydrocarbons, which are associated as a result of numerous molecular interactions and crosslinks of different strengths. At high temperatures, they break down to molecules and pass to solution in the presence of the appropriate solvent.

The conversion of coal in solvent involves the following stages: diffusion of the solvent molecules into the coal's organic mass; solvation of the molecules and fragments within the coal's organic mass; swelling of the coal particles; and their conversion to soluble form. On thermal destruction of weak covalent crosslinks, reactive radical particles are formed. Their sub-

sequent reactions depend on the solvent's properties. In practice, the solvent has two functions: it must ensure effective solvation of the aromatic fragments in the organic mass so as to permit their extraction in solution; and it must act as a hydrogen donor, stabilizing the reactive radical particles by means of active hydrogen.

Note that existing thermal dissolution processes are aimed at maximizing the destruction of the coal's organic mass, so as to obtain light hydrocarbon-fuel fractions. That usually requires elevated temperatures ( $>400^{\circ}\text{C}$ ). The preferred raw material is coal of poor metamorphic development, containing fragments with relatively weak bonds [5–8]. Pitch products may be obtained at low temperatures, since such high degrees of destruction of the coal's organic mass are not required in that case.

The literature regarding the thermal dissolution of coal to produce high-boiling pitch was reviewed in [9, 10]. Research at the Institute of Fossil Fuels and Kharkov Coal-Chemistry Institute has shown that the product yield in thermal dissolution is largely determined by the properties of the solvent and the activity of the coal [11, 12]. Partially hydrogenated polycyclic aromatic hydrocarbons, which are able to act as hydrogen donors, are found to be relatively effective solvents. The action of polycyclic aromatic hydrocarbons such as pyrene and phenanthrene is associated with their ability to donate hydrogen and also to add hydrogen. In other words, they transfer hydrogen from hydrogen-saturated coal fragments to radicals.

Active research on extractive pitches is underway in China, the United States, and Japan [13–17]. The Japanese technology for the thermal dissolution of subbituminous and bituminous coal in the production of ash-free HyperCoal has undergone the most development [17–20]. The process is carried out at  $360\text{--}380^{\circ}\text{C}$ ; mixtures of bicyclic aromatic hydrocarbons are used as solvents. HyperCoal has plastic and clinkering properties and may be used to replace scarce clinkering coal in coking batch. It may also be used to produce variable carbon materials, such as binder, strong coke, graphitized carbon, and coal electrodes [19]. In the United States, a proposal for pitch production is based on the thermal dissolution of coal with 78–84% C at  $400^{\circ}\text{C}$  in anthracene oil, at an autogenous pressure of 1.4 MPa [21–23]. The softening temperature of the pitch obtained is  $200\text{--}240^{\circ}\text{C}$  [24, 25].

During thermal dissolution in the anthracene fraction of coal tar, the yield of pitch-bearing products is high for GZh and Zh coal, as we showed in [26–28]. The technical and structural properties of the pitch produced resemble those of hybrid pitches based on mixtures of coal tar and petroleum [29, 30]. Their content of environmentally hazardous polycyclic aromatic hydrocarbons such as benzo(*a*)pyrene is 2–3 times less than that of the coke-plant pitch currently employed.

In the present work, we study the thermal dissolution of GZh and Zh coal in the anthracene fraction of coal tar as a function of the temperature and duration of the process.

## EXPERIMENTAL

We use coals of ranks 1GZhR (Kaa-Khemsk field, Tuva) and ZhR (Chertinskaya-Koksovaya mine, Kuznetsk Basin). According to published data, these coals have coking properties. The plastic-layer thickness  $y = 19\text{--}21$  and  $30\text{--}34$  mm, respectively, while the softening temperature  $T_{\text{so}} = 340\text{--}360^{\circ}\text{C}$ . In experiments on thermal dissolution, we use crushed coal samples ( $<1$  mm class, with mean particle size 0.4 mm), dried in a vacuum chamber at  $85^{\circ}\text{C}$ . The solvent employed is the anthracene fraction of coal tar from PAO Koks.

A Flash EA<sup>TM</sup> 1112 instrument is used for elementary analysis of the coal, the solvent, and the products. IR spectra are recorded on a Bruker Tensor-27 IR Fourier spectrometer (at the Krasnoyarsk Regional Collective-Use Center, Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences). The preparations for recording the IR spectra are introduced in a KBr matrix.

The mineral composition in the coal and the spatial structure of the coal's organic mass are determined from X-ray diffraction patterns recorded on a PANalytical X'Pert PRO instrument in Cu  $K_{\alpha}$  radiation. The parameters of the spatial structure are calculated analogously to [31].

The group composition of the pitch-like products is characterized in terms of the solubility in toluene and quinoline, by standard methods (State Standard GOST 10200–83). The softening temperature is determined in accordance with State Standard GOST 9950–83 (ring and ball method).

The apparatus used for the thermal dissolution of coal is equipped with rotating 80-mL autoclaves (speed 90 rpm) and a 2-L autoclave with a mechanical stirrer (rotating at 120–160 rpm). In each small autoclave, we charge 4 g of dry coal and 8 g of the anthracene fraction of coal tar. The temperature employed is between  $105$  and  $400^{\circ}\text{C}$ . The gaseous products are collected for determination of its volume and composition by a chromatographic method. The contents of the autoclave are transferred to a filter. The residue on the filter is extracted by toluene and then quinoline. The yield of soluble products is determined from the change in ash content of the residues after extraction by toluene and quinoline.

In experiments with the 2-L autoclave, we add 250 g of coal to 550 g of the anthracene fraction of coal tar. At the end of the reaction, the temperature is reduced to  $250^{\circ}\text{C}$ , and then the contents of the autoclave are discharged in molten form through the lower drain to a heated cylinder, where solid particles (consisting of minerals and coal residue) are deposited. After stand-

**Table 1.** Characteristics and composition of coal samples and solvent

Sample	$A^d$ , %	$V^{daf}$ , %	$y$ , mm	$T_{so}$ , °C	Content ( <i>daf</i> ), wt %				
					C	H	N	S	O
ZhR coal	25.9	37.5	30–34	340–360	86.0	5.6	2.7	0.5	5.2
1GZhR coal	5.2	35.8	19–21	340	84.0	5.4	1.1	0.6	8.9
Anthracene fraction					87.6	5.2		7.2*	

\* Sum of N, S, and O.

ing for 3 h at 250°C, cooling, and separation of the lower (ash) fraction, we obtain an ash-free pitch-bearing extract.

## RESULTS AND DISCUSSION

Table 1 presents the characteristics of the solvent and the coal samples. In thermal analysis of the solvent, the liberation of volatiles begins at ~150°C; the rate of mass loss is greatest at 291°C [28]. At 350°C, volatilization is practically complete, and the crucible contains a small coke residue (2–3%).

The IR spectrum of the anthracene fraction of coal tar includes intense absorption bands due to vibrations of the bonds in the aromatic compounds at 3048, 1600, and 700–900  $\text{cm}^{-1}$  (Fig. 1). In the range 700–900  $\text{cm}^{-1}$ , corresponding to out-of-plane vibrations of aromatic C–H bonds, we observe several peaks corresponding to the presence of molecules with different degrees of substitution in the aromatic rings. Judging from the most intense band at 730  $\text{cm}^{-1}$ , molecules with low levels of substitution predominate. The absorption bands at 2800–3000  $\text{cm}^{-1}$  and 1370–1460  $\text{cm}^{-1}$  indicate that aliphatic compounds are present. Noting that the band at 2960  $\text{cm}^{-1}$  is less intense than the band at 2920  $\text{cm}^{-1}$ , we conclude that the content of  $\text{CH}_3$  groups is considerably less than the content of  $\text{CH}_2$  groups.

1GZhR coal is characterized by low ash content (5.2%), in contrast to ZhR coal (25.9%). According to X-ray diffraction data, the mineral components are mainly kaolin and quartz, with a small content of dolomite and calcite. In 1GZhR coal, we also see impurities of rhodochrosite  $\text{MnCO}_3$ .

From the IR spectra, we determine the molecular composition of the coal's organic mass and the solvent, as follows.

1. We calculate the aromatic index  $H_{ar}$  from the integral intensity of the absorption bands associated with valence vibrations of the aromatic C–H bonds in the region 3000–3100  $\text{cm}^{-1}$  ( $A_{ar}$ ) and the aliphatic C–H bonds in the region 2800–3000  $\text{cm}^{-1}$  ( $A_{al}$ )

$$H_{ar} = \frac{A_{ar}/0.22A_{al}}{1 + (A_{ar}/0.22A_{al})} \times 100, \% \quad (1)$$

2. We calculate the ratio of  $\text{CH}_3$  and  $\text{CH}_2$  groups in the aliphatic fragments from the intensities of the absorption bands at 2960 and 2930  $\text{cm}^{-1}$

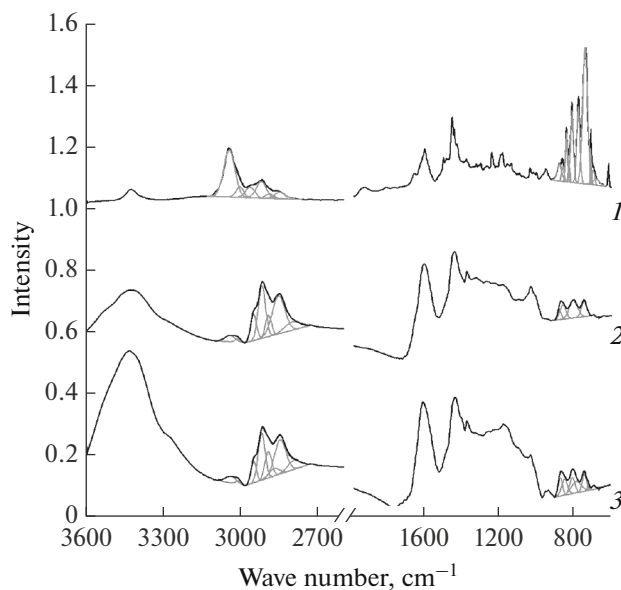
$$\text{CH}_3/\text{CH}_2 = 0.5(A_{2958 \text{ cm}^{-1}}/A_{2920 \text{ cm}^{-1}}). \quad (2)$$

3. We calculate the relative degree of substitution in the aromatic rings (the degree of condensation) from the intensity of the absorption band at 730  $\text{cm}^{-1}$  ( $A_{730}$ ) and the total intensity of the bands in the region 700–900  $\text{cm}^{-1}$  ( $A_{700-900}$ )

$$A_{730}/A_{700-900}. \quad (3)$$

In these equations, we take into account that the ratio of the extinction coefficients for aromatic C–H bonds and aliphatic C–H bonds in coal is 0.22, on average, while the ratio of the extinction coefficients for C–H bonds in  $\text{CH}_2$  and  $\text{CH}_3$  groups is 0.5 [32]. Numerical values calculated from Eqs. (1)–(3) are presented in Table 2.

It is evident from Table 2 that  $H_{ar}$  for the solvent is 0.87. In other words, aromatic hydrogen accounts for 87% of the total hydrogen in the molecules. In ali-



**Fig. 1.** IR spectra of the anthracene fraction of coal tar (1), ZhR coal (2), and 1GZhR coal (3).

**Table 2.** Molecular composition of solvent and coal samples on the basis of the IR spectra

Sample	Aromatic index $H_{ar}$	$A_{730}/A_{700-900}$	$CH_3/CH_2$
Solvent AΦ	0.87	0.47	0.29
ZhR coal	0.28	0.25	0.20
1GZhR coal	0.25	0.20	0.18

phatic structures,  $CH_2$  groups predominate:  $CH_3/CH_2 = 0.29$ . The low  $CH_3/CH_2$  ratio is also confirmed by the ratio of the deformational vibration bands at  $1378\text{ cm}^{-1}$  (for  $CH_3$  groups) and at  $1420\text{--}1460\text{ cm}^{-1}$  (for  $CH_2$  groups). Note that the region  $1420\text{--}1460\text{ cm}^{-1}$  includes several peaks, indicating that  $CH_2$  groups are present in different structural positions.

In the high-frequency region, we observe a band with a peak at  $3430\text{ cm}^{-1}$ , which may be assigned to nitrogen-bearing heterocyclic compounds (such as carbazole, quinoline, and their derivatives) and phenols. We know that such compounds have solvating properties and may facilitate the transfer of coal fragments to the solution.

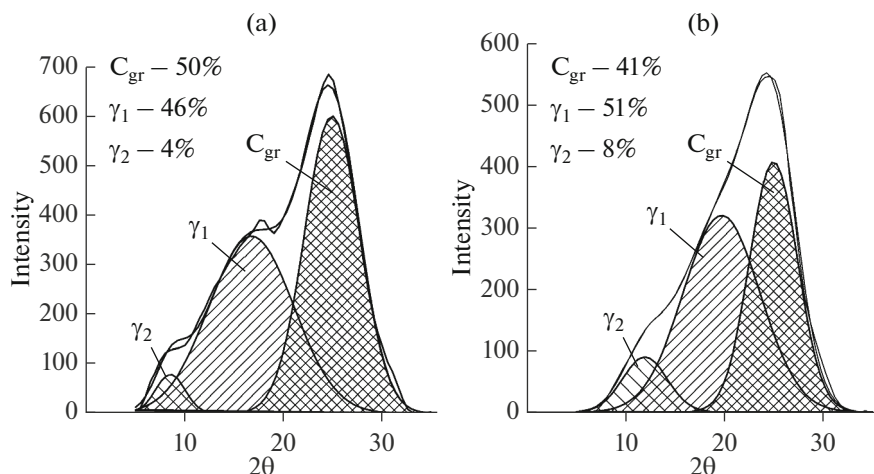
According to the IR spectra, the molecular composition is similar for the 1GZhR and ZhR coal. For the coal samples,  $H_{ar} = 0.25\text{--}0.28$ . That is considerably less than for the solvent. The degrees of substitution in the aromatic rings is higher for the coal ( $A_{730}/A_{700-900} = 0.20\text{--}0.25$ ) than for the solvent (0.47). In other words, the degree of condensation is lower for the coal. The content of methylene chains is significantly higher for the coal ( $CH_3/CH_2 = 0.18\text{--}0.20$ ) than for the solvent. The broad high-frequency absorption band with a peak at  $3450\text{ cm}^{-1}$  indicates that the coal contains

hydrogen-bound phenolic hydroxyl groups. Analysis of other oxygen-bearing fragments in the coal on the basis of the bands in the region  $1000\text{--}1300\text{ cm}^{-1}$  is difficult on account of the superposition of mineral bands.

In the X-ray diffraction patterns of the coal, we see broad reflexes in the ranges  $2\theta = 7\text{--}34^\circ$  and  $34\text{--}52^\circ$ , corresponding to ordered fragments in the coal's organic mass. In Fig. 2, we show fragments of the diffraction patterns with an asymmetric (002) reflex consisting basically of three Gaussian curves. They may be attributed to a relatively ordered graphite-like component with a peak at  $2\theta = 25^\circ$ , containing flat polyaromatic molecules ( $C_{gr}$ ) in packets, and two poorly ordered  $\gamma$  components at the periphery, with peaks at  $2\theta = 17^\circ$  and  $9^\circ$ , according to [31, 33]. In 1GZhR coal, the relatively disordered  $\gamma_1$  component predominates (51%); the content of the graphite-like component is 41%. ZhR coal has a more ordered structure, with 50% of the graphite-like component. The graphite-like packets in the coal consist, on average, of 4.4 graphene layers at a spacing of  $3.6\text{ \AA}$  (diameter  $\sim 17\text{ \AA}$ ).

#### THERMAL DISSOLUTION OF COAL

In the extraction of ZhR coal by means of quinoline at  $\sim 90^\circ\text{C}$ , the bitumen yield is 6%. During extractive processing in the presence of the anthracene fraction of coking tar at  $105^\circ\text{C}$ , the bitumen yield increases over time. After two weeks, the yield of quinoline-soluble components is 14%; and the yield of toluene-soluble components is 8% (Fig. 3). Raising the temperature to  $250^\circ\text{C}$  slightly boosts the yield of quinoline-soluble components (to 18%). Significant acceleration of thermal dissolution begins at  $300^\circ\text{C}$ . After 1 h, the yield of quinoline-soluble components is 36%; after 6 h, it is 42%. The highest yield of quinoline-soluble components (67–70%) is noted at  $350\text{--}380^\circ\text{C}$ .

**Fig. 2.** Fragments of X-ray diffraction patterns for ZhR coal (a) and 1GZhR coal (b).

**Table 3.** Influence of holding time on the conversion of 1GZhR and ZhR coal in thermal dissolution

Coal	$T_{ts}$ , °C	Time, h	Conversion of coal's organic mass, wt %	Content of quinoline-insoluble residue in product, wt % of coal's organic mass
1GZhR	350	1	49	16
		2	73	9
1GZhR	380	1	69	12
		2	52	16
ZhR	300	1	36	17
		6	42	16
ZhR	350	0.5	52	13
		1	70	8

The temperature dependence of the yield of quinoline-soluble components is analogous for 1GZhR coal. At 380°C, the yield of quinoline-soluble components is practically the same for both coals (67–69%). Further heating to 400°C provokes sharp drop in the solubility for both coals. Regardless of the temperature, only a small quantity of toluene-soluble components (8–10%) is extracted. This may not represent the depolymerization or destruction of the coal; these components may have been present all along in the coal's organic mass.

The duration of thermal dissolution affects the yield. At 350°C, the dissolution of 1GZhR coal increases if the duration of the process is extended to 2 h (Table 3). At 380°C, conversely, the yield of quinoline-soluble components falls over time, while the content of the quinoline-insoluble residue increases. This may be attributed to intensification of the secondary reactions: polycondensation of the soluble components to obtain insoluble products. For ZhR coal, increase in the reaction time somewhat increases the solubility at 300 and 350°C. It follows from the results that the temperature for the extraction of quinoline-soluble components from ZhR and 1GZhR coal is 350–380°C, and the optimal duration of the process is 1–2 h.

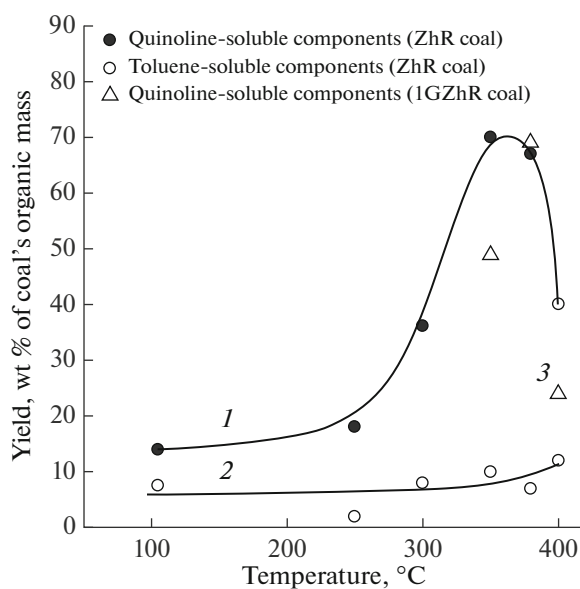
In a 2-L autoclave, we conduct experiments in these optimal conditions, so as to obtain pitch-bearing extracts in sufficient quantity to permit the determination of their characteristics. As an example, Table 4 presents the material balance of the process for the thermal dissolution of 1GZhR coal at 380°C, with 1-h holding. The basic product at room temperature is a hard pitch-like plastic mass with dark coloration, but with lustrous fracture surfaces. We obtain only a small quantity of distillate (0.9%), condensed from the vapor phase at 250°C; and a small quantity of gas (0.2%). The gaseous products consist mainly of CO<sub>2</sub> (55.8%), H<sub>2</sub>S (29.1%), and H<sub>2</sub> (9.9%), with 1.6% CO. Note that practically no methane or other hydrocarbon gases are formed.

Table 5 presents data regarding the thermal dissolution of coal in a 2-L autoclave, at different temperatures. The products obtained at 350–380°C contain

**Table 4.** Mass balance for the thermal dissolution of 1GZhR coal products

Characteristic	Mass, g	Content, wt %
Input to autoclave:		
dry coal	250	31.2
solvent	550	68.8
Total	800	100
Output from autoclave:		
pitch-like ashy product	756	94.5
gas	1.5	0.2
distillate	7.4	0.9
Total	764.9	95.6
Losses	35.1	4.4
Total	800.0	100

Thermal dissolution for 1 h at 380°C in an autoclave with a mixer (working pressure 1.4 MPa). The solvent is the anthracene fraction.

**Fig. 3.** Yields of quinoline-soluble and toluene-soluble components from ZhR coal (1, 2) and 1GZhR coal (3) as a function of the temperature.

**Table 5.** Properties of pitch-like products from 1-h thermal dissolution of coal at different temperatures  $T_{ts}$ 

Coal	$T_{ts}$ , °C	composition of pitch-like product, wt % of organic mass			$T_{so}$ , °C
		$\alpha$ fraction	$\alpha_2$ fraction	$\alpha_1$ fraction	
1GZhR	350	26	13	13	76
1GZhR	380	27	20	7	76
ZhR	250	24	0	24	123
ZhR	350	27	23	4	76
ZhR	380	26	23	3	81

The  $\alpha$  fraction consists of toluene-insoluble components; the  $\alpha_1$  fraction consists of quinoline-insoluble components; and the  $\alpha_2$  fraction consists of quinoline-soluble but toluene-insoluble components.

**Table 6.** Elementary composition of ash-free extracts obtained from coal at 380°C

Coal	Content, wt %				
	C	H	N	S	$O_{dif}$
1GZhR	89.8	5.5	1.4	0.8	2.5
ZhR	89.9	5.4	1.9	0.6	2.2

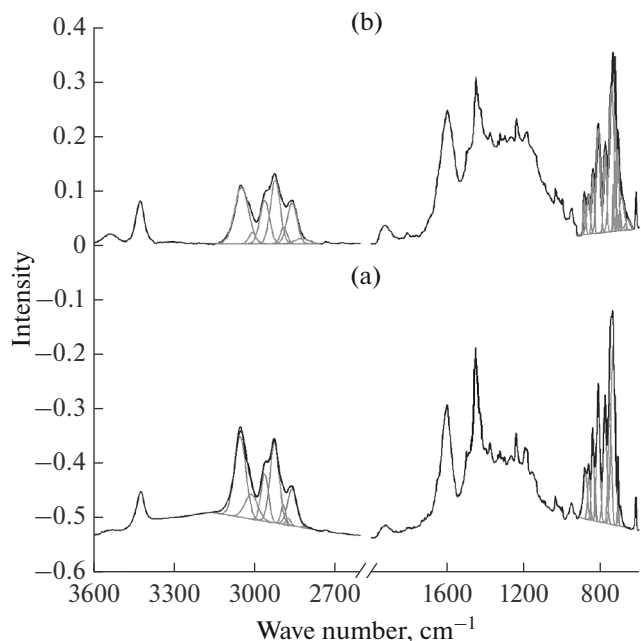
24–27% toluene-soluble components ( $\alpha$  fraction) and 3–13% quinoline-insoluble material ( $\alpha_1$  fraction). The softening temperature of the plastic mass obtained is 76–123°C, depending on the type of coal and the temperature of dissolution. The carbon content in the products is 89.8–89.9%; the hydrogen content is 5.4–5.5%; the nitrogen content is 1.4–1.9%;

the sulfur content is 0.6–0.8%; and the oxygen content is 2.2–2.5% (Table 6). After separation of the ashy material by hot sedimentation, the ash content is 0.2–1.5%.

According to the IR spectra (Fig. 4), the aromatic index  $H_{ar}$  of the product is 0.72–0.78; the degree of substitution in the aromatic rings is low ( $A_{730}/A_{700-900} = 0.42-0.44$ ), and  $CH_3/CH_2 = 0.24-0.33$  (Table 7). The weak bands at 3550, 3420, and 1925  $cm^{-1}$  indicate the presence of a small quantity of phenols, nitrogen-bearing heterocyclic compounds, and unsaturated compounds with accumulated double bonds, respectively.

At 380°C, the X-ray diffraction patterns for the products of thermal dissolution include broad asymmetric reflexes in the region  $2\theta = 8-35^\circ$ , with a peak at around  $25^\circ$ , and in the region  $2\theta = 34-60^\circ$ , with a peak at  $2\theta \sim 43^\circ$ . Fragments of the diffraction patterns are shown in Fig. 5. Computer analysis of the reflex in the region  $2\theta = 8-35^\circ$  shows that product consists mainly (63–69%) of poorly ordered  $\gamma$  components. The proportion of relatively ordered graphite-like packets is 31–37%. Each packet contains five stacked polycyclic aromatic molecules of diameter 17 Å, separated by intervals of 3.5 Å.

In the analysis of the factors determining the thermal dissolution of the coal, it is important to distinguish between effects that may be associated with the chemical properties of the solvent and effects due to structural properties of the coal. We know that the anthracene fraction of coal tar contains significant quantities of compounds with solvating properties (quinoline, carbazole, indole, phenol), hydrogen-donor properties (dihydroanthracene, dihydropyrene), and compounds capable of transporting hydrogen, which may relatively easily add or shed hydrogen (phenanthrene, anthracene, pyrene). The coal employed contains a considerable quantity of polyaromatic fragments, which are present in two main structural components with different degrees of order: in graphite-like packets containing close-packed flat polyaromatic molecules; and in looser structures containing substituted aromatic molecules and other hydrocarbon fragments

**Fig. 4.** IR spectra of products from the thermal dissolution of 1GZhR coal (a) and ZhR coal (b) at 380°C.

**Table 7.** Composition of ash-free pitch-like products obtained by thermal dissolution of coal at 380°C

Coal	Content, wt %					Aromatic index $H_{ar}$	$A_{735}/A_{700-900}$	$CH_3/CH_2$
	C	H	N	S	$O_{djf}$			
ZhR	89.9	5.4	1.9	0.6	2.2	0.78	0.44	0.33
1GZhR	90.0	5.5	1.4	0.8	2.3	0.72	0.42	0.24

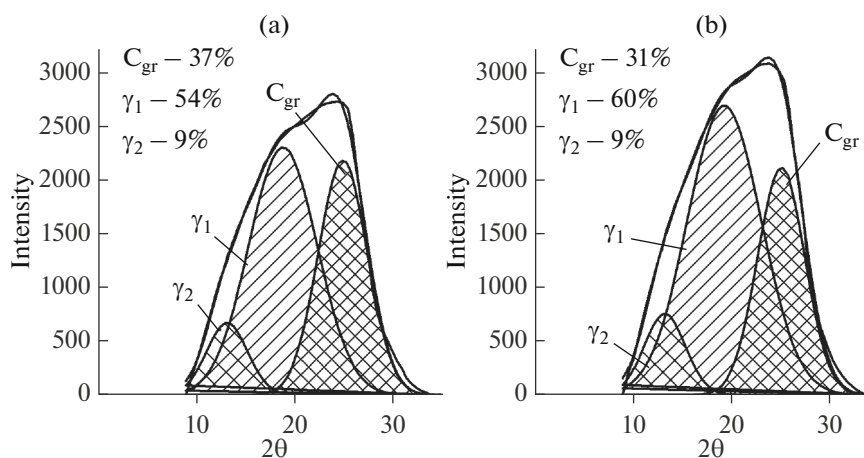
(including naphthene–aromatic, heterocyclic, and aliphatic fragments). The association of molecular fragments in the organic mass of coal at an intermediate metamorphic stage is largely due to multiple non-covalent interactions between aromatic and heterocyclic molecules, according to [34, 35].

Investigation of the thermal dissolution of coal shows that, at low temperature (105°C), the yield of quinoline-soluble products is no more than 14%. That is associated with the predominant micropore structure of the coal's organic mass, which is sterically inaccessible (or largely inaccessible) to large polycyclic molecules of the anthracene fraction. With increase in temperature, the molecular association weakens and hence the mobility of the fragments in the coal's organic mass increases. That permits more effective penetration of the solvent molecules into the coal's organic mass. Considerable increase in the yield of quinoline-soluble products is observed at 300–350°C—that is, in the range at which softening of the coal begins. That facilitates effective interaction of the solvent molecules with fragments in the coal's organic mass, solvation of those fragments, and their transition to solution. At 350°C, Zh coal, whose content of plastic mass is greater than that of GZh coal (for the Zh coal,  $\gamma = 30-34$  mm), has a higher yield of quinoline-soluble products. The influence of the coal's plastic properties on its disintegration was noted in [36, 37].

The thermal solution of coal in the anthracene fraction is a selective process, in which the main products are quinoline-soluble materials. The yield of toluene-soluble components is modest, and the gas yield is very small. Practically no methane or other hydrocarbon gases are formed, although they are usually observed in coal pyrolysis. This may indicate that thermal dissolution occurs without significant thermal destruction of the coal's organic mass, evidently because of disruption of the molecular association and rupture of the oxygen- and sulfur-bearing bonds on solvation. The lack of hydrocarbon gases may also be due to alkylation of the aromatic molecules during thermal dissolution of low-molecular radicals in liquid solvent. That ultimately prevents gas liberation and ensures selective transformation of the coal's organic mass to quinoline-soluble products. Alkylation of pyrene by the decomposition products of the coal's organic mass was noted in [38].

## CONCLUSIONS

We have studied the influence of the temperature and holding time on the thermal dissolution of two samples of 1GZhR and ZhR coal in the anthracene fraction of coal tar. The yield of quinoline-soluble products increases considerably in the temperature range of coal softening.



**Fig. 5.** Fragments of the X-ray diffraction patterns for pitch-like products of the thermal dissolution of ZhR (a) and 1GZhR (b) coal at 380°C.

Optimal thermal-dissolution conditions are determined for selective production of quinoline-soluble pitch-like products from 1GZhR and ZhR coal: 1–2 h at 350–380°C. In those conditions, the yield of quinoline-soluble products is 70–73%. The yield of toluene-soluble components is no more than 10%. The yields of the distillate fraction and the gas are 0.9% and 0.2%, respectively.

The ash-free pitch-like product is a plastic mass with a softening temperature of 76–123°C. It consists mainly of polycyclic aromatic hydrocarbons with a few short alkyl substituents in the aromatic rings. The spatial structure mainly includes poorly structured polycyclic aromatic molecules. The proportion of relatively ordered graphite-like packets is 31–37%. Each packet contains five stacked polycyclic aromatic molecules of diameter 17 Å.

In terms of its composition and plasticity, the product is suitable as a source of alternatives to coal pitch.

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