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Study of the Semicoking Tar of High-Sulfur Oil Shale from the Volga Basin

A. L. Lapidus[a,b,*], **N. Yu. Beilina**[c,**], **D. S. Khudyakov**[a,***], **and A. M. Kozlov**[a,****]
[a] *Gubkin State University of Oil and Gas, Moscow, 119991 Russia*
[b] *Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[c] *Research Institute of Structural Graphite Materials (AO NIIgrafit), Moscow, 111524 Russia*
**e-mail: albert@ioc.ac.ru*
***e-mail: beilinan@mail.ru*
****e-mail: ltybc672@rambler.ru*
*****e-mail: kozlov.a@gubkin.ru*

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Abstract—The semicoking tar of shale oil from the Perelyubskoe deposit was studied. The following characteristics of the tar were determined: density, fractional and elemental compositions, and lead and manganese contents. The detailed analysis of the light gasoline fractions of this tar was carried out.

Keywords: oil shale, tar, semicoking, pyrolysis, thiophene
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A search for alternative sources of hydrocarbon raw materials and the development of complex technologies for their processing is a problem of considerable current interest in the context of limited oil reserves and relatively high costs of petroleum production. Oil shale, whose proven reserves in Russia and abroad are very large, can be an inexpensive raw material [1].

Oil shale is characterized by a high H/C atomic ratio in the organic matter (close to that in oil) and a unique composition of the organic matter [2].

Shale from the Perelyubskoe deposit of the largest in Russia Volga basin was chosen as the test material [3].

The highest yield of tar from processed shale was achieved in the thermal decomposition process of oil shale at a temperature of 500–550°C.

The thermal decomposition of the oil shale from the Perelyubskoe deposit without air access was carried out in a reactor with a capacity of 8 kg of crushed dry oil shale in 1 h at a temperature of 560°C and an oil shale feed rate of 23.5 cm/min for 7 min.

The resulting shale tar was divided into two parts by simple sedimentation. The upper (light) portion of the tar was separated into fractions in an ARN-2 oil rectification apparatus. Table 1 summarizes the characteristics of the light portion of the tar. From the beginning of boiling to 410°C, 17 fractions were separated from the tar at regular intervals of 20°C, and the residue after rectification with losses amounted to 29.3 wt %.

Table 1. Characteristics of the light shale tar

Characteristic	Value
Density, g/cm^3	1.036
Fractional composition, wt %:	
initial bp–100°C	2.2
100–120°C	1.6
120–140°C	2.4
140–160°C	3.4
160–180°C	4.7
180–200°C	6.3
200–220°C	0.8
220–240°C	1.5
240–260°C	2.5
260–280°C	1.8
280–300°C	4.6
300–320°C	5.7
320–340°C	5.0
340–360°C	7.3
360–380°C	6.3
380–400°C	7.7
400–410°C	6.9
Above 410°C + losses	29.3

Table 2. Elemental composition of the fractions of tar, wt %

Fraction	N	C	H	S
initial bp–100°C	0.0	61.8	8.2	11.5
100–120°C	0.0	64.4	8.1	11.7
120–140°C	0.1	67.5	8.5	11.2
140–160°C	0.1	67.3	8.9	9.5
160–180°C	0.0	64.6	7.7	7.1
180–200°C	0.1	65.6	8.0	6.1
200–220°C	0.1	68.0	8.2	7.5
220–240°C	0.2	63.1	7.9	7.8
240–260°C	0.1	68.2	8.0	7.6
260–280°C	0.2	73.1	8.8	8.6
280–300°C	0.4	73.2	8.4	7.8
300–320°C	0.5	75.1	8.6	7.6
320–340°C	0.6	76.2	8.7	7.2
340–360°C	0.7	76.3	8.6	6.7
360–380°C	0.7	76.9	8.4	6.8
380–400°C	0.7	76.4	8.3	6.6
400–410°C	0.7	76.7	8.4	6.9
Above 410°C + losses	1.2	78.5	7.9	6.9
Shale tar	0.7	74.2	8.4	8.0

CHNS analysis was performed using an EA-3000 elemental composition analyzer (EuroVector).

Table 2 shows the experimental data of the elemental analysis of the shale tar and its fractions. The presence of high sulfur content in low-boiling fractions (11.2–11.7 wt %) was most likely due to the high concentrations of thiophene and its homologs. The sulfur content of the samples separated above 140°C was lower than that of the gasoline fraction, and it varied unevenly over a wide range from 6.1 to 9.5 wt % depending on the boiling point of the fraction.

The pyrogenetic synthesis of hydrogen sulfide and organic sulfur compounds during the thermal processing of Volga basin shale occurred due to a set of interrelated processes. It is likely that a significant part of thiophene and its homologs was formed due to the destructive transformations of kerogen, including alkyl-substituted thiophene rings and more complex cycloalkyl-substituted structures. The pyrogenetic synthesis of thiophene and simple methyl derivatives from the intermediate products of thermal destruction of kerogen and the transformation of some compounds of the mineral matter of shale were also possible [4]. Organosulfur (thiophene) compounds can be separated from the tar by an extraction method used in petrochemistry and converted into valuable chemical products: herbicides, polymers, fuel additives, adsorbents, antioxidants, and flotation reagents (with consideration for the fact that these products are currently almost not produced in Russia).

Oil is rich in hydrogen: the weight ratio of carbon to hydrogen in the organic matter of oil reaches 6–7, which is not the case with other types of solid fossil fuels, where this ratio is higher than 10–15. Tar obtained as a result of the processing of coal is also different in this characteristic. However, the above ratio in oil shale tars is closer to that in oil; therefore, these tars can be the most likely substitute for oil in the future. In the course of elemental analysis, we found the ratios of carbon to hydrogen in the organic matter of the fractions of the test shale tar; they were 7.6–10.0 (7.6–8.4 for light fractions boiling up to 200°C, 8.0–8.7 for medium fractions boiling in a range of 200–300°C, and 8.7–10.0 for heavy fractions boiling above 300°C). The ratio of carbon to hydrogen in the starting shale tar was 8.8. Hence, it follows that the light distillates of shale tar can be considered as an alternative to the traditional types of motor fuel. However, in the case of using the Volga basin shale as a raw material for this fuel, desulfurization (for example, hydrotreating) is necessary.

Figure 1 shows the dependence of the weight ratio of carbon to hydrogen on the fractional composition of shale oil.

We carried out the detailed chromatographic analysis of gasoline fractions boiling up to 140°C. Table 3 summarizes the molecular weights of fractions, relative densities, and saturated vapor pressures. Table 4 presents the concentrations of individual classes of organic substances in gasoline fractions (the group composition).

The gasoline fractions of oil consist of 6–28 wt % aromatic hydrocarbons, 21–75 wt % naphthenes, 1–32 wt % *n*-paraffins, and 18–40 wt % isoparaffins [5]. The test fractions of shale tar contained 17.6–22.6 wt % aromatic hydrocarbons, 7.9–12.5 wt % naphthenes, 2.5–3.4 wt % *n*-paraffins, and 18.9–35.3 wt % isoparaffins. In the analysis of a wider total gasoline fraction of shale oil, these values can be slightly different from

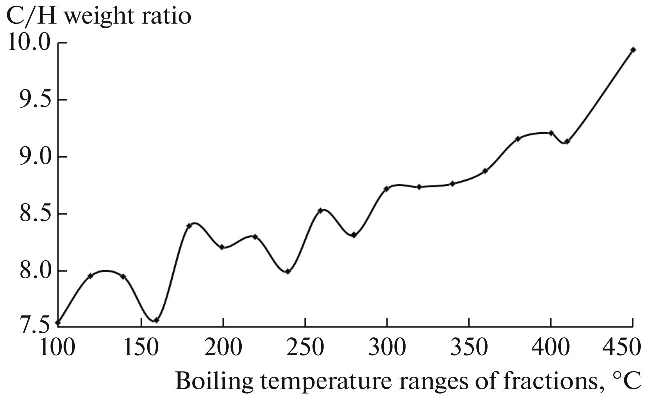

Fig. 1. Dependence of the weight ratio of carbon to hydrogen in the organic matter on the fractional composition of shale oil.

Table 3. Characteristics of gasoline fractions

Gasoline fraction	Molecular weight, g/mol	ρ_4^{20}	ρ_{15}^{15}	Saturated vapor pressure, kPa
Fraction 1 (initial bp–100°C)	108.029	0.748	0.752	12.711
Fraction 2 (100–120°C)	117.078	0.757	0.761	6.955
Fraction 3 (120–140°C)	125.411	0.769	0.773	2.307

Table 4. Concentrations of the classes of substances in gasoline fractions, wt %

Class of substances	Fraction 1 (initial bp–100°C)	Fraction 2 (100–120°C)	Fraction 3 (120–140°C)
n-Paraffins	3.4	2.7	2.5
Isoparaffins	18.9	27.9	35.3
Aromatic hydrocarbons	17. 6	18.5	22.6
Naphthenes	7. 9	10.5	12.5
Olefins	41.5	27.6	18.5
Oxygenates	4.8	0.3	0.1
Unidentified	5.9	12.5	8.5
Total	100	100	100

The detailed analysis of the light gasoline fractions of the tar for hydrocarbons was carried out by capillary gas chromatography in accordance with GOST 32507-2013 (method B) on a Khromatek-Kristall 5000 chromatograph (a FID detector and a BP1-PONA quartz capillary column, 100 m × 0.25 mm).

the obtained values. With the use of the light fractions of shale oil as motor fuel components, their additional processing is necessary. The test gasoline fractions can also be used to manufacture products similar to petroleum solvents (mainly, mixed solvents) [6].

The olefin hydrocarbon contents of fractions 1 (initial bp–100°C), 2 (100–120°C), and 3 (120–140°C) were 41.5, 27.6, and 18.5 wt %, respectively. The highest oxygenate content of 4.8 wt % was obtained in fraction 1 (initial bp–100°C). The concentrations of aromatic hydrocarbons in each of the test gasoline fractions of the tar were no higher than 20 vol %

The concentrations of lead and manganese in shale tar and its fractions were determined by atomic absorption spectroscopy (AAS SavantAA, GBC Scientific Equipment) in accordance with GOST [State Standard] 32350–2013 and GOST 33158–2014, respectively.

Because of the high viscosity of the tar and its fractions, the test samples were diluted by a factor of 12 : 10 mL of 4-methyl-2-pentanone and 1 mL of toluene were added to a 1-mL sample; toluene was added because not all of the fractions were sufficiently soluble in 4-methyl-2-pentanone. As a result of the analysis, it was found that the lead content of the shale tar and its fractions was no higher than 1 mg/L.

Table 5. Manganese content of the shale tar and its fractions, mg/L

Sample no.	Concentration in a diluted sample	Concentration in a test sample
1	0.00	0.00
2	0.00	0.00
3	0.01	0.12
4	0.01	0.12
5	0.01	0.12
6	0.01	0.12
7	0.02	0.24
8	0.00	0.00
9	0.00	0.00
10	0.00	0.00
11	0.00	0.00
12	0.02	0.24
13	0.02	0.24
14	0.26	3.12
15	0.00	0.00
16	0.00	0.00
17	0.00	0.00
18	0.04	0.48

Sample nos. 1–17 correspond to the initial bp–100°C–400–410°C shale tar fractions, respectively; sample no. 18 is shale tar.

Table 5 summarizes the manganese content of the test products. In all of the samples other than nos. 14 and 18, the manganese content did not exceed 0.02 mg/L; therefore, the concentrations of manganese were higher than 0.24 mg/L only in a fraction of 340–360°C (manganese content, 3.12 mg/L) and in shale tar (manganese content, 0.48 mg/L).

Thus, shale tar similar to petroleum was obtained in the process of the thermal decomposition of high-sulfur oil shale from the Perelyubskoe deposit at 560°C, and this tar is suitable for the manufacture of motor fuels and a number of valuable chemical products.

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