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Comparative Analysis of the Properties of Extractive and Coal Tar Pitches

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Abstract

The properties of the pitch samples obtained by means of the thermal dissolution of coal were studied using a unit with a flow tubular reactor. Their main differences were analyzed in comparison with coal-tar pitch. It was shown that in terms of elemental composition, extractive pitches are characterized by lower carbon content and a high percentage of oxygen, compared to the traditional binder. Their technological parameters are characterized by increased softening point and low coke residue. These features are a consequence of molecular composition. According to IR and NMR spectroscopy, the aromaticity factor of the alternative binder is relatively low, the organic matter contains a large number of aliphatic groups ($-CH_2-$ and $-CH_3$), as well as polar oxygen-containing groups such as carbonyl, ether, etc. The latter groups have a negative effect on the rheological properties of the extractive pitch. The influence of coal type and coal-oil paste composition on the yield and quality indicators of the pitch-like products of thermal dissolution was analyzed. The use of a coal-solvent mixture with the high percentage of coal is not reasonable because of the high viscosity of final extractive pitches, which hinders the preparation of a homogeneous mixture for the formation of carbon-graphite products.

Keywords: thermal dissolution of coal, extractive pitch, molecular composition

INTRODUCTION

During the recent decade, the especially rapid development of the production of iron and non-ferrous metals, in particular steel and aluminium, is observed in many countries [1, 2]. The major amount of cast iron and steel (60–70 %) is manufactured according to the most efficient traditional blast-furnace technology using metallurgical coal coke. Coal tar pitch (about 4 %) is formed as a side product of its production. The non-volatile residue of the coal tar pitch (pitch, about 50 % of the yield of coal tar pitch) serves as a valuable raw material for obtaining carbon materials for various purposes and is mainly used as a binder in anodes for aluminium electrolysis.

During recent years, as a result of innovations in ferrous metallurgy, a substantial decrease in the consumption of expensive metallurgical coke was achieved. In the majority of countries, this has led to a decrease in its production and, as a consequence, to a decrease in the production of the side product – pitch. The planned increase in the number of blast furnaces with the injection

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of dust-like coal, natural gas and oil fractions (as reducing agents to replace a part of coke) into the hearth, as well as large-scale development of promising competitive out-of-furnace processes of steel preparation, in particular fusion in electroarc furnaces or reducing fusion (Corex®-process), will cause a substantial decrease in the need for coke and therefore to even stronger decrease in the production of pitch [3].

Meanwhile, the need for pitch and the requirements to its quality are continuously increasing in various branches of industry, especially in the dynamically developing production of aluminium and high-tech carbon materials. It should be stressed that the large-scale development of the promising competitive external fusion technology in electroarc furnaces with graphitized electrodes under the conditions of a decrease in the production of metallurgical coke will inevitably encounter a serious problem of the lack of pitch, which is indispensable in the production of these electrodes. Except for China, the mentioned trends of the production and consumption of pitch are characteristics of the majority of countries, which defines the urgent necessity to develop the methods of obtaining substituents leaving aside the coking process.

The problem connected with the search for an alternative to the coke pitch is also dictated by a number of other factors, among which the high content of carcinogenic substances in it is of special importance.

In this connection, the process of the thermal dissolution of coal is attracting increased attention during the recent years because this process allows obtaining a high-boiling extract under rather mild conditions, and this extract is suitable for processing into a carbon binder [4–7]. The development of this process will allow us also to solve the problem of the ecological safety of pitch materials because ecologically dangerous carcinogenic materials are practically absent from initial coal.

Different versions of the implementation of thermochemical coal processing are known, traditionally aimed at obtaining an increased yield of liquid products intended for use as fuel. The majority of these processes involve hydrogenation processing, in particular with the help of catalysts, and require the autoclave-type apparatuses [8, 9]. However, autoclave reactors are the least suitable version to carry out chemical technological processes under industrial conditions. Their main disadvantage is their periodic action, with loading and unloading procedures often insufficiently automated due to the construction features. This has a negative effect on the final net cost of the products. Reactors of this type are considered by designers as the last and the worst possibility for real industrial production.

The goal of the present work was to study the properties of alternative extractive pitch obtained from the products of the thermal dissolution of coal at the medium stage of metamorphism in a flow tubular reactor, and a comparison with the properties of traditional coal tar pitch.

EXPERIMENTAL

The raw material for thermal dissolution was the coal of 1GZh grade (Chadan deposit, LLC Tuvinskaya Gornorudnaya Kompaniya) and Zh grade (the Kuznetsk coal basin, LLC Raspadskaya Ugolnaya Kompaniya). After grinding to particle size not more than 0.2 mm and drying, coal was mixed with solvents to form the paste. The paste-forming solvents were tar pitch and the heavy product of oil processing in equal relations similar to the case described in [10].

The extractive pitch was obtained in the laboratory tubular flow reactor. The temperature in the furnace was kept at a level of 400 °C, the pressure was 10–20 atm. After passing along the reaction coil, the products entered the distillation zone for the purpose of separating the volatile hydrocarbons with boiling temperatures below 300 °C.

Elemental and technical analyses of initial coal were carried out using standard methods according to GOST R 53357–2013 (Table 1).

The softening temperature of the resulting extractive pitch was determined according to GOST 9950–83 (the ring and rod method), the coke number was determined according to GOST R ISO 6998–2017. The group composition was characterized on the basis of solubility in toluene and quinoline using standard methods according to GOST 10200–2017.

To compare the properties, we used commercial coal tar pitch manufactured by the PC Altay-Koks.

The features of the molecular composition of the pitch were determined from IR spectra recorded with the help of the IR Fourier spectrometer Nicolet 380-IR (Thermo Electron Corp., USA), and from the spectra of ^{13}C nuclear magnetic resonance (NMR) and proton magnetic resonance

TABLE 1

Elemental and technical composition of coal samples

Coal grade	Technical analysis, mass %				Elemental composition, mass % per daf				H/C atomic ratio
	W^a	A^d	V^{daf}	S_t^d	C	H	N	O	
1GZh	0.6	5.0	38.2	0.25	86.60	5.80	1.20	6.15	0.80
Zh	1.8	11.2	34.5	0.55	87.54	5.55	0.91	5.45	0.76

Note. W^a is analytical moisture, A^d is ash content, V^{daf} is the yield of volatile substances, S_t^d is total sulphur, daf is dry ash-free state of the sample.

(PMR) recorded with an Avance III 600 spectrometer (Bruker, Germany). PMR spectra were recorded for the pitch fraction soluble in toluene. NMR spectra were recorded using a standard cross-polarization procedure with the suppression of proton signals and with magic angle spinning (CPMAS).

RESULTS AND DISCUSSION

Thermal dissolution parameters and technical characteristics of resulting pitch

The material balance of thermal dissolution of coal in the paste composed of 33 mass % coal and 67 mass % solvent is presented in Table 2. The yield of the major products was determined after the reaction carried out for 1 h.

The data show that coking coal samples close to each other in composition and properties form almost the same amount of extractive pitch. Taking into account the increased ash content of Zh grade coal, the target product is distinguished by higher ash content in this case.

The major characteristics of the obtained pitch-like products of thermal dissolution of coal are presented in Table 3. It may be stated that the properties of extractive pitch depend on the grade of initial coal and the composition of the thermally dissolved mixture. An increase in coal metamorphism degree and the fraction of coal in the suspension cause an increase in the temperature of product softening above 100 °C, its dynamic viscosity and coke number. The major differences between traditional coal tar pitch and extractive pitch are well pronounced if we compare these parameters. One can see that the yield of the coke residue, which provides the quality of coal graphite products – their porosity, mechanical strength [11] – for experimental samples are much lower than in the case of the traditional binder.

Viscosity is of great practical importance, too, because it affects the distribution of the binder during mixing with the filler. Results of viscosity measurements show that an increase of the coke number is always accompanied by worsening (in some cases substantial) of the viscosity characteristics of the alternative pitch. These circumstances hinder its use in the electrolysis production. Quite the contrary, the high content of the most valuable α_2-fraction (the substances soluble in quinoline but insoluble in toluene) which is responsible for binding properties [12] are higher in extractive pitch than in traditional pitch. It is also necessary to mention that the resulting samples contain extremely low benz(a)pyrene content, which will have a positive effect on the ecological aspects of the use of this binder under industrial conditions.

TABLE 2

Material balance of thermal dissolution of coal of different grades, mass %

Product	1GZh		Zh	
	Yield	Yield, % per daf	Yield	Yield, % per daf
Extractive pitch	78.9/1.87[a]	79.0	78.5/2.66[a]	79.8
Strippant	12.6	12.9	11.3	11.9
Gases, mechanical losses (from the difference)	8.5	8.1	10.2	8.3

[a] Ash content of extractive pitch, mass %.

TABLE 3

Major characteristics of coal tar pitch (CTP) and extractive pitch

Parameter	CTP	Extractive pitch from coal of grade		
		Zh	1GZh	
		Composition of suspension[a], mass %		
		33/67	33/67	40/60
Softening temperature (R&R)[b], °C	90	101	87	104
α-fraction, mass %	33.1	37.7	36.0	39.8
α_1-fraction, mass %	9.0	8.5	8.0	12.6
α_2-fraction, mass %	24.1	29.2	28.0	27.2
Coke number, mass %	55.0	47.3	45.1	48.6
Dynamic viscosity at 185 °C, mPa · s	433	704	404	2814
Benz(a)pyrene content, mg/g of pitch	10.3	2.6	2.8	3.2

Note. 1. CTP is coal tar pitch (PC Altay-Koks). 2. α-fraction – substances insoluble in toluene, α_1-fraction – substances insoluble in quinoline, $\alpha_2 = \alpha - \alpha_1$.

[a] Here and in Tables 4–7: composition of suspension (coal/solvent), mass %.

[b] R&R – the Ring and Rod method (GOST 9950–83)..

Characteristics of the chemical and molecular composition of pitch

The data on the elemental composition of pitch are presented in Table 4. Attention should be paid to the increased oxygen content in the organic mass of the resulting pitch-like products: its concentration in the pitch from 1GZh coal is 3 times higher than in the coal tar pitch.

The IR spectra of coal tar pitch and extractive pitch contained intense absorption bands related to aliphatic structures – in the regions of 3000–2800 and 1460–1370 cm^{-1}; the bands characteristic of aromatic compounds were detected in the regions 3100–3000 and 1600 cm^{-1}; those related to out-of-plane deformation vibrations of aromatic bonds (C_{ar}–H) appeared at 900–700 cm^{-1} (Fig. 1). The general view of the IT spectra of pitch-like products of thermal dissolution with the variation of initial coal and the composition of thermal-soluble suspension exhibited almost no differences. Judging from the intensity (*A*) and profile of absorption bands within the range 3100–2800 cm^{-1}, the coal tar pitch is characterized by substantially higher aromaticity than extractive samples.

For the semi-quantitative estimation of the molecular composition of pitch-like products, we determined the IR spectral characteristics demonstrating the relative content of aromatic hydrocarbons, the degree of cycle substitution and the fraction of methyl (CH_3) groups with respect to the total amount of aliphatic groups [13–15]. The collected data are listed in Table 5. In spite of the close degree of metamorphism of initial coal samples, pitch samples obtained on their basis differ from each other in composition for the same composition of thermal-soluble paste. The extractive pitches based on 1GZh coal grade are characterized by the lower relative amount of aromatic hydrogen (C_{ar}–H), calculated from

TABLE 4

Elemental analysis of coal tar pitch and extractive pitch

Pitch sample	Coal grade/ composition of suspension[a], mass %	Elemental analysis, % per daf					H/C atomic ratio
		C	H	N	S	O	
Extractive	1GZh/(33/67)	89.1	5.1	1.5	0.4	3.9	0.69
	Zh/(33/67)	90.3	4.8	1.3	0.7	2.9	0.64
Coal tar	–	92.7	4.4	1.2	0.5	1.2	0.57

[a] See footnote to Table 3.

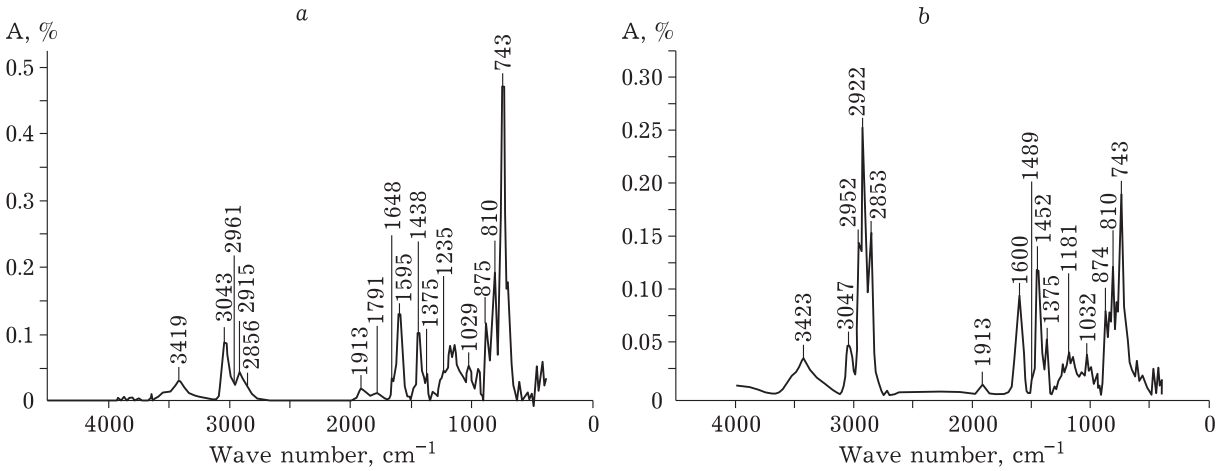

Fig. 1. The general view of IR spectra for coal tar pitch (*a*) and extractive (GZh1) pitch (*b*).

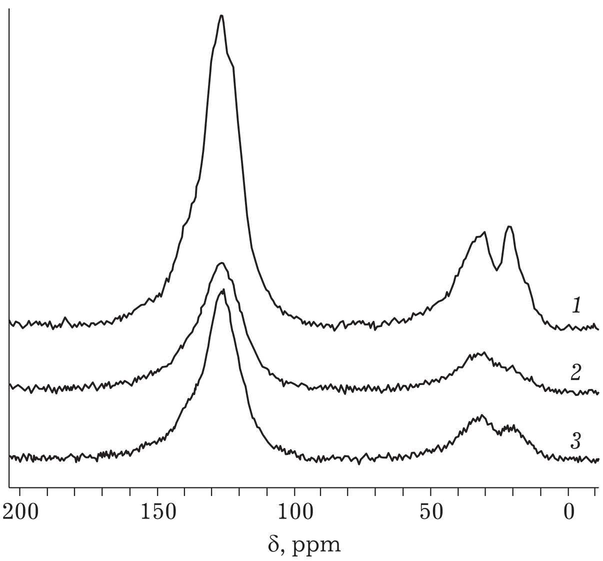

Fig. 2. ^{13}C CPMAS NMR spectra of extractive pitch obtained from coal of different grades and the compositions of suspensions (coal/solvent), mass %: *1* – GZh (40/60), *2* – GZh (33/67), *3* – Zh (33/67).

the ratio of the intensities of absorption bands at 3050 and 2920 cm^{-1} (A_{3050}/A_{2920}). For this sample, the relative amount of CH_3 groups with respect to the total amount of aliphatic groups is higher. An increase in the fraction of coal in the coal-oil paste, with the same conditions of thermal dissolution, leads to an increase in the aromaticity of the extractive pitch. In this case, it is characterized by the low degree of aromatic ring substitution, mainly by methyl substituents.

The ^{13}C CPMAS NMR spectra of the solid samples are shown in Fig. 2. The qualitative analysis of the spectra showed that the composition of the studied samples is represented by the aromatic and aliphatic fragments, as well as by a set of different functional groups. The major differences relate to their quantitative relations.

The relative distribution of carbon atoms over structural groups in the samples under study, determined by integrating the corresponding signals, is shown in Table 6. Analysis of the data shows that hydrocarbons within the extractive pitch have mainly aromatic nature. The degree of aromaticity f_a, calculated taking into account the data of elemental analysis, approaches the

TABLE 5

Molecular composition of pitch according to the data of IR spectroscopy

Pitch sample	Coal grade/ composition of suspension[a], mass %	Substitution degree ($A_{730}/A_{700-900}$)	CH_3/CH_2 ratio (A_{2950}/A_{2920})	$(C_{ar}-H)/CH_2$ ratio (A_{3050}/A_{2920})
Extractive	1GZh/(33/67)	59.00	0.51	0.38
	1GZh/(40/60)	70.00	0.71	0.56
	Zh/(33/67)	61.20	0.63	0.41
Coal tar	–	83.20	0.75	2.01

[a] See footnote to Table 3.

TABLE 6

Fragment composition of the samples of extractive pitch (data of ^{13}C NMR spectra)

Coal grade/ composition of suspension[a], mass %	Distribution of carbon atoms over structural fragments, rel. %								f_a
	CH_3	CH_2	OCH_3	C–O–C	C_{ap}–H	C_{ap}–C	C_{ap}–O	C=O, COOH	
	Range of the chemical shifts of resonance absorption, ppm								
	0–25	25–51	51–67	67–93	93–129	129–148	148–171	171–187	
1GZh/(33/67)	1.81	10.60	0.81	2.37	60.98	17.94	2.18	3.32	0.81
1GZh/(40/60)	5.46	9.92	0.47	0.87	63.17	18.79	1.46	1.50	0.82
Zh/(33/67)	3.42	9.80	1.33	0.51	62.28	17.95	1.86	1.19	0.82

Note. f_a is the degree of aromaticity, which is equal to $(C_{ar}-C+C_{ar}-H)/(C_{ar}-C+C_{ar}-H+C_{alk})$, $C_{alk} = CH_3+CH_2$.

[a] See footnote to Table 3.

TABLE 7

Structural parameters of toluene-soluble fraction (data of PMR spectra)

Pitch sample	Coal grade/ composition of suspension[a], mass %	Distribution of hydrogen atoms over structural fragments, rel. %					σ	*n*
		H_{ar}	H_{olef}	H_α	H_β	H_γ		
		Range of chemical shifts of resonance absorption, ppm.						
		9.0–6.7	6.7–4.5	4.5–2.0	2.0–1.0	1.0–0.0		
Coal tar	–	79.42	1.11	11.52	4.03	3.34	0.07	1.5
Extractive	Zh/(33/67)	46.77	0.58	25.15	19.63	7.87	0.21	2.0
	GZh/(33/67)	44.39	0.62	24.71	22.55	7.74	0.22	2.1
	GZh/(40/60)	47.68	0.71	24.20	20.57	6.83	0.20	2.0

Note. 1. σ is the degree of substitution in aromatic rings. 2. *n* is the average length of alkyl substituent. 3. H_{ar} means hydrogen atoms bound to carbon in the aromatic compounds, H_{olef} means hydrogen atoms bound with carbon having unsaturated bond, H_α, H_β, H_γ means hydrogen atoms in aliphatic substituents in α, β, γ-positions.

[a] See footnote to Table 3.

values characteristic of the typical coal tar pitch. No significant differences are observed in the aromaticity of samples obtained from different coal grades. The fraction of carbon atoms of alkyl groups reaches 15 rel. % with the high fraction of methylene groups, which is not characteristic of the traditional binder.

It may be also stressed that the characteristics of the molecular composition of the extractive pitch, in particular the content of methyl, methoxyl, ether and carbonyl groups, are to a definite extent dependent on the grade of coal and on the composition of the coal-oil paste, that is, on coal content in it. Oxygen atoms, which were found by means of elemental analysis to be present in high concentrations, are incorporated in phenol and carboxyl groups, and also form ethers and methoxy substituents. The relative percentage of the latter is maximal in the case of thermal dissolution of Zh grade coal, while ethers and carboxylic acids dominate in the pitch obtained from coal of the lower degree of metamorphism. Comparing the effect of coal grade and the composition of the thermal-soluble mixture on the content of aliphatic chains in the final product, one may state the prevailing effect of coal type and its fraction in the suspension on the content of methyl and methylene groups in the extractive pitch.

Investigation of the composition and structure of the substances soluble in toluene was carried out with the help of PMR spectroscopy. It was established preliminarily that the yields of soluble substances extracted with toluene and its deuterated analogue were almost the same. A general view of the PMR spectrum for extractive pitch obtained from 1GZh coal grade is shown as an example in Fig. 3 (paste composition: 33 % coal and 67 % solvent). Estimation of hydrogen distribution over molecular fragments showed that the relative amount of aromatic protons (H_{ar}) of this fraction of extractive pitch is about 46–48 %, while for standard pitch their fraction is 79 % (Table 7). The number of aliphatic protons in the substituents in α-, β- and γ-positions (H_α, H_β and H_γ) is 25, 21 and

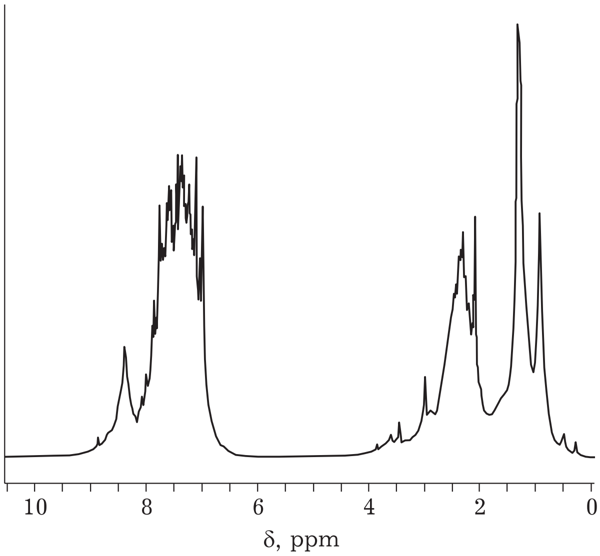

Fig. 3. PMR spectrum of extractive pitch. Coal grade: GZh1, composition of suspension (coal/solvent), mass % – 33/67.

7 % as average, respectively.

So, the degree of substitution (σ) of the aromatic rings of hydrocarbon molecules included in the toluene-soluble substances of the pitch product of thermal dissolution of coal is more than 3 times more than in coal tar pitch. The aromatic molecules of extractive pitch (in comparison with coal tar pitch) have somewhat longer aliphatic substituents.

It should be stressed that the PMR spectra of toluene-soluble substances did not contain a noticeable signal related to the protons bounds to oxygen atoms. A comparison of this circumstance with the data obtained by means of ^{13}C NMR spectroscopy for the whole pitch allows us to suppose that phenol functional groups are concentrated mainly in the toluene-insoluble part of the extractive pitch.

CONCLUSION

As a result of the studies, the features of the chemical and molecular composition of extractive pitch obtained by thermal dissolution of two samples of medium-metamorphized coal in a flow reactor were established. It was demonstrated that the presence of a large amount of oxygen-containing and other heteroatomic components within extractive pitch has a negative effect on viscosity and softening temperature of the material due to intermolecular interactions, and relatively low content of aromatic hydrocarbons leads to a lower yield of the coke residue.

A comparison of the properties of extractive pitch with the corresponding properties of commercial coal tar pitch was carried out. It was established that extractive pitch is distinguished by somewhat increased softening temperature, relatively high viscosity and lower coke number than the traditional coal tar pitch. These differences are a consequence of differences in their molecular composition. Comparatively low aromaticity degree characteristic of extractive pitch depicts the lack of highly aromatic precursors which would be able to form the coke residue during thermal treatment. The presence of relatively high fraction of aliphatic fragments and heteroatoms has a negative effect on the rheological properties of the resulting samples. Oxygen-containing functional groups that are present in extractive pitch and its fractions are prone to the formation of intermolecular interactions of the type of hydrogen bonds, which explains increased viscosity and softening temperature in comparison with traditional pitch.

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