CHEMICAL COMPOSITION OF ORGANIC MATTER OF THE MONGOLIAN KHOOT OIL SHALE

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On the basis of the results obtained by IR, NMR and GC-MS analysis it is supposed that organic matter of Khoot oil shale is a complex mixture of high-molecular organic compounds mainly of naphthene-aliphatic character with long aliphatic chains connected with naphthene rings as well as with some substituents such as aromatic rings, carboxylic, carbonyl and hydroxyl groups. Such a structure is evidenced by obtaining aliphatic, naphthenic, aromatic and heterocyclic substances of different molecular mass by pyrolysis (decomposition) of the organic matter of oil shale.

Introduction

Kerogen in oil shale is a complex heterogeneous mixture of organic compounds, and shale oil produced by pyrolysis is formed by many different reactions involving these components.

The kinetics of kerogen decomposition and conversion have been studied rather extensively by many investigators, using various oil shales [1–11], whereas less attention has been paid to the investigation of oil shale and shale oil composition. The studies in this field were carried out by Fainberg and other researchers [12–15]. Investigation of oil shale by IR has also been reported [13–15]. These papers usually present the results of oil shale qualitative analyses. At present the use of quantitative IR spectroscopy is one of the important methods for studying chemical structure of solid fuels such as coal and oil shale as well as changes in the structure under the influence of physical-chemical factors [16]. The studies of Mongolian oil shale describe its main characteristics, pyrolysis conditions, thermal degradation and kinetic study [17–18].

The present paper describes studies made to characterize and investigate oil shale from the Khoot deposit, Mongolia, using IR, NMR and GC-MS.

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Experimental

The Khoot mining area is located to the northwest of Bayanjargalan in the province of Dundgovi Aimag. Khoot oil shale belongs to the Jurassic period of the Mesozoic era. The estimated resources are 612 million t that is equivalent to 42 million t of shale oil. The Khoot deposit is featured by abundant supplies of good-quality brown coal underlying oil shale and that doubles the importance of the Khoot oil shale study.

The investigations were carried out on oil shale samples taken from the 46th ditch and the Eedemt region of the deposit. Petrographic and mineral analysis revealed their composition: approximately 51 % clay minerals, 25 % organic matter, 5 % limonite, 10 % calcite and dolomite, 1 % feldspar, 1 % quartz, 5 % epidote, and 2 % getite. Both samples had schistose structure and brown-yellow colour. The density was 1.9371 and 1.9335 g/cm³, and high calorific value 2120 and 2010 kcal/kg for 46th ditch and Eedemt samples, respectively.

The results of proximate and ultimate analyses of oil shale are given in Table 1 and characteristics of shale oil obtained in experiments in Table 2.

Table 1. **Proximate and Ultimate Analysis Data of Khoot Oil Shale**

Indices	46th ditch	Eedemt
Moisture W^a, %	5.88	5.52
Ash A^d, %	61.12	62.46
Organic matter, % (on dry matter)	28.82	26.27
$(CO_2)^d_M$, %	10.06	11.27
C, %	66.12	62.84
H, %	10.2	7.65
N, %	2.64	2.79
S_{total}, %	0.19	0.45
O, % (by difference)	20.85	26.27
H/C atomic ratio	1.85	1.46

Table 2. **Characteristics of Shale Oils**

Indices	46th ditch	Eedemt
Density*, g/cm³	0.893	0.891
Index of refraction*	1.51	1.50
Elemental analysis**, wt.%:		
Carbon	84.27	82.88
Hydrogen	10.49	11.36
H/C atomic ratio	1.49	1.64
Average molecular mass	211	208

* Determined at 20 °C.
** On shale oil basis.

Separation of shale oil into different groups of components was investigated according to the general scheme described in [12], in which pyridine bases were extracted from shale oil by the acid and phenols by the alkali method.

Khoot oil shale was investigated by means of IR and shale oil by gas chromatography and ^1H NMR spectral analysis. The samples for taking IR spectra were prepared in the form of a thin film pressed between the plates of KBr. Spectra were recorded between 4000 and 400 cm^{-1} using a Bruker model Vacuum-FT-IR-Spectrometer IFS. The intensity of IR spectra is characterized by the optical density of a sample calculated for the mass unit of the 1-cm^2 sample and is expressed as [18]:

$$A_v = \frac{1}{f} \lg \frac{I_0}{I_v}$$

For the absorption bands of 700–900cm^{-1} the integral intensity of the absorption was determined by the following formula:

$$B = \frac{1}{f} \int_{700}^{900} \lg \frac{I_0}{I_v} d_v$$

where f is the concentration of the sample for a 1-cm^2 square area of the tablet;

I_0 and I_v are the intensities of the incoming and reflected by the sample light, respectively.

The percentages of hydrogen and carbon in the kerogen were calculated according to the Oelert [19] formulas as:

$$
\begin{aligned}
H_{CH_3} &= 4.6 \times 10^{-2} \times A_{1380}; \\
H_{AR} &= 1.14 \times 10^{-4} \times B_{650-910}; \\
C_{CH_3} &= 4H_{CH_3} \times (100/C_{EL}); \\
C_{AR} &= 12H_{AR} \times (100/C_{EL})
\end{aligned}
$$

where H_{CH_3}, H_{AR}, C_{CH_3}, and C_{AR} are the percentages of the aliphatic and aromatic hydrogen and aliphatic and aromatic carbon, respectively;

A and B are optical densities;

C_{EL} is the amount of the carbon calculated from elemental analysis data.

Proton NMR spectra were obtained on a spectrometer Bruker AC 200 using deuterated chloroform as the lock solvent. The quantitative distribution of H atoms was calculated from the ratio of the integral of the functional group region to the total integral.

Gas chromatography was carried out using a Finnigan Mat GC-MS system. A HP-5MS 30 m × 0.25 mm capillary column was used. The temperature program was as follows: 50 to 150 °C at 5 °C per minute, 150 to 250 °C

at 8 °C per minute, 250 to 300 °C at 20 °C per minute, and the oven was maintained at 50, 150, 250 °C for 5 min. The mass-spectrometric data were acquired and processed with a computer data system. Each sample was first dissolved in a mixture of pentane and benzene (10 : 1).

Results and Discussion

IR Analysis

The investigations were performed using the samples of the Khoot 46th ditch and Eedemt oil shale. Spectra of the two oil shales were identical (Fig. 1).

The IR spectra show peaks [13] at:

- 3434 cm^{-1} (hydroxyl groups)
- 2930, 2850 and 1380 cm^{-1} (aliphatic CH_2 and CH_3 groups)
- 1710 cm^{-1} (carboxyl and carbonyl groups)
- 1630 cm^{-1} (aromatic C=C bonds), 1430 and 870 cm^{-1} (CO_3^- or carbonate)
- 1030, 530 and 470 cm^{-1} (Si–O–mineral bonds of clay minerals and quartz)
- 800 and 776 cm^{-1} (Si–O bonds)
- 710 cm^{-1} (aromatic C–H
- 427 cm^{-1} (Me–OH bonds)

The optical density of spectra was calculated using IR spectra (Table 3). These data demonstrate that Khoot oil shale consists mainly of clay minerals, carbonate and organic matter the latter being dominantly of aliphatic and naphthene-type structure. There are also a few aromatic fragments in the oil shale structure.
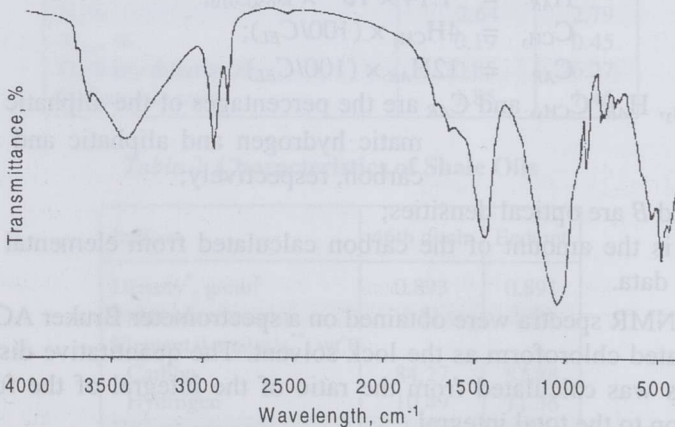

Fig. 1. IR spectra of oil shale samples

The relative intensities of the oil shale from the Khoot deposit (Table 4) were calculated on the basis of optical density and compared with similar results for Estonian oil shale [20]. Table 4 shows that the ratio of Si–O–mineral/CH$_3$ for the Mongolian samples is higher than that for the Estonian shale. The mineral matter content of the Khoot oil shale is higher than that of the organic matter. The ratio of OH...O/CH$_3$ is also higher for the Mongolian samples and shows that the organic matter is mainly connected with active groups of clay minerals.

The quantitative distribution of different-type hydrogen and carbon in the kerogen was calculated using the results of IR and Oelert formulas (Table 5).

Table 3. **Characteristics of IR Spectra**

Wave length, cm^{-1}	46th ditch	Eedemt
Optical density A 10^2 cm^2/g		
3424	2.18	2.12
2924	2.65	2.35
2852	1.75	1.55
1704	0.96	–
1631	1.56	1.49
1434	4.67	4.50
1384	1.92	1.71
1032	9.0	8.0
526	2.8	1.6
471	4.8	2.1
Optical density B 10^4 cm^2/g		
874	3.53	1.33
800	2.0	1.87
714	0.63	0.4

Table 4. **Relative Intensities of the Oil Shale Spectra**

Relative intensities	Oil shale			
	Russian (Turov)	Estonian	Mongolian (Khoot)	
			46th ditch	Eedemt
D_{3400}/D_{2930}	1.2	0.4	0.82	0.90
D_{1430}/D_{2930}	1.1	2.2	1.76	1.91
D_{1030}/D_{2930}	8.0	1.1	3.4	3.4
D_{1030}/D_{1430}	5.7	0.8	2.2	1.9
D_{1430}/D_{800}	2.1	32.0	2.33	2.4

Table 5. **Distribution of Hydrogen and Carbon in Kerogen, %**

Group	46th ditch	Eedemt
Hydrogen:		
aliphatic (or naphthenic)	8.83	7.86
aromatic	0.72	0.46
Carbon:		
aromatic	13.09	8.76
aliphatic (or naphthenic)	53.41	49.90

The results of IR analysis show that the kerogen of the Khoot oil shale is a complex mixture with predominant aliphatic and naphthene-type structures and less aromatics with attached carbonyl and hydroxyl groups. The peaks at 400–500 cm^{-1} are indicative of organic-mineral structural elements in the Khoot oil shale.

The first step in the shale oil research was the determination of the chemical composition of shale oil. This was as follows: 0.84 % substances insoluble in benzene, 1.78 % pyridine bases, 0.27 % organic acids, 0.67 % phenols, 3.96 % asphaltenes and 92.48 % neutral oils. As one can see, the share of organic acids and phenols is low. A further investigation of the chemical nature and possibilities of using them in chemical synthesis may be useful.

^{1}H NMR Analysis of Shale Oil

The shale oils from the 46th ditch and Eedemt oil shales were analyzed by ^{1}H NMR. Their spectra are shown in Fig. 2.
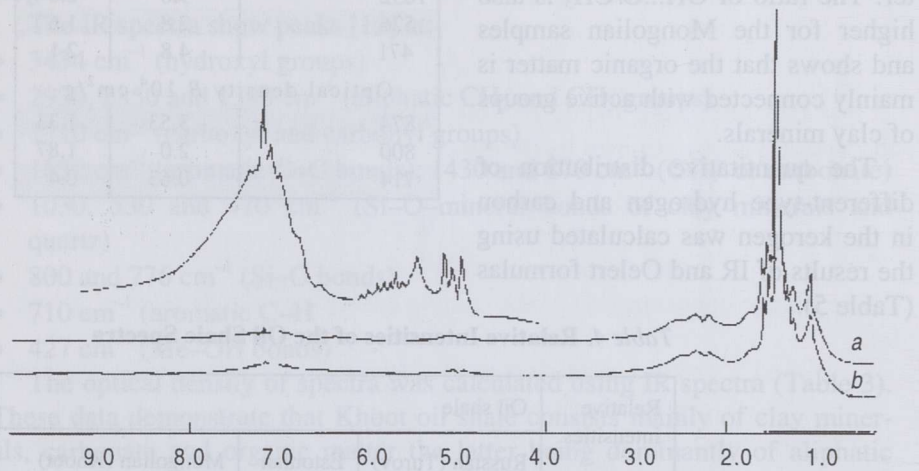

Fig. 2. ^{1}H NMR spectra of shale oils from 46th ditch (*a*) and Eedemt (*b*) oil shale

The aim of NMR analysis in our case was to elucidate the quantitative distribution of H atoms among different functional groups. We calculated the quantitative distribution of H atoms (Table 6).

Table 6. **Distribution of H Atoms in Shale Oil**

Group	Chemical shift δ, ppm	Distribution of H atoms, %	
		46th ditch	Eedemt
CH₃	0.5–1.1	11.6	13.3
CH₂ and CH of the long alkyl chains in β-position to an aromatic ring	1.1–1.6	41.7	39.5
CH₂ in the naphthene	1.6–1.9	10.0	11.3
CH₂ and CH in α-position to an aromatic ring	1.9–2.8	20.0	18.0
Olefins	4.0–6.0	3.3	5.05
Aromatics	6.0–7.8	13.4	12.85

Table 6 shows that most of the H atoms present in shale oil (39.5–41.7 %) are located in –CH_2– and –CH– of long alkyl chains in the β-position to an aromatic ring. The results of the NMR analysis follow that of the IR analysis – the organic matter of oil shale is dominated by aliphatic and naphthene-type structures.

Study of Shale Oil by GC-MS

Shale oils obtained from the 46th ditch and Eedemt oil shale samples were investigated by gas chromatography. The chromatograms of these two samples were similar. The chromatogram of the Eedemt shale oil is shown in Fig. 3.

The shares of different carbon types in shale oil were calculated using the spectrum of the Khoot shale oil. It contains 45 % aliphatic and 30 % aromatic compounds. The results show that the percentage of aromatic compounds in oil exceeds that in the Khoot oil shale organic matter. It means that during decomposition of oil shale a redistribution of hydrogen occurs increasing the content of aromatic compounds.
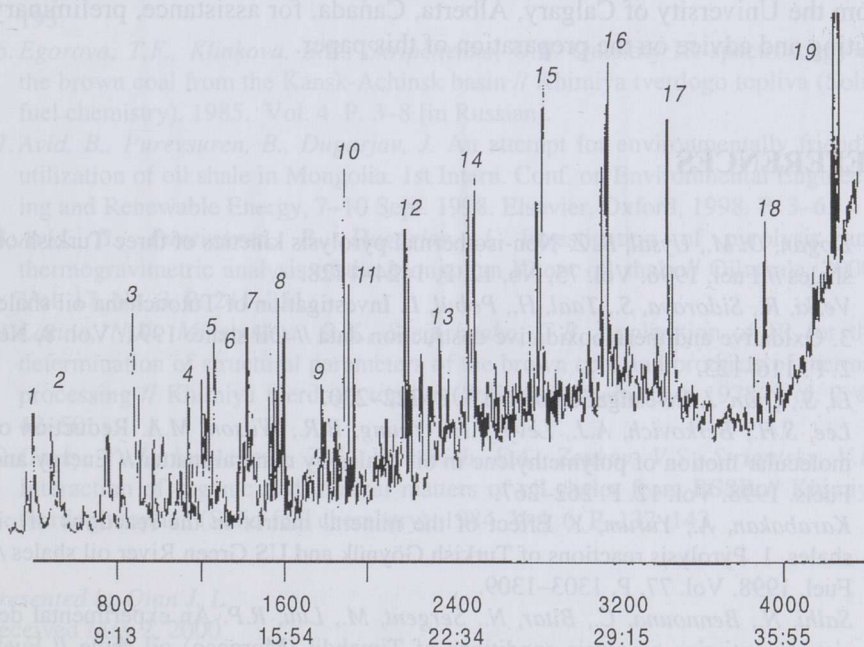

800	1600	2400	3200	4000
9:13	15:54	22:34	29:15	35:55

Fig. 3. Chromatogram of shale oil from Eedemt oil shale:
1 – 1,4-dimethylbenzene; *2* – 1,2-dimethylbenzene; *3* – 1,2,3-trimethylbenzene;
4 – 1,2,3,4-tetra-methylbenzene; *5* – heptadecane; *6* – octadecane;
7 – 2-ethyl-1,4-dimethylbenzene; *8* – 1,4-dimethylcyclohexene;
9 – tetrahydronaphthopyrone; *10* – 2,5-dihydroxy-1,4-benzoquinone;
11 – 2,6,10,14-tetramethylnonadecane; *12* – 2,2,6,6-tetramethylpiperidinyloxi;
13 – dimethylnaphthalene; *14* – tetracosane; *15* – heptatriacontane;
16 – 1-dotriacontanol; *17* – 5-eicosene; *18* – tetratetracontane; *19* – tritetracontane

Conclusions

1. The IR analysis shows that the kerogen of the Mongolian Khoot oil shale is a complex mixture with predominant aliphatic- and naphthene-type structures. A lesser part of the kerogen is of aromatic structure with attached carbonyl and hydroxyl groups.

2. Most of H atoms present in the shale oil (39.5–41.7 %) are located in CH_2 and CH of long alkyl chains in the β-position to an aromatic ring. The results of the NMR analysis follow those of the IR analysis – aliphatic and naphthene-type structures dominate in the shale organic matter.

3. The shale oil from the Khoot oil shale contains 45 % aliphatic and 30 % aromatic compounds.

Acknowledgements

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