

## Catalytic Alkylation of Brown Coal and Peat

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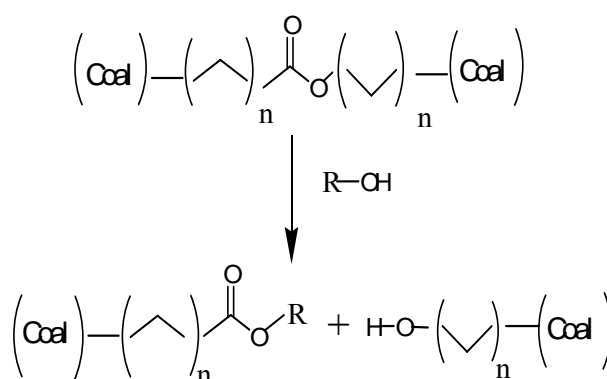
### Abstract

The alcohol alkylation of low-grade metamorphic coal and peat in the presence of mineral and organic acids was studied using FTIR, NMR, and GC-MS. The impact of the reaction conditions on the yield of extractable matter was investigated experimentally, and relevant regression equations were obtained. Changes in the group and individual compositions of the wax fractions of bitumen in the process of brown coal and peat alkylation were studied. It was found that the esters of alkylated coal waxes consisted of native esters of fatty acids, and alkyl esters of these acids formed as a result of the alkylation reaction. Esterification and transesterification were predominant in the reactions of the bitumen fraction components. The positive effect of alcohol alkylation on the increase of the bitumen yield was found.

### Introduction

Fossil solid fuels (FSF), brown coal, and peat bitumen are promising sources of a wide range of valuable chemicals and products [1]. The composition and applications of the wax fraction of native coal and peat bitumen have been studied in the most detail. It is generally accepted that waxes mainly consist of a mixture of fatty acids, alcohols, esters, and paraffin hydrocarbons. It was recently found that the catalytic methylation of coal considerably increased the bitumens—substances soluble in organic solvents (methanol, hexane, and an alcohol–benzene mixture) – yield [2]. The yield of the hexane extract, which corresponds to deresined wax, can be increased to more than double its original yield. The soluble products are characterized by a much higher hydrogen-to-carbon ratio than that of native coal and peat. It is likely that this effect can be explained by a high degree of depolymerization of coal matter because of the occurrence of both degradation and addition reactions (coal alkylation with methanol).

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It was proposed that esterification and transesterification reactions play a predominant role in the depolymerization of coal using this method [3]. So, the reaction of the alkylation agents on the organic matter of native coal and peat under acid catalysis conditions can be considered an efficient method for increasing the yield of soluble substances from coal and peat [4].

### Experimental

This work is devoted to a detailed study of the changes in the composition of bitumens and, especially, the wax fraction of bitumen in the process of the prealkylation of brown coal at

different stages of metamorphism and peat. In our study, we ascribed the substances from the hexane extract to the wax fraction.

The following typical low-grade metamorphism coal samples were used in the experiments: flame coal from the Karakan deposit in the Kuznetsk Basin (Russia) with properties that are close to the samples used for alkylation in references [5-7]; brown coal from the Itatskoe deposit in the Kansk-Achinsk Basin (Russia); brown coal from the Aleksandriiskoe deposit (Balakhovsky open-pit mine), Dnieper Basin (Ukraine); brown coal from the Tyul'ganskoe and Mayachnoe deposits, South Ural Basin (Russia).

High-moor peat, with a degree of decomposition  $R = 25\%$ , from the Krapivinskoe deposit (Russia) was studied. The bituminosity of the initial peat was 2.5% on the dry ash free (DAF) basis, including a wax fraction of 1.6% on the DAF basis. Table 1 summarizes the characteristics of the coal and peat samples.

The samples of coal and peat (5g) have been alkylated by methanol and n-butanol in the presence of acids, in accordance with a previously published procedure [2]. The process was carried out at the boiling temperature of an alcohol–acid–solid fuel mixture of confined particles (0,2 mm) at atmospheric pressure with a variation of the acid-to-alcohol ratio and duration, according to the experimental design matrices (Table 2) [8, 9]. Then, samples were exposed to extraction processing in a Grefe apparatus [10] serially hexane and a 1:1 ethanol–benzene mixture.

For a comparison of the amount and composition of bitumen extracted from the original samples and from the alkylated samples, the samples were processed by the same solvents under identical conditions in the absence of a catalyst. The alcohol, hexane, and ethanol-benzene extracts were summarized for the calculation of the total extractable substance.

**Table 1**  
Characteristics and elemental composition of samples, weight %.

The sample of coal or peat	W <sup>a</sup>	A <sup>d</sup>	V <sup>DAF</sup>	C <sup>DAF</sup>	H <sup>DAF</sup>	(O+N+S) <sup>DAF</sup> on a difference
Karakan flame coal	5,50	8,7	37,7	77,3	5,2	17,5
Itatskoe brown coal natural-oxidised	22,3	23,5	54,5	70,1	4,8	25,1
Aleksandriiskoe brown coal (Balakhovsky open-pit mine)	15,5	18,2	40,9	67,0	6,1	26,9
Mayachnyi brown coal	5,3	20,0	63,6	58,6	6,8	34,6
Tyul'gansky brown coal	6,5	23,5	67,3	66,2	9,9	23,9
Krapivinsky peat	11,2	12,3	72,6	46,8	8,1	45,1

**Table 2**  
Factor coding in the experiments

Level of factor	Amount of alcohol, ml (x <sub>1</sub> )	Acid concentration in alcohol, % (x <sub>2</sub> )	Duration, h (x <sub>3</sub> )
Karakan flame coal, benzenesulphonic acid (BSA) catalyst, methylated			
-1	25	5	1
0	44	10	3
+1	63	15	5
Itatskoe brown coal natural-oxidised, BSA catalyst, methylated			
-1	25	1	0,5
0	50	5	3
+1	75	9	5,5
Aleksandriiskoe brown coal, BSA catalyst, methylated			
-1	50	1	0,5
0	50	10	3
+1	50	19	5,5
Krapivinsky peat, orthophosphoric acid (OPhA), butylated			
-1	70	1	0,5
0	120	5	3
+1	170	9	5,5

The butanol extract formed in the course of the peat alkylation was washed with water to remove the catalyst; then, butanol was distilled off to obtain bitumen, which was separated into wax and resin fractions through the extraction with n-heptane. For comparison, butanol bitumen was also extracted from the initial peat (Table 3).

The composition of the wax fractions of the initial and modified FSF was studied using FTIR,  $^{13}\text{C}$  NMR, and  $^1\text{H}$  NMR spectroscopy, thin-layer chromatography (TLC) and gas chromatography–mass spectrometry (GC–MS). The FTIR spectra were recorded on a Bruker TENZOR-27 spectrometer at a resolution of  $2\text{ cm}^{-1}$  in the accumulation of 64 scans over the range of  $4000\text{--}400\text{ cm}^{-1}$ . Thin layer chromatography (TLC)

conditions: Silufol UV 254 plates; eluent – benzene–acetic acid (99:1). The spots of separated substances were visualized using a quartz lamp and iodine vapor. The GC–MS analysis was performed on Hewlett Packard G1800 and Agilent 6890N/5973 GC-MS chromatographs (column, HP5-MS; carrier gas, helium (1 ml/min); column temperature programming was  $50^\circ\text{C}$  for 2 min,  $4^\circ\text{C}/\text{min}$  to  $280^\circ\text{C}$ , and  $280^\circ\text{C}$  for 15 min; and ionizing electron energy was 70 eV. The concentrations of the individual compounds were measured using total ion current. The reliability of the identification, based on the NIST-2 library of mass spectra, was higher than 90%. The NMR spectra were measured on a WP-200 instrument from Bruker Physik AG.

**Table 3**

Yields of extracts from investigated samples, % of weights on DAF

The sample of brown coal or peat	Wax fractions		The sum of the extracted	
	Initial	modified	initial	Modified
Karakan flame coal	n. a.	n. a.	5,00	34,7
Itatskoe brown coal natural-oxidised	1,2	4,6	4,2	45,6
Aleksandriiskoe brown coal (Balakhovsky open-pit mine)	3,5	12,0	11,8	35,6
Mayachnyi brown coal	2,2	23,2	12,5	51,3
Tyul'gansky brown coal	11,8	17,4	14,6	39,1
Krapivinsky peat	1,6	8,2	2,5	38,0

## Results and Discussion

After processing the experimental results, a number of regression equations, adequate at a confidence level of 0,05 for response functions were obtained:

Yield of total extractable matter, % DAF:

Karakan coal metylated, BSA catalyst:

$$Y = 3,3 + 3,8x_1 + 5,1x_2 + 6,1x_1^2 + 2,0x_2^2 + 2,7x_3^2 + 4,1x_1x_2 - 2,6x_1x_3 - 1,1x_2x_3; \quad (1)$$

Itatskoe coal metylated, BSA catalyst:

$$Y = 17,2 + 8,2x_1 + 7,2x_2 + 2,2x_3 - 0,25x_1^2 + 13,0x_2^2 - 10,9x_3^2 + 0,1x_1x_2 + 7,9x_1x_3 - 5,9x_2x_3; \quad (2)$$

Aleksandriiskoe coal metylated, BSA:

$$Y = 28,3 + 7,9x_2 - 3,6x_2^2 + 0,3x_3 - 4,6x_3^2 - 0,7x_2x_3; \quad (3)$$

Krapivinsky peat butylated, OPhA catalyst:

$$Y = 21,6 + 1,9x_1 + 0,15x_1^2 + 8,0x_2 - 3,9x_2^2 + 7,8x_3 - 3,4x_3^2 - 1,2x_1x_2 + 1,8x_1x_3 + 3,6x_2x_3. \quad (4)$$

In general the regression models revealed a positive effect of the alkylation treatment of coal on both the total increase in the bitumen content and the yield of the hexane extract. The maintenance of an acid catalyst concentration and a reaction time at high values positively affected the increase in the yield of bitumen components, as shown in Fig. 1, 2.

The extraction of the alkylated samples has shown substantial growth in extractables, including an aliphatic structure. The fractional composition of the wax fraction (hexane extract) from the Alexandria coal, according to TLC and GC-MS, is presented in the Table 4.

It was noted that the hexane extract (wax) of methylated coal also contained methyl esters of fatty acids  $\text{C}_{24}\text{--}\text{C}_{32}$  ( $R_f = 0,72$ ), which is not characteristic of natural wax. The amount of fatty acids presented in the hexane extract of alkylated coal was much lower than that in native wax (Table 5). Moreover the chromatogram of wax obtained from alkylated coal exhibited a considerable increase in the spot area that corresponded to wax alcohols with  $R_f = 0,32$ . This can be explained by the transesterification of the corresponding wax esters with methanol and the release of alcohols:

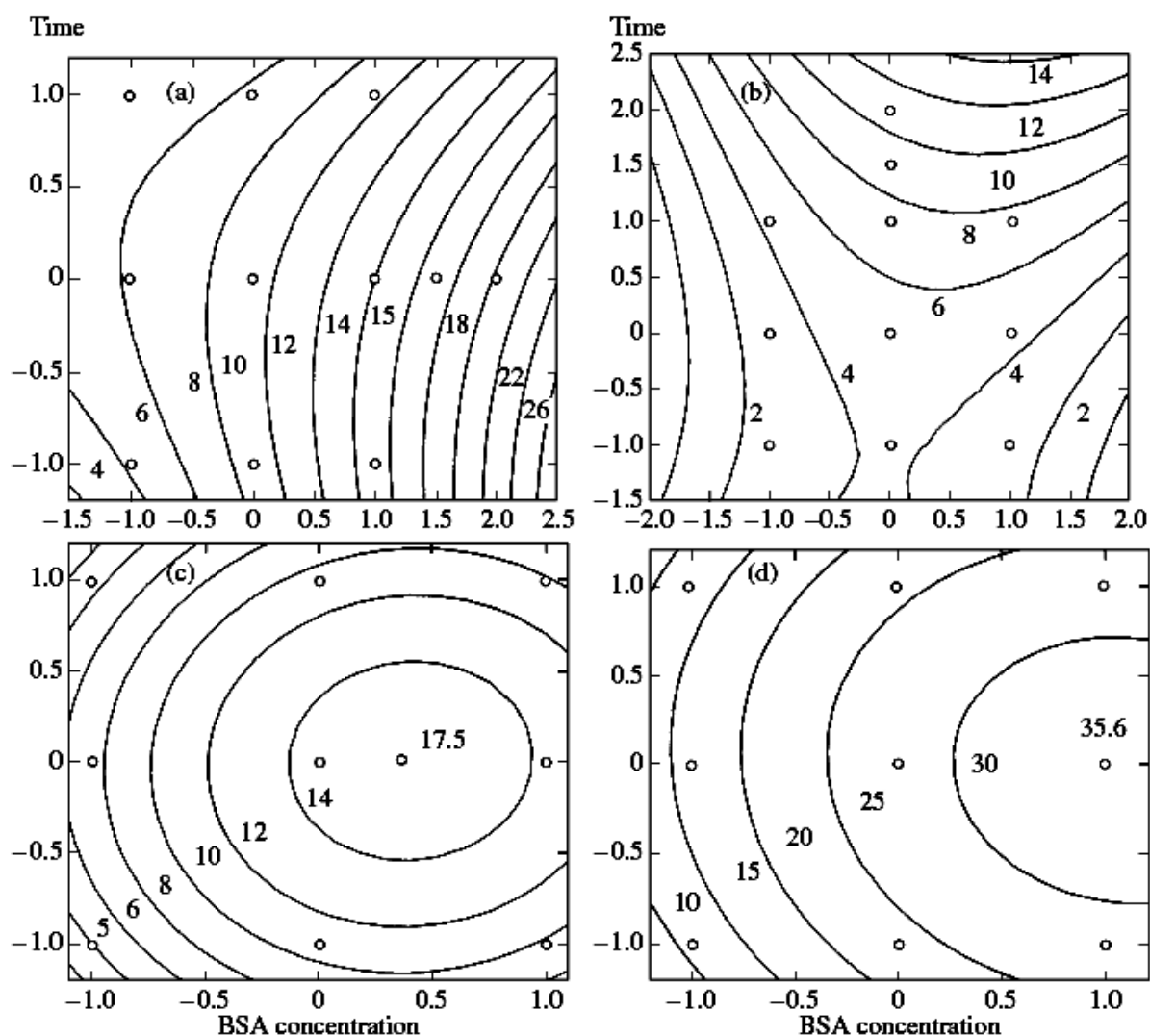
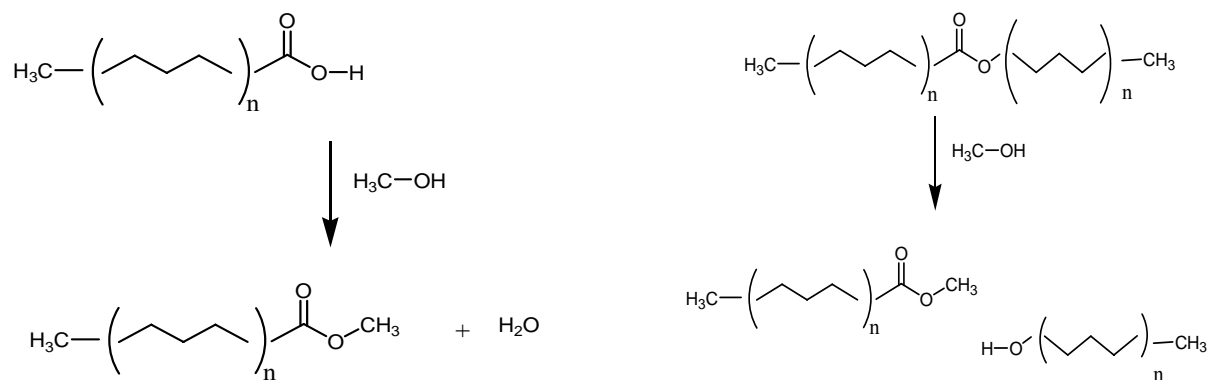


Fig. 1. The dependence of the yield (figures at curves, % on a DAF basis) of extractable matter from alkylated samples of Aleksandriiskoe brown coal: (a) methanol extract, (b) hexane extract, (c) ethanol–benzene extract, and (d) total extractables at the various conditions.

The increase in the amount of the alcohols in wax prepared from alkylated coal is also illustrated by the relative decrease in the saponification

number to 53 (Table 5), because alcohols belong to the unsaponifiable matter of wax.

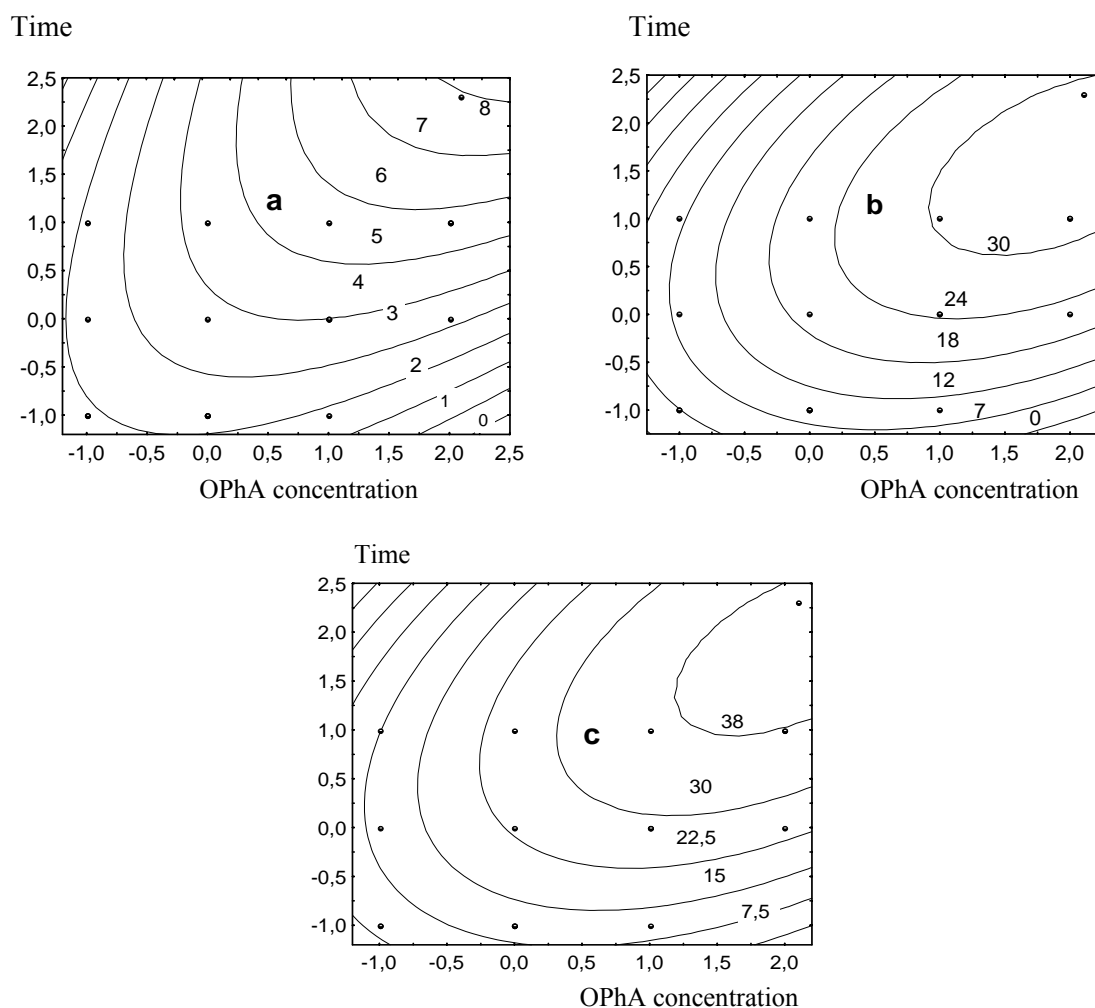


Fig. 2. The dependence of the yields (figure on curves, % on DAF) of the extractables from alkylated Krapivinsky peat under modification conditions: (a) the wax fraction (heptane extract); (b) resin fraction; and (c) the total extractables.

**Table 4**

Fraction composition of Alekdandriisky brown coal wax samples according to TLC and GC-MS data

Wax fraction	Deresined wax from initial coal		Deresined wax from modified coal		Published data [11]	
	R <sub>f</sub>	%	R <sub>f</sub>	%	R <sub>f</sub>	%
Acids	0,20	8	0,19	5	0,18	13
Alcohols	0,27	6	0,32	25	0,26	10
Natural esters	0,55	68	0,50	27	0,79	62
Methyl esters	-	-	0,72	25	-	-
Paraffins	0,84	18	0,84	18	0,94	15

Considering the physical and chemical characteristics of methylated coal wax – absence of resins, low acid value (1 mg KOH/g) and saponification value (53 mg KOH/g) received (Table 5) – the coal can be assigned as a high-grade product, comparable with some industrial esterified waxes or vegetative (Carnauba) wax. It is necessary

to note that esterified waxes are traditionally produced by a multiphase rehash of raw mountain wax.

The IR spectra of all the samples of the hexane extracts of alkylated brown coals (Fig. 3.) were almost identical in the regions of 3000-2800 and 725-720 cm<sup>-1</sup> in relation to the stretching vibrations

of methyl and methylene groups and the pendular vibrations of the methylene groups of long alkane chains, respectively [12-14]. Bands due to aromatics were absent. In the region of 1750–1710  $\text{cm}^{-1}$ , changes in the relative intensities of bands due to the carbonyl groups of esters were observed – the intensity of the band at 1709  $\text{cm}^{-1}$  ( $\nu$  C=O of the natural esters of long-chain carboxylic acids and long-chain aliphatic alcohols) in alkylated samples

decreased when compared with that in the initial sample, whereas the intensity of the band at 1735  $\text{cm}^{-1}$  ( $\nu$  C=O of the methyl esters of carboxylic acids) increased. These changes suggest the occurrence of the transesterification reaction with the replacement of the long-chain alkyl radical of a natural alcohol by a shorter radical of the alkylating agent (methanol).

**Table 5**  
Physicochemical characteristics of waxes

Extractant	Wax yield, % on a DAF basis	Color	Dropping temperature, °C	Gasoline insoluble, %	Resins, %	Acid value, mg KOH/g	Saponification value, mg KOH/g
Aleksandriisky coal wax							
Extraction gasoline (Tb = 70°C)	4.0	Dark brown	82	0.3	18.7	26	81
Methylated Aleksandriisky coal wax							
Hexane	8.6	Light beige	78	Not detected	Not detected	1	53
Carnauba wax [1]							
–	–	Yellow	86–88	Not detected	Not detected	2	75–80
Romonta 751							
–	–	dark brown to black	85-105	Not detected	Not detected	15-32	70-95

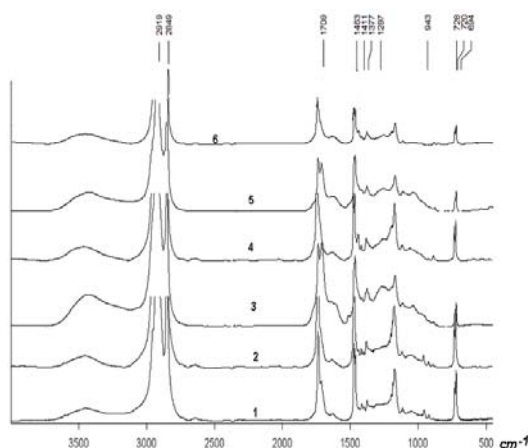


Fig. 3. FTIR spectra of hexane extracts of Aleksandriiskoe brown coal (1 - original, 2 - alkylated); Tyul'gansky brown coal (3 - original, 4 - alkylated); Mayachnyi brown coal (5 - original, 6 - alkylated).

According to the IR spectra, the wax fraction of peat bitumens (Fig.4.) is presented as a mixture of alkanes - substituents free and present in the capacity of (2958; 2916; 2873; 2848  $\text{cm}^{-1}$ ), the

normal saturated esters (1736  $\text{cm}^{-1}$ ), olefins (1635  $\text{cm}^{-1}$ ), secondary alcohols (3400; 1243; 1068  $\text{cm}^{-1}$ ), and small amounts of the normal saturated carboxylic acids (1720  $\text{cm}^{-1}$ ). The wax fraction of

alkylated peat differs by the presence of higher quantities of esters of fatty acids ( $1736\text{ cm}^{-1}$ ).

In the  $^{13}\text{C}$  NMR spectrum of hexane extract of the alkylated coal, a signal at 51.18 ppm belonging to the methoxy group ( $-\text{O}-\text{CH}_3$ ) is presented. The corresponding signal in the spectrum of the extract of native coal is absent. These facts prove the

passing of the methylation reaction of the carboxylic acids (esterification) or their esters (transesterification).

The signals of the aromatic components in the spectra are not observed. The signal at 173.76 ppm was assigned to the carbonyl group in the esters ( $\text{R}-\text{COO}-\text{R}$ ) (Fig.5).

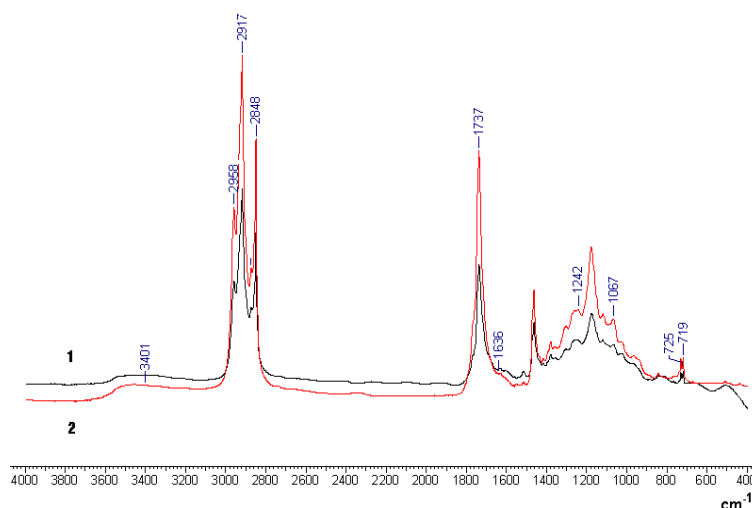


Fig. 4. The FTIR spectra of the wax fraction of peat bitumens (1 - original, 2 - alkylated)

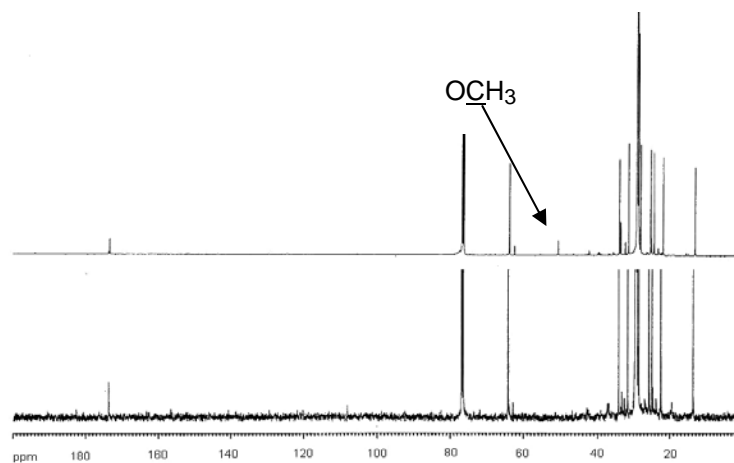


Fig. 5. The  $^{13}\text{C}$  NMR spectrum of the hexane extract of Aleksandriisky coal methylated in the presence and without the presence of benzenesulfonic acid.

The group compositions of wax fractions of Tyul'gansky brown coal, Mayachnyi brown coal and Krapivinsky peat determined by GC-MS are presented in Table 6. The wax fractions of the original coals are presented in the core from the monobasic linear carboxylic acids consisting of mainly with an even number (from 16 to 32) of carbon atoms. There are alkanes, alcohols, and esters of fatty acids from the natural origin also

presented. After alkylation, a part of fractions, belonging to alkanes and not identified compounds that are produced from the destruction of the organic matter in the coal, increases. The formation of methyl and butyl esters with the simultaneous decrease of the amount of carboxylic acids again proves the reactions of esterification and transesterification, which lead to the disappearance of esters from the natural origin.

**Table 6.**  
Group composition of waxes according to GC–MS data, % at a mixture

Groups of compounds	Parent	Alkylated
Tjulgansky brown coal		
Alkanes	5,10	3,41
Natural esters	1,91	Not detected
Methyl esters	Not detected	80,81
Carboxylic acids*	73,25	0,85
Ketones	Not detected	4,90
Unidentified	19,75	10,02
Mayachnyi brown coal		
Alkanes	3,64	3,68
Alkenes	Not detected	5,22
Natural esters	0,91	0,97
Methyl esters	Not detected	82,98
Carboxylic acids*	63,64	Not detected
Ketones	10,91	0,58
Alcohol	7,73	1,74
Aldehydes	0,45	1,74
Others	1,36	0,77
Unidentified	11,36	2,32
Krapivinsky peat		
Monocarboxylic acids*	60,98	Not detected
Dicarboxylic acids*	6,10	Not detected
Alcohol	2,44	3,41
Alkanes	6,10	1,70
Butyl esters monocarboxylic acids	Not detected	41,36
Butyl esters dicarboxylic acids	Not detected	12,17
Others (unidentified)	24,39	41,36

\*- Determined in the form of methyl esters after processing of treatment by diazomethane

The peat processing conditions promote a gain in the yield of the aliphatic fraction. At the optimum combination of parameters, the maximum yield is 8,2 % from organic matter, whereas complete extraction from the lack of alkylation yields 1,6 %.

The general yield growth of five times the wax fraction is accompanied by a non-uniform gain in the yield of its individual components (Tables 3,6). So, for monocarboxylic acids (in the form of esters), yield growth was made three-fold, dicarboxylic acid yield growth was 10-fold, alcohol growth was 7-fold, alkanes were 1-4 fold. The wax fraction of butylated peat was presented in the core from the butyl esters of dicarboxylic acids C<sub>4</sub>-C<sub>30</sub>, monocarboxylic acids C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub>, C<sub>30</sub>, and in small quantities of alkanes. The esters of the dicarboxylic acids in the appreciable quantities occur only after peat processing through butanol alkylation in the presence of inorganic acids, and it

leads the assumption interaction that these acids react with metal ions existing in the peat in form of organomineral complexes and salts (Table 6) [15]. The increase in the total yield of the wax fraction is reached primarily as a result of the formation of butyl esters of mono- and dicarboxylic acids (esterification), and alcohol during transesterification. The growth of the ester yield from the monobasic carboxylic acids considerably exceeded the gain in the yield of alcohol, which specifies the destruction reactions of organomineral complexes in the peat matter, which is characterized by a high ash content in the initial peat (12,3 %) and a rather basic property of ash (8,3 mmol HCl/g).

## Conclusions

The substantial yield of the extractable matter was achieved in the alcohol alkylation of low-grade



metamorphic coal and peat in the presence of mineral and organic acids under various reaction conditions. The FTIR, NMR, and GC-MS analysis of the group and individual compositions of the wax fractions from the bitumen in the process of brown coal and peat alkylation elucidated that the wax fractions of the original coals were present in the core from the monobasic linear carboxylic acids consisting of mainly with an even number (from 16 to 32) carbon atoms, some alkanes, alcohols, and esters of fatty acids from its natural origin. The esters of alkylated coal waxes consisted of the native esters of fatty acids, and the alkyl esters of these acids formed as a result of the alkylation reaction. Esterification and transesterification were predominant among the reactions of the bitumen fraction components. A positive effect of alcohol alkylation on the increase in the yield of the bitumen was found.

### Aacknowledgments

We are grateful to L.M. Pokrovskii and M.M. Shakirov (Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences) for their assistance in the identification of substances through GC-MS analysis and NMR spectroscopy.

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Received 3 March 2011