Structural-Group and Componential Composition of Bitumen Fractions of Tyulgan Brown Coal

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Abstract

The paper presents data for structural-group and component compositions of bitumoid fractions derived upon sequential extraction of brown coal of the Tyulgan deposit with the following solvents: ethanol, *n*-heptane, and alcohol-benzene. As demonstrated by FT-IR, ^{13}C CPMAS NMR, and GC-MS, the resulting bitumen is a multicomponent mixture of compounds mainly consisting of alkanes, fatty alcohols, unsaturated hydrocarbons, aromatic compounds found in trace amounts, carboxylic acids, and phenols. Bioactive compounds, such as *Lignoceic alcohol*, *Ceryl alcohol*, *Behenic alcohol*, *Ferruginol*, β-*Amyrin*, and *Heneicosane*, were detected therein.

Key words: solid fossil fuel bitumen, component composition, bioactive compounds

INTRODUCTION

The issue of the advanced processing of solid fossil fuels (SFF) is of relevance. One of the challenges addressed within this problem is linked to the advanced processing of lignite to yield a number of products, such as waxes and humic compounds promising from the standpoint of practical use [1–3]. The major technique to extract such species is extraction.

Upon SFF treatment with various organic solvents, there are produced extracts, bitumens, the composition and yields of which depend on a number of factors: extraction techniques, the chemical nature of the solvents used and SFF treated. The use of solvents with boiling points not higher than the temperature of thermal decomposition of SFF organic matter ensures the extraction of compounds without changing their composition, which is critical when exploring the chemical structure of SFF [4]. The contents and quantities of bitumoids are different for all types of SFF: 5–28 %, 5–33 %, and about 5 % for turf, brown coal, and coal, respectively. [5]

Bituminous brown coal is a promising source of a broad number of compounds and products that are of practical importance [6 and 7]. Nowadays, it has been found that bitumen is comprised of carboxylic acids, carbonyl compounds, steroids, *n*-, *iso*- and cycloalkanes, and also of alcohols. Nevertheless, the amount of unidentified compounds is also great. Large concentrations of bioactive compounds that may be extracted from bitumen and find applications in medicine, pharmacology, agriculture, and other industrial areas are of special interest [8].

Bituminous SSF, including fossil wax fractions, may also exert a binding effect [9] on soil substrate components, which opens up bitumen use perspectives to recultivate disturbed soils.

In this regard, it is required to more profoundly investigate the componential composition of bituminous SSF.

This research deals with examining the group and componental composition of bitumen fractions produced of coal of lignite phase of diagenesis.

EXPERIMENTAL

The research subject was 1B brown coal (TBC) of the Tyulgan deposit of the Southern Ural basin. Hereafter, bitumen was sequentially extracted from the investigated coal sample.

Extraction was carried out according to the Graefe method [5] at boiling points of solvents with the sequential use of ethanol, n-heptane, and alcohol-benzene (1 : 1). As a consequence of sequential extraction, there were obtained three appropriate extracts and a sample of residual coal left after extraction: ethanol extract (EE), n-heptane extract (NHE), alcohol-benzene extract (ABE), and residual coal (RC). Table 1 reports the performance of the initial sample and residual coal after extraction, whereas Table 2 gives extraction conditions and the yield of extracted compounds.

Hereafter, for the purposes of additional fractioning, the resulting extracts were divided into saponifiable (S) and non-saponifiable (N) components. Figure 1 reports the diagrammatic view of the separation procedure into S and N components.

The composition of the resulting extracts, their saponifying and non-saponifying components, and also residual coal was analysed by FTIR, ^{13}C NMR, and gas chromatography-mass spectrometry (GC-MS).

Infrared spectra were recorded in dry KBr using an Infralum FT-801 IR-Fourier spectrophotometer at a resolution of 4 cm^{-1} with an accumulation of 16 scans in the 4000–550 cm^{-1} range.

NMR spectra were recorded on a Bruker Physic AG WP-200 spectrometer. High-resolution solid-state ^{13}C NMR spectra were recorded at a frequency of 75 MHz using a standard cross-polarization technique with proton decoupling and cross-polarization magic-angle-spinning (CPMAS), a contact time of 2000 μs, an FID-acquisition period of 40 ms, a scan delay of 5 s. A sample was placed into a zirconium rotor with an external diameter of 7 mm and a Kel-F lid and rotated at a frequency of 5 kHz. The accumulation of 1024 scans

TABLE 2

Extraction condition and the yield of extractable compounds (a sample of 7 g, a solvent volume of 100 mL, an extraction time of 3 h)

Solvent	Extract yield, g	E^{daf}, %
Ethanol	0.61	12.22
n-Heptane	0.06	1.20
Alcohol-benzene	0.13	2.60
Total	0.80	16.02

Note. E^{daf} is the yield of extractable compounds on dry ash-tree basis.

was carried out at room temperature. TMS was used as an internal standard.

GC-MS analysis was carried out using Agilent 6890N GCMS with Agilent 597 mass-selective detector (HP-5 ms capillary column (30 m × 0.25 mm × × 0.25 μm). The parameters were as follows: an evaporator temperature of 290 °C, solvent removal for 4 min, 50 : 1 split ratio, a helium carrier gas flow rate of 1 mL/min, an analytical sample volume of 5.0 μL, a programmed column temperature increase between 50 °C and 290 °C with a retention of 3 min at a rate of 5 °C/min, and 60 min exposure at 280 °C. The content of individual compounds was recorded according to total ion current. Identifying the componental composition of the investigated samples was performed according to mass spectra using NIST-8 Wiley spectral library and was higher than 90 %. The results of spectroscopic research are discussed below.

Absorption band assignments in IR spectra were based on literature data [10−16]. The relative experimental error was 3−5 %, a significance level of α = 0.05.

RESULTS AND DISCUSSION

Table 3 presents IR spectroscopy data for brown and residual coal, the resulting extracts, and their saponifiable and non-saponifiable components. Figure 2, *a* demonstrates IR spectra the original and residual coal after extraction. It can be seen that the TBC-recovered extract is a multicomponent mixture of compounds, such as alco-

TABLE 1

Technical and elemental analysis data of the initial and residual coal samples after extraction

Sample	W$^{\mathrm{a}}$, %	A$^{\mathrm{d}}$, %	V$^{\mathrm{daf}}$,%	C$^{\mathrm{daf}}$	H$^{\mathrm{daf}}$	H/C (at.)	(O + N + S), according to difference
Initial	9.1	21.5	65.9	57.3	6.3	1.3	36.4
Residual	7.5	27.0	64.4	63.6	5.9	1.1	30.5

Bitumen fraction   KOH

                          Butanol as solvent

Saponification
(3 h, 118 °C)

Distilled   Saponified/
water   non-saponified

Separating
funnel

Organic phase   Solvent (butanol)   HCl
(non-saponifiable), pH 7   Aqueous phase

Analysis   Acidified
                                  aqueous phase (pH 1−2)

                    Extraction
                    in separating funnel
                    at precipitate
                    dissolution
                    temperature

Organic phase   Aqueous phase
(saponifiable), pH 7
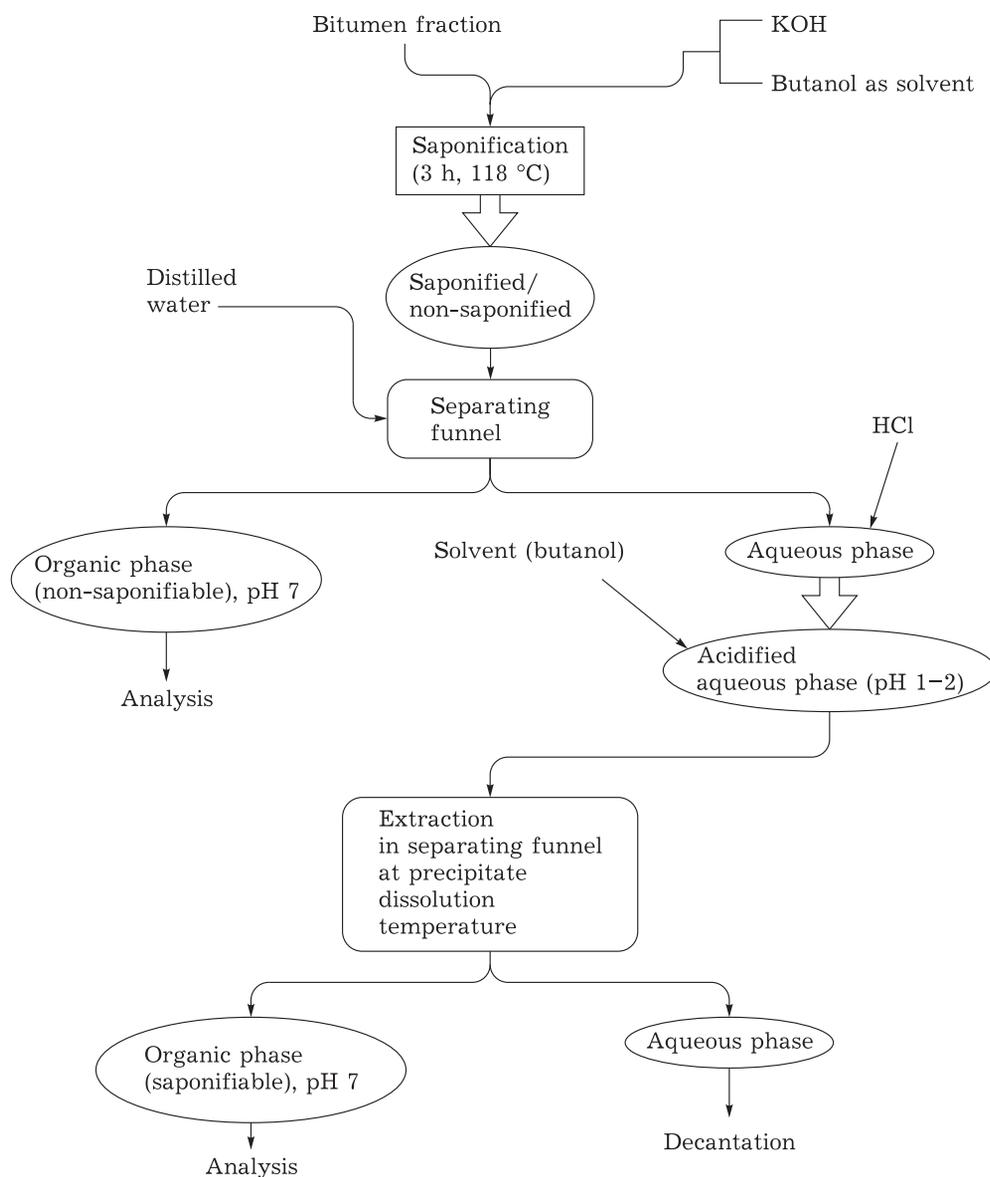
Analysis   Decantation

Fig. 1. Scheme for separation of the resulting extracts onto fractions of saponifiable and non-saponifiable components.

hols, phenols, alkanes, carboxylic acids, and little aromatics.

Figure 2, *b* reports IR spectra of a sample of ethanol extract (EE) and its saponified (EES) and non-saponified (EEN) fractions. EE is a mixture of alcohols, phenols, *n*-saturated esters, unsaturated hydrocarbons, carboxylic acids, and some aromatic compounds. Carboxylic acids that have almost completely transferred from the initial extract to the saponifiable fraction and some alkanes are prevailing in the saponifiable component. Alcohols are present in the saponifiable fraction as hydrolysis products of esters under saponification conditions. Alkanes and alcohols are prevailing in the non-saponifiable fraction of EE togeth-

er with free carboxylic acids and RCOOH generated upon the decomposition of natural esters in minor amounts are present in small amounts.

Figure 2, *c* presents IR spectra of a sample of *n*-heptane extract (NHE) and its saponifiable (NHES) and non-saponifiable (NHEN) sections. The NHE is a mixture of alkanes, alcohols, phenols, *n*-saturated esters, and unsaturated hydrocarbons, and also carboxylic acids and aromatic compounds, whereas alkenes and alcohols are prevailing. Substance group distribution upon separation into saponifiable and non-saponifiable components is similar to their partitioning in EES and EEN.

Figure 2, *d* gives IR spectra of a sample of alcohol benzene extract (ABE) and its saponified

TABLE 3

IR analysis results of the investigated samples

Sample	Optical densities in absorption band maximum, unit fractions								
	Absorption band, cm^{-1}								
	3650−3200	2926±10	2853±10	1725−1690	1630−1575	1465±20	1200−1275	1070−1030	721±10
	1	2	3	4	5	6	7	8	9
TBC	0.20	0.19	0.12	0.13	0.20	0.12	0.10	0.19	0.03
RC	0.13	0.08	0.06	0.09	0.13	0.08	0.07	0.15	−
EE	0.17	0.70	0.49	0.22	−	0.17	−	0.16	0.07
EES	0.07	0.26	0.17	0.19	−	0.10	0.11	0.07	0.02
EEN	0.09	0.64	0.40	0.06	0.24	0.12	−	0.05	0.04
NHE	0.02	0.65	0.41	0.13	−	0.10	−	0.09	0.04
NHES	0.08	0.25	0.17	0.11	−	0.07	0.06	0.06	0.02
NHEN	0.06	0.52	0.36	0.06	0.21	0.12	−	0.05	0.06
ABE	0.02	0.35	0.22	0.12	0.05	0.08	−	−	0.02
ABES	0.11	0.37	0.22	0.31	−	0.12	0.18	0.08	−
ABEN	0.04	0.37	0.25	0.05	0.14	0.09	0.03	0.03	0.04

Note. 1 − alcohols, phenols (νOH), 2 − alkanes (νCH$_3$), 3 − alkanes (νCH$_2$), 4 − carboxylic acids νC=O), 5 − aromatic compounds (νC=C), 6 − alkanes (δCH$_2$), 7 − aromatics (νC−O), 8 − alcohols (νC−O), and 9 − paraffins more than C$_{26}$.

(ABES) and non-saponified (ABEN) portions. The alcohol benzene extract is a mixture of alkanes, alcohols, *n*-saturated esters, unsaturated hydrocarbons, carboxylic acids, and some aromatic compounds. Carboxylic acids and alkanes are prevailing in the saponifiable portion of ABE. Alcohols are present in the saponifiable portion as hydrolysis products of esters under saponification conditions. Alkanes and alcohols are prevailing in the non-saponifiable fraction of ABES. In addition, free carboxylic acids and RCOOH formed under decomposition of natural esters are present in small amounts therein.

The initial coal and coal after extraction, extracts, as well as their saponifiable and non-saponifiable components, were also investigated by ^{13}C NMR (CPMAS). Signal assignments were made on the basis of literature data [15−20].

As demonstrated by the resulting ^{13}C NMR (CPMAS) data for Tyulgan brown coal, compounds with long alkyl chains are prevailing therein. These species are mainly related to fatty esters, acids and alcohols. Peaks in the 5−48 ppm range demonstrate the presence of straight alkyl chains and alkyl groups. Peaks in the 90−48 ppm

range show the availability of alcohol compounds. There are peaks in the 108−90 ppm range that indicate the presence of C$_{O-alk-O}$ groups. Peaks in the 145−108 ppm range are typical for aromatic compounds, while those near 165−145 ppm are characteristic for phenols. Peaks in the 187−165 ppm range represent acid compounds, whereas those in the 220−187 ppm range indicate the presence of carboxylic species. Table 4 reports integral intensities of spectral ranges of this sample. Data for residual coal after extraction are also presented here.

As can be seen, compounds of various types, mostly alkanes, are extracted upon sequential extraction of the initial coal. Substances of other groups are extracted to a lesser degree, which is indicated by an increase in the integral intensity in the ranges of these moieties.

Table 5 gives integral intensities of spectral ranges for a sample of ethanol extract. As can be seen, this sample consists of alkanes, acids, alcohols, and aromatics. The integral intensity of alkanes is reduced in the non-saponifiable fraction and on the contrary, that of other groups is increased for integral intensities of spectral ranges

TABLE 4

Integral intensities of spectral regions of ^{13}C CPMAS spectra of Tyulgan and residual coal samples after sequential extraction, %

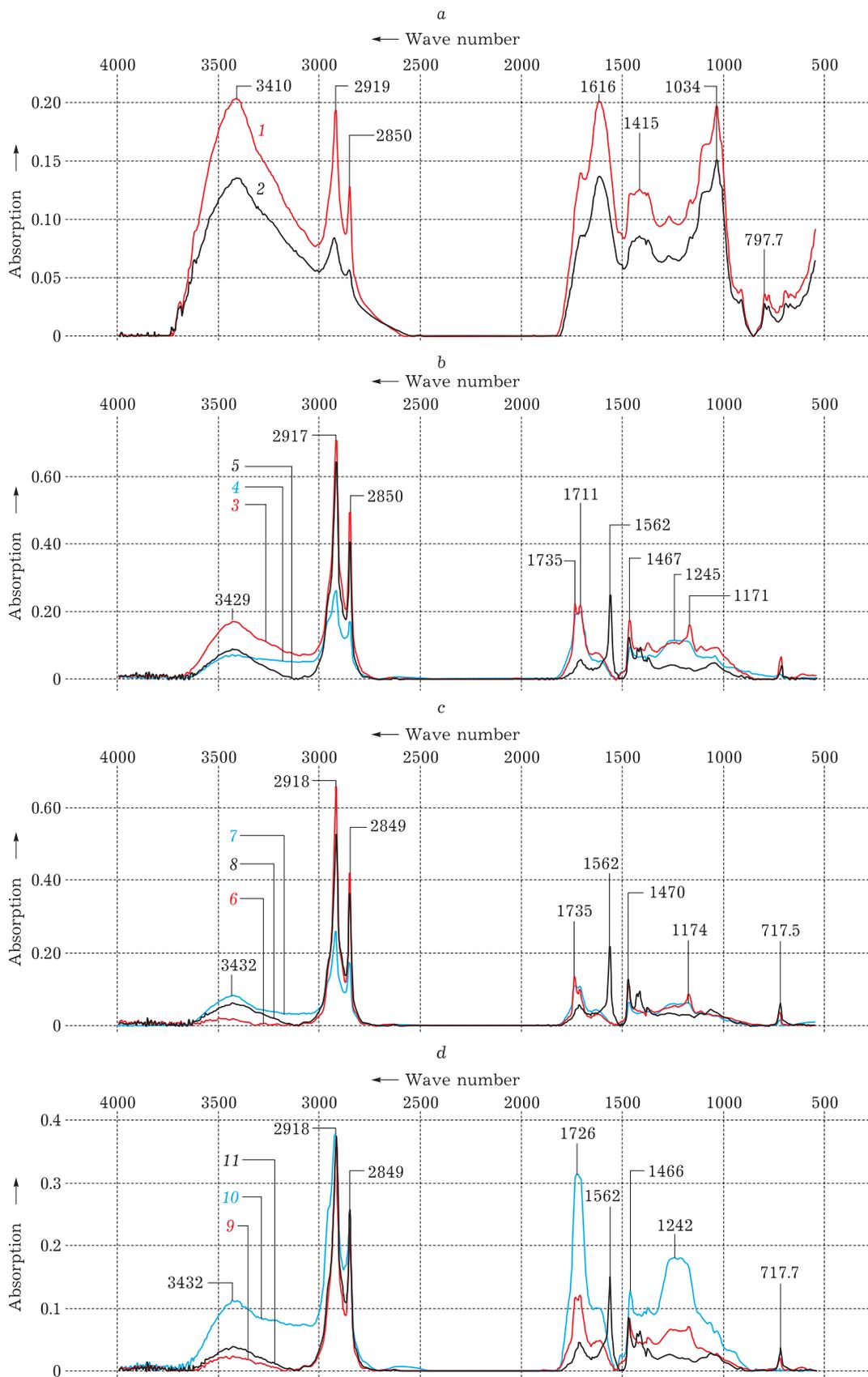| Coal sample	220−187 C=O	187−165 COOH	165−145 C$_{ar}$-O	145−108 C$_{ar}$	108−90 C$_{O-alk-O}$	90−48 C$_{alk-O}$	48−5 C$_{alk}$
Tyulgan brown	4.40	4.52	4.31	15.32	4.23	18.95	47.41
Residual	5.11	4.94	5.08	17.71	4.50	20.91	35.09

Fig. 2 IR spectra of initial Tyulgan brown coal (*1*) and residual coal after extraction (*2*) of ethanol extract. EE (*3*) and its saponified EES (*4*) and non-saponified, EEN (*5*) fractions, *n*-heptane extract (*6*) and its saponified (*7*) and non-saponified (*8*) portions, alcohol-benzene extract (*9*) and its saponified (*10*) and non-saponified (*11*) sections.

TABLE 5

Integral intensities of spectral regions of ^{13}C CPMAS spectra of the ethanol extract sample and its saponifiable and non-saponifiable fractions, %

Sample	220−187	187−165	165−145	145−108	108−90	90−48	48−5
	C=O	COOH	C_{ar}-O	C_{ar}	$C_{O\text{-}alk\text{-}O}$	$C_{alk\text{-}O}$	C_{alk}
EE	2.31	2.86	1.90	6.91	2.58	11.64	70.96
EES	2.88	3.88	2.69	9.07	2.75	13.81	64.18
EEN	1.62	1.79	1.29	4.83	2.23	9.83	77.96

of EES. That indicates a decrease in the concentration of alkanes and concentrations of compounds of other groups. Groups of compounds, whereof the initial ethanol extract is comprised, present this sample.

According to Table 5, there is an increase in integral intensities in the 48−5 ppm range. The latter corresponds to the alkane moiety. The integral intensity of other moieties is reduced. This indicates an increase in the concentration of alkanes in the sample and a decrease in the content of compounds of other moieties. Compounds that are similar to compound groups of the ethanol extract and its saponifiable component present this sample.

In analysing ^{13}C NMR (CPMAC) data for samples of *n*-heptane extract and its saponifiable and non-saponifiable components, there was the appearance of similar peaks in the same ranges but with different intensities. That attests to the presence of compounds of similar groups in the samples but in different concentrations. As it follows from the data of Tables of integral intensities for NHE, NHES, and NHEN samples (Table 6), the integral intensity in the ranges of acids, phenols, $C_{O\text{-}alk\text{-}O}$ compounds and carbonyl species is increased in the saponifiable fraction of *n*-heptane extract. The integral intensity in the ranges of compounds belonging to alkanes and alcohols is decreased. There is a decrease in integral intensities in the ranges of compounds belonging to acids, phenols, aromatics, $C_{O\text{-}Alk\text{-}O}$, alcohols, and carbonyl species for NHEN sample. However, there is an increase for the range of compounds of

alkane series. The acquired data indicate that compounds belonging to acids, phenols, aromatics, $C_{O\text{-}alk\text{-}O}$, and carbonyl species are concentrated in the saponifiable fraction of *n*-heptane extract.

Alkane compounds are concentrated in the non-saponifiable fraction. Almost identical indicators for integral intensities in the 90−48 ppm range indicate essentially identical distributions of compounds of this type in saponifiable and non-saponifiable fractions.

When the acquired data of 13C NMR (CP MAC) for ABE extract, and also its saponifiable and non-saponifiable fractions are compared, there are peaks in the same ranges but at different intensities. That indicates the presence of compounds of similar types but in different concentrations in the samples. Upon the analysis of the data of integral intensities (Table 7), it can be noted that integral intensities are increased in the non-saponifiable fraction in the ranges of compounds of acid, phenol, aromatics, alcohol types, whereas the integral intensity of alkane series is decreased. They are reduced in all ranges of substance groups for ABE sample, except for the 48−5 ppm range (alkane series). As demonstrated by this data, compounds of acid, phenol, aromatics, alcohol, and carbonyl types are concentrated in the first fraction when separating ABE into saponifiable and non-saponifiable fraction, whereas in the second fraction, alkane species are collected. Integral intensity indicators within the 108−90 ppm range ($C_{O\text{-}alk\text{-}O}$) indicate that compounds of this type increasingly pass to the saponifiable fraction upon separation.

TABLE 6

Integral intensities of spectral regions of ^{13}C CPMAS spectra of the n-heptane (NHE) extract sample and its saponifiable and non-saponifiable fractions, %

Sample	220−187	187−165	165−145	145−108	108−90	90−48	48−5
	C=O	COOH	C_{ar}-O	C_{ar}	$C_{O\text{-}alk\text{-}O}$	$C_{alk\text{-}O}$	C_{alk}
NHE	1.55	2.25	1.29	4.35	2.49	8.10	79.9
NHES	1.75	2.60	1.67	5.11	2.56	7.93	77.79
NHEN	1.43	2.26	1.06	3.74	2.09	7.98	81.26

TABLE 7

Integral intensities of spectral regions of ^{13}C CPMAS spectra of the alcohol-benzene extract sample and its saponifiable and non-saponifiable fractions, %

Sample	220−187	187−165	165−145	145−108	108−90	90−48	48−5
	C=O	COOH	C_{ar}-O	C_{ar}	$C_{O-alk-O}$	C_{alk-O}	C_{alk}
ABE	2.97	3.57	2.66	8.75	3.07	12.81	64.57
ABES	3.07	4.25	3.01	10.33	2.94	13.5	62.19
ABEN	1.31	1.68	1.10	4.12	2.16	8.75	79.83

TABLE 8

Structural-group parameters of the investigated samples

Parameter	TBC	SC	EE	EES	EEN	ENH	ENHS	ENHN	ABE	ABES	ABEN
f_a	19.63	22.79	8.81	11.76	6.12	5.64	6.78	4.8	11.41	13.34	5.22
f_{al}	70.59	60.5	85.18	80.74	90.02	90.49	88.28	91.33	80.45	78.63	90.74
f_a/f_{al}	0.27	0.37	0.10	0.14	0.06	0.06	0.07	0.05	0.14	0.17	0.05

As demonstrated by the data of integral intensities for EE, NHE, and ABE see Tables 5−7), ethanol and alcohol-benzene extract the highest quantities of compounds of acid, phenol, aromatic, $C_{O-Alk-O}$, alcohol and carbonyl series upon sequential extraction, whereas n-heptane extracts the largest amounts of alkanes.

Structural-group parameters (Table 8) [21] were also calculated for all investigated samples according to ^{13}C NMR (CPMAS) data:

degree of aromaticity f_a:

$f_{ar} = C_{ar}$−O + C_{ar}

degree of aliphaticity:

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

aromaticity/aliphaticity f_{ar}/f_{al}:

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

According to the former, Tyulgan brown coal is notable for low contents of aromatics. When sequential extraction is carried out, aromatics in only small portions are extracted, which is indicated by an increase in the f_{ar} parameter in RC. As indicated by the calculated structural-group parameters, aromatic compounds were mainly extracted with ethanol and alcohol-benzene. Aliphatic compounds are more readily extracted with n-heptane. Aromatics are mainly concentrated in the saponified fraction when separating extracts onto saponified and non-saponified components.

The group and componential composition of the resulting extracts, and also their saponified and non-saponified components, was investigated by GC-MS (Table 9). As demonstrated by the acquired data, compounds of alcohol, alkene, acid, stearin, phenol, and terpene series are prevailing in EE. NHE extract is mainly comprised of compounds of alcohol, alkane, alkene, ketone, and

TABLE 9

Group composition of the investigated extracts and their saponified and non-saponified component for compounds with matching according to NIST databases of over 70 % (acquired by GC-MS)%

Sample	Groups of compounds											
	1	2	3	4	5	6	7	8	9	10	11	12
EE	0.26	3.59	1.44	1.03	0.36	7.04	1.31	1.16	1.44	−	0.06	−
EES	1.16	1.50	5.39	0.94	1.42	0.18	−	0.77	0.21	−	0.84	0.94
EEN	1.62	4.66	2.54	1.80	0.41	13.85	0.99	1.46	3.51	0.26	−	1.07
NHE	2.23	3.09	1.60	1.41	2.45	9.46	0.15	0.77	0.35	−	0.21	0.18
NHES	1.02	0.88	9.10	0.06	2.63	1.20	0.39	1.08	0.25	0.22	−	0.95
NHEN	1.89	1.99	2.93	1.30	0.15	17.70	1.22	1.37	1.31	0.27	0.05	0.73
ABE	0.03	4.39	6.32	0.92	0.22	9.46	−	1.20	1.27	0.34	−	0.53
ABES	1.18	−	14.4	−	2.88	−	0.25	0.82	0.68	−	−	0.63
ABEN	1.21	3.98	4.11	1.20	0.56	10.69	−	0.21	1.24	0.52	0.36	0.89

Note. 1 − alkanes, 2 − alkenes, 3 − acids presented as butyl esters, 4 − ketones, 5 − natural esters, 6 − alcohols, 7 − sterols, 8 − phenols, 9 − terpenes, 10 − aldehydes, 11 − amines, 12 − others.

TABLE 10

Bioactive compounds detected in bitumens by GC-MS

Fraction	Substance name [22]	Content in mixture, %	Matching with NIST,%
	Saponifiable		
EES	1-Docosene	0.9	95
NHES	Oleic acid, butyl ester	1.0	99
ABES	Butylparaben	0.8	99
ABES	Decanedioic acid, dibutyl ester	1.7	91
	Non-saponifiable		
EEN	Ferruginol	0.7	87
	Sugiol	0.7	95
	Lignoceric alcohol	4.5	99
	Podocarpa-8,11,13-triene-7β,13-diol, 14-isopropyl+Totarol	0.9	90
	β-Amyrin	0.4	92
	Bнtyl stearate	0.3	96
	Ceryl alcohol	4.0	99
NHEN	Behenic alcohol	2.0	99
	Ceryl alcohol	3.8	99
ABEN	Behenic alcohol	2.0	99
	γ-Tocopherol	0.2	99
	Butyl palmitate	0.9	99

natural ester series. Compounds of alcohol, acid, alkene, phenol, and terpene types are prevailing in ABE.

As demonstrated by GC-MS data, Tyulgan brown coal bitumens are a multicomponent mixture of compounds, wherein compounds of alkane, alcohol, acid, terpene, and ester series are prevailing. Aromatic compounds are present in the resulting extracts in small amounts. There is also a substantial number of unidentified compounds. BAS attract the most attention as a bitumen component. Table 10 reports BAS [22] found in bitumens by GC-MS; the contents were maximum in the specified fractions.

Most highly concentrated BAS in Tyulgan brown coal bitumens have turned out to be the following: *Lignoceric alcohol, Ceryl alcohol,* and *Behenic alcohol.* The acquired data have also demonstrated the efficiency of the procedure used to separate the resulting extracts onto saponifiable and non-saponifiable components. The former was used as a measure of additional fractionation to increase the fraction of identifiable compounds upon GC-MS analysis and the quality of separating onto more narrow fractions upon column chromatographic separation that is likely to be used in the future.

prising free and substituted alkanes, alcohols, and unsaturated hydrocarbons, and also aromatic compounds, acids and phenols in small amounts. Fractions of saponifiable substances in all extracts are mainly comprised of carboxylic acids, alcohols, esters, fragments of organic matter of acid type, and phenols. Alcohols are present in the saponifiable portion as products of ester hydrolysis under saponification conditions. Fractions of non-saponifiable substances of extracts contain alkanes, alcohols, fragments of organic matter of neutral type.

As identified, bitumens contain *Lignoceric alcohol, Ceryl alcohol, Behenic alcohol, Ferruginol, Butylparaben, Betulin,* and β-*Amyrine.* Bioactive substances (BAS) are concentrated in the non-saponifiable fraction of the resulting extracts. The detected BAS may find use in various branches, such as medical science, pharmacology, and agriculture.

Acknowledgements

CONCLUSION

As ascertained, bitumoids of Tyulgan brown coal are a multicomponent mixture mainly com-

REFERENCES

1 Zherebtsov S. I. Alkylation by alcohols of solid fuels of a low degree of coalification: dis. … dr. chemical sciences.

Russian University of Chemical Technology D. I. Mendeleev, Moscow, 2017.

2 Zherebtsov S. I. Extraction technologies and products of processing of brown and off-grade coal, *Coal.* 2009. No. 7. P. 63−66.

3 Zherebtsov S. I. Non-fuel use of Itatsky brown coal. In the collection: Experience and prospects of high technologies in the coal industry of Kuzbass. Proceedings of the scientific and technical conference. Kemerovo: Institute of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences, 1998. P. 258−262.

4 Belkevich P. I. Bitumens of Peat and Brown Coal / P.I. Belkevich, N. G. Golovanov, E. F. Dolidovich. Minsk: Science and Technology, 1989. 125 p.

5 Aronov S. G. Chemistry of solid combustible minerals / S. G. Aronov, L. L. Nesterenko. Kharkov: Publishing House of Kharkov State. University, 1960. 371 p.

6 Zherebtsov S. I. The composition of the wax fraction of methylated brown coal bitumoids / S. I. Zherebtsov, A. I. Moiseev, *Chemistry of Solid Fuels.* 2009. No. 2. P. 12−21.

7 Zherebtsov S. I. Complex technologies and products of processing of peat, brown and substandard Kuzbass coals / S. I. Zherebtsov, A. I. Moiseev, *Gorny Information-Analytical Bulletin.* 2008. No. S7. P. 114−124.

8 Shpakodraev K.M. Extraction and composition of bitumen solid fuels (review) / K. M. Shpakodraev, S. I. Zherebtsov, Z. R. Ismagilov, *Bulletin of the Kuzbass State Technical University.* 2018. No. 1. P. 169−180.

9 Filippov M. M. Schungite Rocks of the Onega Structure. Petrozavodsk: Karelian Research Center of the Russian Academy of Sciences. 2002. 280 p.

10 Bellamy L. D. Infrared Spectra of Molecules. Moscow: Foreign Literature Publishing House, 1957. 444 p.

11 Nakanisi K. Infrared Spectra and the Structure of Organic compounds. Moscow: World, 1965. 219 p.

12 Bellamy L. D. New Data on the IR Spectra of Complex Molecules. Moscow: World, 1971. 318 p.

13 Pretsch E. Structure Determination of Organic Compounds: Tables of Spectral Data / E. Pretsch, P. Biihlmann, C. Affolter. − 3., completely rev. and enl. engl. ed. Berlin, Heidelberg, New York, Barcelona, Hong Kong, London, Milan, Paris, Singapore, Tokyo: Springer, 2000. 404 p.

14 V. A. Mironov, Yankovsky S. A. Spectroscopy in Organic Chemistry. M.: Chemistry, 1985. 232 p.

15 Nyquist R. A. Interpreting Infrared, Raman, and NMR Spectra. V. 1. San Diego: Academic press, 2001. 448 p.

16 Silverstein R. M. Spectrometric Identification of Organic Compounds. Seventh edition. / R. M. Silverstein, F. X. Webster, D. J. Kiemle. Hoboken: John Wiley & Sons. Inc., 2005. 502 p.

17 Gordon A., Ford R. Chemist's Satellite. M.: Mir, 1965. 216 p.

18 Kazitsina L. A. The Use of UV, IR and NMR Spectroscopy in Organic Chemistry: Uch. manual for universities / L. A. Kazitsina, N. B. Kupletskaya. M.: Higher School, 1971. 264 p.

19 Kalaitzidis S. Early coalification features as approached by solid state 13C CPMAS NMR spectroscopy / S. Kalaitzidis, A. Georgakopoulos, K. Christanis, A. Iordanidis, Geochimica et Cosmochimica Acta. 2006. Vol. 70. P. 947−959.

20 Mao J.-D. Structural Features of a Bituminous Coal and Their Changes during Low-Temperature Oxidation and Loss of Volatiles Investigated by Advanced Solid-State NMR Spectroscopy / J-D. Mao, A. Schimmelmann, M. Mastalerz *et al.*, Energy and Fuels. 2010. No. 24. P. 2536−2544.

21 Kalabin G. A. Quantitative NMR Spectroscopy of Natural Organic Raw Materials and Products of its Processing / G. A. Kalabin, L.V. Kanitskaya, D.F. Kushnarev. M.: Chemistry, 2000. 408 p.

22 PubChem [Electronic resource]: [scientific database of data.]. Chemical Compounds and Mixtures. USA: National Center for Biotechnology Information, 2004 Access mode: https://pubchem.ncbi.nlm.nih.gov, free. Title From the screen. Date of appeal: 10.17.2018.