

Stimulation of Low-Temperature Dissolution of Organic Matter of Brown Coal, Composition of Bitumoids

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ABSTRACT

The paper presents data on the yield, chemical composition of bitumen extracted from the brown coal of the Tyulgan deposit. Bitumens were extracted from brown coal by the following methods: I) sequential extraction with ethanol, n-heptane, alcohol-benzene according to the Grefe method, II) low-temperature dissolution of the organic mass of coal (OMC) by alkylation and subsequent extraction of bitumoids; III) stimulation of alkylation by ultrasound and subsequent extraction of bitumoids. It is shown that the use of ultrasonic exposure during the O-alkylation process has a positive effect on the yield of bitumoids - the yield increased to 52%. The obtained samples were studied using the methods of IR spectroscopy, ¹³C NMR (CPMAS), gas chromatography-mass spectrometry (GC-MS). A number of individual compounds were identified in the composition of bitumen and bitumoids during the study by the GCMS method: gamma-tocopherol, Stigmast-4-en-3-one, beta-Hydroxyallobetulan, 1-Hexadecanol, Oleyl alcohol, etc. Among the identified compounds, various biologically active substances are present.

Keywords: Bitumen, Brown coal, Extraction, O-alkylation, Ultrasonic action, Biologically active substances

1. INTRODUCTION

Brown coals are usually burned to generate heat and electricity, while the colossal chemical potential that is concentrated in them is irretrievably lost. Coal chemistry processing is one of the most significant methods in the complex use of brown coal. The most promising method is extraction using various methods of stimulating low-temperature dissolution of organic matter of brown coal. This makes it possible to extract the numbers of valuable products from brown coal: humic substances and bitumen (mountain wax) [1,2].

Bitumen is a valuable product in high demand on the world market, the cost of which in its "raw" form reaches 3000 € per ton. When processing bitumen, it is customary to distinguish two components, wax and resin. Wax in its structure and characteristics of use is very similar to natural plant essential waxes and is used in cosmetics, for the manufacture of protective and polishing compositions, precision casting, et al. In addition, terpenoids, hopanes, sterols, and some vitamins, and other biologically active substances (BAS) characteristic of vegetation, were found in waxes and resins. Therefore, special attention is attracted by studies aimed at studying the possibility of extracting biologically active substances in pure form or in the form of narrow fractions, which can

find their application in cosmetics, medicine, agriculture [1-5].

This work is devoted to the study of the group and component composition of fractions of brown coal bitumen, as well as ways to increase the yield of bitumen during their extraction, such as O-alkylation and O-alkylation under the influence of ultrasound.

2. EXPERIMENTAL

To study the group and component composition of bitumen, several experiments were carried out, during which bitumen was extracted from coal with successive extraction according to Grefe method (I), from O-alkylated coal (II), and O-alkylated coal under the influence of ultrasound (III).

Brown coal (1B) (Table 1) of the Tyulgan deposit of the South Ural Basin (TBC) was used as a raw material for the extraction of bitumen.

2.1. The Grefe Extraction

The Grefe extraction was carried out with the sequential use of solvents: ethanol, n-heptane, ethanol-benzene 1:1 [4]. As a result of the process carried out, 3 fractions were obtained: I R1, I W, I R2. The volume of each of the solvents used was 100 mL, the duration of extraction with each of the solvents was 3 h, the total yield of extraction bitumen was 16.0% (Table 2). The results of the proximate and ultimate analysis of de-bituminated coal (CR1) are presented in Table 1.

2.2. O-Alkylating Treatment and Extraction of Bitumoids

O-alkylating treatment and extraction of bitumoids were carried out under conditions calculated for the maximum yield of bitumoids [6]. Process parameters: 5 g of coal; 69.75 mL of n-butanol, n-heptane 100 mL, 9.8% of the volume of the OPA solution ($w=79.9\%$, $\rho=1.626 \text{ g/cm}^3$), the duration of the alkylation process is 6.0 h. The resulting bitumoids were separated into wax (II W) and resin (II R) fractions using a methodology based on the dissolution of resins in acetone [2, 7, 8].

After the completion of the process, residual resins were extracted from the remaining coal mass with alcohol-benzene (1:1), according to the Grefe method. As a result, the total yield of bitumoids was 44.4% (Table 2). The results of the proximate and ultimate analysis of the obtained de-bituminated coal (CR2) are shown in Table 1.

Table 1. Results of the proximate and ultimate analysis of initial and de-bituminated coals

Sample	W ^a	A ^d	V ^{daf}	C ^{daf}	H ^{daf}	H/C _{at}	(O+N+S) ^{daf} by difference
TBC	9.1	21.5	65.9	57.3	6.3	1.3	36.4
CR1	7.5	27.0	64.4	63.6	5.9	1.1	30.5
CR2	3.1	37.5	64.1	65.9	5.0	0.9	29.1
CR3	1.9	39.3	63.8	67.8	4.5	0.8	27.7

Note. ^{daf} - dry ash-free state of the sample; W^a - analytical moisture in accordance with GOST R 52917-2008; A^d - ash content on a dry sample in accordance with GOST 11022-95; V^{daf} - content of volatile substances according to GOST 6382-2001. Measurement error-no more than 2%.

2.3. O-Alkylation Treatment and Extraction of Bitumoids During the Intensification of the Process by Ultrasound

O-alkylation treatment and extraction of bitumoids during the intensification of the process by ultrasound were carried out with the following process parameters: associated solvent - n-heptane, 100 mL; alkylating alcohol - n-butanol, 50 mL; the catalyst of the process is OPA ($w=79.9\%$, $\rho=1.626 \text{ g/cm}^3$), 5% by volume of the mixture; brown coal - 5 g; the duration of the process is 0.5 h; the process was carried out at the boiling point of the mixture ($98\pm 5^\circ\text{C}$). Ultrasound was generated by an UZDN-2T unit, frequency 22 kHz. After the completion of the process, residual resins were extracted from the remaining coal mass with alcohol-benzene (1:1), according to the Grefe method The bitumoids yield under these conditions was 52.0% Table 2.

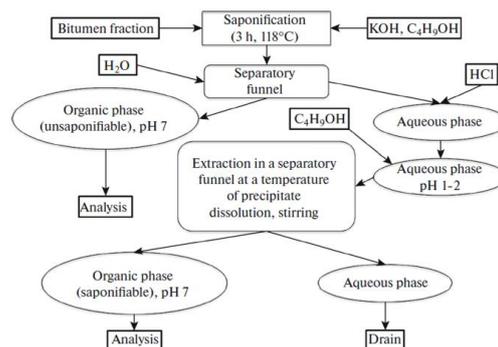


Figure 1. Schematic diagram of separation into saponifiable and unsaponifiable components

The obtained bitumoids were subsequently fractionated into wax (III W) and resin (III R) [2, 7, 8]. The results of the proximate and ultimate analysis of the obtained de-bituminated coal (CR3) are shown in Table 1. All the obtained samples for additional fractionation were divided into saponifiable and

unsaponifiable components [4, 9]. The separation Figure 1 was carried out using a saponification

reaction (butanol, KOH to pH = 11-12, process temperature 118°C, duration 3 h).

Table 2. Bitumen yield during extraction according to Grefe method (I)

Fraction	E ^{daf} , %	E _{total} ^{daf} , %	Results of separation into saponifiable and unsaponifiable components			
			sap., %	unsap., %	losses, %	total, %
Grefe sequential extraction (I)						
I R1 (resin extracted with ethanol)	12.2	16.0	34.7	61.9	3.4	100
I W (wax extracted with n-heptane)	1.2		18.1	80.3	1.6	100
I R2 (resin extracted with alcohol-benzene)	2.6		49.3	49.5	1.2	100
Alkylating process with <i>n</i> -butanol (II)						
II W (wax)	16.5	44.4	72.5	25.4	2.1	100
II R (resin)	27.9		76.8	17.3	5.9	100
Alkylating process with <i>n</i> -butanol under the influence of ultrasound (III)						
III W (wax)	23.2	52.0	68.6	28.5	2.9	100
III R (resin)	28.8		85.9	10.2	3.9	100

For narrower fractionation, the obtained fractions were separated using the method of liquid column chromatography (LC) [9, 10]. Glass columns with the following parameters: diameter - 10 mm; length - 500 mm. Silica gel, GOST 3956-76, was used as a filler, the grain size of silica gel was 0.2-0.5 mm. Following the recommendations [11] and to avoid overloading the column, the loading of the sample for separation was 0.06 g. Solvents were sequentially used as eluents: toluene, ethyl acetate, butanol, ethanol, ethanol-formic acid (1:1). The residual fraction was recovered with hot butanol ($t=118^{\circ}\text{C}$). The yield of fractions was monitored using a refractometer - according to the refractive index of the eluent used.

The samples obtained were studied using IR spectroscopy, ^{13}C -NMR (CPMAS) spectroscopy, chromatography-mass spectrometry (GC-MS).

The IR spectra were recorded on an Infracum-FT 801 FTIR spectrophotometer at a resolution of 4 cm^{-1} with the accumulation of 16 scans in a range of $4000\text{--}500\text{ cm}^{-1}$ in dry KBr.

High-resolution solid-state NMR spectra were recorded on a Bruker Avance III-300 instrument at 75 MHz using standard methodology cross-polarization with rotation at a magical angle (CP/MAS) and the accumulation of 1024 scans at room temperature. Chemical shifts are reported relative to tetramethylsilane (TMS).

The GC-MS analysis was carried out on an Agilent 6890N chromatograph instrument with an Agilent 5973 mass-selective detector under the following conditions: HP-5ms capillary column,

injector temperature, 290°C ; solvent removal, 4 min; split ratio, 50:1, helium carrier gas flow rate, 1 mL/min, injected sample volume, $5.0\ \mu\text{L}$, and column temperature programming from 50°C after a 3 min exposure to 280°C at a rate of $5^{\circ}\text{C}/\text{min}$ and holding at 280°C for 60 min. The concentrations of individual compounds were measured on a total ion current basis. The components of the test samples were identified using the NIST-11 and Wiley libraries of spectra.

3. RESULTS AND DISCUSSION

The data obtained Tables 2 show that the O-alkylation process allowed a significant increase in the yield of bitumoids, up to 44.4%, which is 28.4% more than in the case of sequential extraction according to Grefe. Intensification of the alkylation process by ultrasound made it possible to increase the bitumoids yield - the yield of 52.0%, with a process duration of 0.5 h. When separating the test samples, as a result of the saponification reaction, the proportion of saponifiable substances changes as follows Tables 2: successive extraction according to Graefe<O-alkylation<O-alkylation under ultrasonic action.

IR spectra of the studied samples are shown in Figure 2. The assignment of absorption bands was carried out on the basis of literature sources [12-15]. The samples under study have an identical group composition and are complex multicomponent mixtures (substances). The absorption bands in the region of $3400\text{--}3200\text{ cm}^{-1}$ are stretching vibrations of

the -OH group of alcohols and phenols linked by hydrogen bonds. The absorption bands in the region of 3000-2800 cm⁻¹ are stretching vibrations of -CH₂ and -CH₃ groups. In the region of 1750-1690 cm⁻¹ there are absorption bands characteristic of stretching vibrations of >C=O saturated aliphatic acids and α-halogen-substituted aliphatic acids, esters of long-chain carboxylic acids. In the range of 1475-1450 cm⁻¹, the spectra of the samples contain absorption bands characteristic of bending vibrations of -CH₂ groups. Absorption bands in the range of 1175-1125 cm⁻¹ are characteristic of plane bending vibrations of 1-, 1,3-, 1,2,3-, 1,3,5-aromatic compounds. The absorption bands in the 730-710 cm⁻¹ region are related to the pendulum vibrations of the methylene groups of long alkane chains.

Analyzing the ¹³C-NMR (CPMAS) data, compounds with long alkane chains predominate in the studied samples, mainly related to esters, carboxylic acids, and alcohols. Aromatic compounds are present in small amounts Table 3. The assignment of signals was carried out based on the literature sources [12-14]. Peaks in the range of 5-48 ppm indicate the presence of straight alkane chains and alkyl groups. Peaks in the range of 48-90 ppm indicate the presence of substances in the alcohol group. In the region of 90-108 ppm, the peaks were indicating the presence of acetal groups. Peaks in the region of 108-145 ppm are characteristic of the aromatic group of substances. The presence of peaks in the range of 145-165 ppm is typical for substances

with an aromatic ring having a hydroxyl group. Substances with a carboxyl group are presented in the spectrum in peaks in the range of 165-187 ppm. Peaks in the 187-220 ppm region indicate the presence of substances with a carbonyl group.

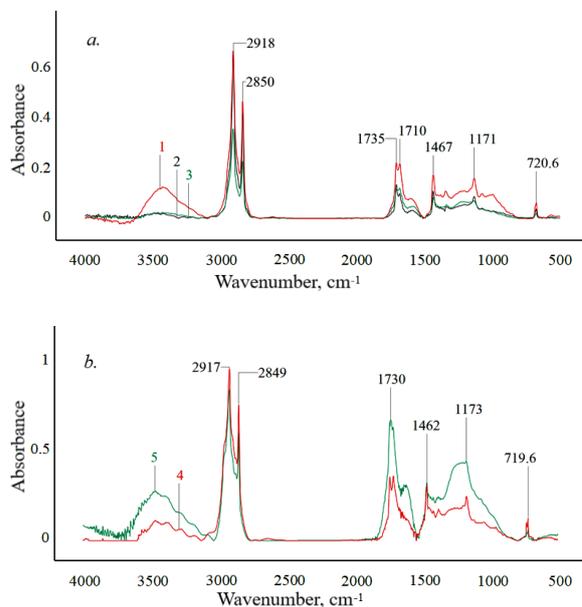


Figure 2. a. - IR-spectra of ethanol (1), n-heptane (2), alcohol-benzene (3) bitumen fractions (I); b. - IR spectra of bitumoids (II) from O-alkylated brown coal (4), bitumoids (III) from O-alkylated brown coal with the intensification of the process by ultrasound (5)

Table 3. Integral intensities (%) of spectral regions in the ¹³C-NMR spectra (CP MAS) of the samples under study

Sample	220-187 C=O	187-165 COOH	165-145 C _{ar} -O	145-108 C _{ar}	108-90 C _{O-Alk-O}	90-48 C _{alk-O}	48-5 C _{alk}	Structural-group parameters		
								f _{ar}	f _{al}	f _{ar/al}
Grefe sequential extraction (I)										
IR1	2.3	2.9	1.9	6.9	2.6	11.6	71.0	8.8	85.2	0.10
IR1S	2.9	3.9	2.7	9.1	2.7	13.8	64.2	11.8	80.7	0.14
IR1U	1.6	1.8	1.3	4.8	2.2	9.8	78.0	6.1	90.0	0.06
IW	1.5	2.2	1.3	4.3	2.5	8.1	79.9	5.6	90.5	0.06
IWS	1.7	2.6	1.7	5.1	2.6	7.9	77.8	6.8	88.3	0.07
IWU	1.4	2.3	1.1	3.7	2.1	8.0	81.3	4.8	91.3	0.05
IR2	3.0	3.6	2.7	8.7	3.1	12.8	64.6	11.4	80.4	0.14
IR2S	3.1	4.2	3.0	10.3	2.9	13.5	62.2	13.3	78.6	0.17
IR2U	1.3	1.7	1.1	4.1	2.2	8.7	79.8	5.2	90.7	0.05
Alkylating process with n-butanol (II)										
Alkyl.	1.6	2.1	1.4	4.9	2.1	8.2	78.5	6.3	88.8	0.07

bitumoids										
II W	2.3	2.1	1.6	5.9	2.3	9.6	74.9	7.5	86.8	0.09
II WS	1.2	2.4	1.3	4.1	2.4	8.2	79.9	5.4	90.5	0.06
II WU	2.3	1.4	1.8	7.9	2.2	12.4	71.2	9.7	85.8	0.11
II R	5.2	6.1	5.0	16.0	4.2	17.9	41.0	20.9	63.1	0.33
II RS	5.0	7.1	5.8	17.6	4.1	17.8	40.8	23.4	62.7	0.37
II RU	2.7	2.3	2.0	8.2	2.2	15.2	66.0	10.3	83.4	0.12
Alkylating process with <i>n</i> -butanol under the influence of ultrasound (III)										
Alkyl. under the infl. of ultrasound bitumoids	3.1	4.0	2.9	9.2	3.2	13.8	61.8	12.2	78.8	0.15
III W	1.9	2.8	1.8	5.6	2.8	10.5	72.9	7.4	86.2	0.09
III WS	1.4	3.0	1.6	5.0	2.5	8.5	77.2	6.6	88.2	0.07
III WU	1.2	1.6	1.2	4.8	2.2	9.2	79.3	6.0	90.7	0.06
III R	6.5	7.3	7.8	23.6	4.7	16.3	31.1	31.4	52.2	0.60
III RS	5.6	7.4	6.7	20.5	4.4	17.4	35.8	27.2	57.6	0.47
III RU	1.6	2.4	1.8	7.3	2.1	11.2	73.1	9.1	86.4	0.10

Note: IR1 ethanol-extracted resin; IR1S saponifiable component of the resin extracted with ethanol; IR1U unsaponifiable component of the resin extracted with ethanol; IW wax, extracted with *n*-heptane; IWS saponifiable component of wax extracted with *n*-heptane; IWU unsaponifiable component of wax extracted with *n*-heptane; IR2 resin extracted with alcohol-benzene; IR2S saponifiable component of the resin extracted with alcohol-benzene; IR2U unsaponifiable component of the resin extracted with alcohol-benzene; IIW wax fraction of bitumoids; IISW saponifiable component of the bitumoids wax fraction; IIWU unsaponifiable component of the wax fraction of bitumoids; IIR resin fraction of bitumoids; IIRS saponifiable component of the resin fraction of bitumoids; IIRU unsaponifiable component of the resin fraction of bitumoids; IIW wax fraction of bitumoids extracted from O-alkylated under the influence of ultrasound; IIWS saponifiable component of the wax fraction of bitumoids extracted from brown coal alkylated under the influence of ultrasound; IIWU unsaponifiable component of the wax fraction of bitumoids extracted from brown coal alkylated under the influence of ultrasound; IIR resin fraction of bitumoids extracted from O-alkylated brown coal under the influence of ultrasound; IIRS saponifiable component of the resin fraction of bitumoids extracted from alkylated under the influence of ultrasound brown coal; IIRU unsaponifiable component of the resin fraction of bitumoids extracted from brown coal alkylated under the influence of ultrasound.

According to Table 3, for all the samples under study, the structural-group parameters [16] were calculated f_{ar} - the aromaticity index, f_{al} - the aliphatic index and f_{ar}/f_{al} - the ratio of aromaticity to aliphaticity, where:

$$f_{ar} = C_{ar-O} + C_{ar};$$

$$f_{al} = C_{O-alk-O} + C_{alk-O} + C_{alk};$$

$$f_{ar}/f_{al} = (C_{ar-O} + C_{ar}) / (C_{O-alk-O} + C_{alk-O} + C_{alk}).$$

Analyzing the calculated structural-group parameters (Table 3), we think that aromatic substances during separation as a result of the saponification reaction are concentrated in the saponifiable components of the studied samples. Comparing the indicators f_{ar} alkylated bitumoids and alkylated under the influence of ultrasound, in the latter we observed an increase in the indicator by 2

times. At the same time, there is a tendency in the concentration of aromatic substances in the saponifiable components of the resin fraction (II RS, III RS).

In the study of bitumen and their fractions by GC-MS, more than 200 individual compounds were identified in their composition, including Oleic acid, Octadecanoic acid, Heneicosane; Heptadecane, Oxirane, hexadecyl-, Podocarpa-5,8,11,13-tetraen-7-one, 13-hydroxy-14-isopropyl-, gamma-Tocopherol, Stigmast-4-en-3-one, beta-Hydroxyallobetulane, 1-Hexadecanol, Oleyl Alcohol, Octacosanoic acid, Nonacosanoic acid, Nonacosenoic acid, Triacotanoic acid and others. Particular attention is attracted by BAS [17, 18], which are present in the composition of bitumen and bitumoids in significant concentrations, some of them are presented in Table 4.

Table 4. Biologically active substances identified in the composition of the test samples

Sample, fraction	Substance [17, 18]*	Relative content in the sample, %	Match according to the NIST11 base, %
I R1U	Ferruginol	0.66	87
	Sugiol	0.69	95
	Betulin	0.36	99
I WS	Ferruginol	0.18	87
	Octadecanoic acid	0.6	91
	Oleic acid	1.02	99
I R2U	Sugiol	0.45	99
	n-Tetracosanol-1	3.55	95
II WS	n-Tetracosanol-1	7.7	95
	Octacosanoic acid	13.2	99
II WU	beta-Amyrin	0.96	99
	Stigmastanol	2.44	99
II RS	Sugiol	5.41	99
	Heptanedioic acid	2.3	83
II RU	Sugiol	7.01	99
	Betulin	4.96	99
III WS	Octacosanoic acid	21.03	91
	Triacotanoic acid	9.48	82
	9-Hexadecenoic acid	2.23	70
III RU	Sugiol	0.35	86
	Octacosanoic acid	9.08	83
	Hexacosanoic acid	6.29	80
	Oleic acid	16.4	90

* - Carboxylic acids are presented as butyl esters

For narrower fractionation and isolation of valuable lipid fractions enriched with BAS, LC separation of samples bitumens and bitumoids was carried out (Table 5).

The LC separation of the samples made it possible to increase the proportion of identified compounds in the GC/MS analysis. From the results obtained, it should be noted that in the fractions eluted with toluene, there is a tendency to extract substances related to alcohols, terpenes, and sterols. Among the substances identified in these fractions, there were biologically active substances such as Sugiol, a plant metabolite with antiviral and antitumor activity, Ferruginol, plant metabolite with antitumor and antibacterial activity, Betulin with analgesic properties, antiviral, anti-inflammatory, and antitumor properties.

Moreover, the elution with ethanol made it possible to extract several fractions with a high relative content of Oleic acid - up to 75.8% (I R2), which is also a BAS. Several fractions eluted with a mixture of ethanol and formic acid from alkylated samples were not able to be analyzed. In the obtained chromatograms of these fractions, the intensity of the peaks of substances relative to the peaks of the solvent is very low.

Changing the chromatographic parameters during the analysis of these fractions, within the operating limits of the device, did not affect the readings obtained for these fractions on the chromatograms. Probably, the operating temperature of the instrument with this hardware is insufficient for evaporation and separation of fractions obtained by elution with a mixture of ethanol and formic acid during LC separation.

Table 5. Substances with the highest relative contents in the obtained fractions during LC separation, according to GC-MS data, (relative contents,%)*

Eluent	Substance **	Relative content in the sample, %	Substance **	Relative content in the sample, %	
					I R1
Toluene	1	n-Tetracosanol-1	21.4	9-Hexadecenoic acid	10.5
		1-Heptacosanol	9.0	n-Tetracosanol-1	7.7
		Octadecanoic acid	7.3	Behenic alcohol	5.3
		β-Sitosterol	4.4		
		Podocarpa-5,8,11,13-tetraen-7-one, 13-hydroxy-14-isopropyl	2.9		
	Sugiol	3.0			
	Tetracosanoic acid	16.3			
	2	n-Tetracosanol-1	16.2		
		1-Heptacosanol	13.9		
		Octacosanoic acid	12.5		
Hexacosanoic acid		9.9			
Octacosanoic acid		16.3	Hexadecanoic acid	9.1	
Ethyl acetate	Hexacosanoic acid	13.1	Octadecanoic acid	3.6	
	Tetracosanoic acid	12.3	Oleic acid	3.9	
	Triacotanoic acid	9.4			
	Hexacosanoic acid	17.2	Hexadecanoic acid	41.3	
Butanol	Oleic acid	15.4	9-Hexadecenoic acid	28.8	
	Tetracosanoic acid	11.6			
	Octacosanoic acid	10.7			
	Oleic acid	71.9			Oleic acid
Ethanol	Hexadecanoic acid	11.1	Hexadecanoic acid	8.8	
	Decanedioic acid	7.7	Decanedioic acid	7.7	
	Tetracosanoic acid	12.9			
Ethanol + formic acid (1:1)	1	Hexacosanoic acid	11.1	Oleic acid	69.9
				Oleic acid	16.8
Butanol (t=118°C)	Octacosanoic acid	11.6	Tetradecanoic acid	6.6	
	Triacotanoic acid	8.4	Hexadecanoic acid	6.4	
	9-Tetradecenoic acid	7.9			
Eluent	Substance **	Relative content in the sample, %	Substance **	Relative content in the sample, %	
	I R2		II W		
Toluene	Oleic acid	8.6	Tetracosanoic acid	8.6	
	n-Tetracosanol-1	4.2	Octacosanoic acid	7.8	
	1-Hexacosanol	3.4	Hexacosanoic acid	6.3	
Ethyl acetate	Hexadecanoic acid	61.9	n-Tetracosanol-1	5.5	
			Tetracosanoic acid	11.5	
			Hexacosanoic acid	11.0	
			Octacosanoic acid	10.8	
Butanol	9-Hexadecenoic acid	30.0	Triacotanoic acid	6.6	
			Tetracosanoic acid	10.4	
			Hexadecanoic acid	9.2	
			9-Hexadecenoic acid	8.5	
			Octacosanoic acid	7.6	
Ethanol	Oleic acid	75.8	Oleic acid	65.1	
			Hexadecanoic acid	7.1	
Ethanol + formic acid	1	Oleic acid	50.9	Oleic acid	28.0
				Decanedioic acid	10.0

(1:1)	2	Oleic acid	38.7		
Butanol (t=118°C)		Oleic acid	14.9	Octacosanoic acid	13.9
	Hexadecanoic acid	10.2	9-Hexadecenoic acid	10.7	
			Hexacosanoic acid	10.7	
			Tetracosanoic acid	7.9	
Eluent	Substance **	Relative content in the sample, %	Substance **	Relative content in the sample, %	
	II R		III W		
Toluene	Hexadecanoic acid	15.0	Octacosanoic acid	18.0	
	9-Hexadecenoic acid	9.3	Tetracosanoic acid	14.8	
	Pentadecanoic acid	6.0	Hexacosanoic acid	14.5	
	Tetradecanoic acid	4.3			
	Sugiol	3.0			
Ethyl acetate	Hexadecanoic acid	19.9	Hexadecanoic acid	27.4	
	Hexadecenoic acid	15.0	9-Hexadecenoic acid	15.6	
	Oleic acid	12.4	Oleic acid	8.7	
Butanol	9-Hexadecenoic acid	20.0	Hexadecanoic acid	24.7	
	Hexadecanoic acid	17.8	9-Hexadecenoic acid	21.7	
	Oleic acid	12.8	Oleic acid	10.3	
			Tetradecanoic acid	6.9	
			Pentadecanoic acid	5.0	
Ethanol	Oleic acid	54.4	Oleic acid	72.2	
	9-Hexadecenoic acid	6.4			
Ethanol + formic acid (1:1)	-	-	-	-	
Butanol (t=118°C)	Oleic acid	18.6	Octacosanoic acid	14.2	
	Hexadecanoic acid	13.6	Hexacosanoic acid	10.0	
			Hexadecanoic acid	8.7	
Eluent	Substance **		Relative content in the sample, %		
	III R				
Toluene	Hexadecanoic acid			24.8	
	9-Hexadecenoic acid			22.2	
	Oleic acid			19.2	
Ethyl acetate	Hexadecanoic acid			32.6	
Butanol	9-Hexadecenoic acid			26.7	
	Hexadecanoic acid			24.7	
	Oleic acid			11.5	
	Tetradecanoic acid			8.7	
Ethanol	9-Hexadecenoic acid			22.4	
	Hexadecanoic acid			21.9	
	Oleic acid			14.6	
Ethanol + formic acid (1:1)	-			-	
Butanol (t=118°C)	Hexadecanoic acid			36.5	
	Octadecanoic acid			25.2	

Note: * - coincidence with NIST11 not less than 70%; ** - carboxylic acids are presented as butyl esters.

4. CONCLUSION

Thus, the alkylation treatment with *n*-butanol in the presence of catalyst H₃PO₄ made it possible to significantly increase the bitumoids yield to 44.4%. The intensification of the process by ultrasonic action made it possible to reduce the duration of the process to 0.5 h and increase the bitumoids yield to 52.0%, which is 7.6% more than in alkylation under conditions calculated for the maximum yield of

bitumoids, and 36.0% more than in sequential extraction according to the Grefe method.

The samples under study are complex multicomponent mixtures of substances of a predominantly aliphatic nature, aromatic substances are present in small quantities. The proportion of saponifiable substances, depending on the processing method, varies as follows: successive extraction according to Grefe<O-alkylation<O-alkylation under

ultrasonic action. Aromatic substances during separation are concentrated in the saponifiable components. Comparison of the structural-group parameters of bitumoids obtained by alkylation and alkylation under ultrasonic action showed that in the latter the aromaticity index (f_{ar}) doubles - this indicates an increase in the extractability of aromatic substances as a result of the intensification of the process by ultrasonic action.

More than 200 individual compounds have been identified in bitumen and their fractions, among which there are various biologically active substances.

The use of LC separation made it possible to increase the number of individual compounds identified in the GC-MS analysis. It should be noted that in the fractions eluted with toluene, there is a tendency to extract substances related to alcohols, terpenes and sterols, among which: Sugiol is a plant metabolite, has antiviral and antitumor activity; Ferruginol is a plant metabolite, has antitumor properties, etc. elution with ethanol made it possible to extract the numbers of fractions with a high relative content of Oleic acid - up to 75.8% (I CM2), which also has biological activity.

The identified biologically active substances can find their application in cosmetics, medicine, veterinary medicine, and agriculture. The method can be useful in the complex processing of brown coal.

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