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LOW-SULPHUR OIL SHALE RESEARCH AND EXPERIMENTAL PROCESSING

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Low-sulphur oil shales which in most cases yield paraffinic oil upon retorting have been studied. Oils obtained have high values for solidification point (25-30 °C) and a relatively low density - about 900 kg/m^3. Compared to high-sulphur oils, low-sulphur ones contain more paraffins and olefins and less aromatic hydrocarbons. The content of phenols in paraffinic oils is negligible - 2-4 %.

Low-sulphur oil shales studied may be divided into two groups. The first group comprises oil shales for which 70-100 % of the total sulphur remains in the semicoke during retorting, for the second group this percentage is 50-70.

The overwhelming majority of oil shale of the world yield low-sulphur paraffinic oil upon retorting. This oil is similar to low-sulphur paraffinic petroleums in its physical and chemical properties [1]. Quite naturally such shale oil is therefore considered a good substitute for petroleum and its subsequent refining can be accomplished with traditional petrochemical methods.

The world-wide experience in processing low-sulphur shales to produce liquid fuel is quite extensive. In China, shales have been processed on an industrial scale since 1927. In the USA, large pilot-scale retorts have been in operation and they still are in Brazil. Several smaller pilot and test units are used for oil shale research in many countries of the world.

The authors' present tests have shown (Tables 1 and 2) that oil shales which yield paraffinic oil upon retorting have a relatively low density (about 900 kg/m^3) and, as a rule, a low content of sulphur (Tables 3 and 4). The majority of oil shales in the world yield retort oils with higher contents of nitrogen compounds than kukersite oil (sample No. 1) produced from Estonian shale. Some oil shales contain arsenic, and the presence of arsenic compounds makes the subsequent processing of such oil more difficult since those compounds poison the catalysts used for hydrogenation.

Table 1. Properties of Low-Sulphur Oil Shales from Various Deposits of the World (Shale Samples *1-9*) (end)

Indices	Estonia, Estonian (kukersite)	Russia		Kazakhstan		Ukraine, Boltysh	Byelorus, Luban	Bulgaria	
		Ukhta	Eckibastuse	Kenderlyck	Ust-Kame-nogorsk			Gurkovo-Nikolayev	Breznik
	Investigated shale sample number								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Fischer assay product yield (shale sample 200 g), %:									
Shale oil	–	–	3.9	–	–	–	–	2.8	–
Pyrogenetic water	–	–	1.8	–	–	–	–	3.2	–
Semicoke	–	–	86.5	–	–	–	–	91.4	–
Gas and losses (by difference)	–	–	7.8	–	–	–	–	2.6	–
Fischer assay oil of organic matter, %	–	–	15.5	–	–	–	–	20.7	–
Ash composition, %:									
SiO_2	28.5	66.4	60.3	57.4	57.2	65.8	36.8	59.9	40.0
Fe_2O_3	5.5	1.5	14.0	6.3	}24.6	8.6	5.8	8.3	7.5
Al_2O_3	6.7	4.5	17.6	14.0		17.6	10.2	19.1	14.0
K_2O	2.1	}1.0	1.2	1.1	}7.2	2.6	–	–	1.9
Na_2O	0.4		0.6	1.6		1.7	–	–	0.9
MgO	4.4	1.3	1.3	1.3	2.9	1.5	2.8	2.0	3.8
CaO	44.8	22.8	2.1	13.4	4.9	2.1	29.4	8.4	23.1
SO_3	6.5	1.6	0.2	3.3	2.5	–	5.0	1.6	8.8
Total	98.9	99.1	97.3	98.4	99.3	99.9	90.0	99.3	100.0

Table 1. **Properties of Low-Sulphur Oil Shales from Various Deposits of the World (Shale Samples *1-9*)**

Indices	Estonia, Estonian (kukersite)	Russia, Ukhta	Eckibastuse	Kazakhstan, Kenderlyck	Ust-Kamenogorsk	Ukraine, Boltysh	Byelorus, Luban	Bulgaria, Gurkovo-Nikolayev	Breznik
Investigated shale sample number	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Moisture of oil shale tested in experimental retort, %	5.1	–	7.3	2.8	1.0	4.4	1.2	10.7	0.7
Content (dry basis), %:									
Carbon dioxide $(CO_2)^d_M$	20.8	13.0	4.0	5.5	3.3	0.5	17.0	4.3	14.9
Ash A^d	46.2	75.5	70.9	57.4	74.7	57.5	67.0	82.2	66.5
Organic matter*	33.0	11.5	25.1	37.1	22.0	42.0	16.0	13.5	18.6
Total sulphur S^d_t	1.90	0.39	1.32	2.1	1.0	1.40	1.6	0.38	2.47
Including:									
Sulphate	0.05	–	0.01	–	–	0.12	0.1	–	0.08
Pyrite	1.30	–	1.08	–	–	1.11	1.1	0.31	2.27
Organic (by difference)	0.55	–	0.23	0.64	–	0.17	0.4	0.07	0.12
Heating value (bomb calorimeter), MJ/kg	12.43	3.56	7.58	12.94	7.91	12.73	5.65	3.27	7.12
Fischer assay product yield (standard retort), %:									
Shale oil	21.8	4.6	5.2	19.8	10.9	17.5	8.8	5.3	9.7
Pyrogenetic water	2.4	0.4	2.1	2.1	0.5	3.9	1.2	1.4	2.4
Semicoke	70.2	93.3	87.8	71.9	83.3	72.9	86.6	90.7	83.5
Gas and losses (by difference)	5.6	1.7	4.9	6.2	5.3	5.7	3.4	2.6	4.4
Fischer assay oil of organic matter, %	66.1	40.0	20.7	53.4	49.5	41.7	55.0	39.3	52.1

* Here and later on organic matter content is equal to: $100 - (CO_2)^d_M - A^d$.

Table 2. **Properties of Low-Sulphur Oil Shales from Various Deposits of the World (Shale Samples *10-19*)**

Indices	USA, Green River	Brazil, Paraiba valley oil shale		Yugoslavia, Aleksinac	Roumania, Anin	Thailand, Mae Sot	Australia, Stuart	China		
		papery	lump sized					Hua-dian	Fu-shun	Mao-ming
	Investigated shale sample number									
	10	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
Moisture of oil shale tested in experimental retort, %	–	3.2		2.5	1.5	–	–	–	–	–
Content (dry basis), %:										
Carbon dioxide $(CO_2)^d_M$	17.3	0.2	0.3	6.6	3.8	10.5	1.8	5.4	3.9	1.0
Ash A^d	68.3	60.3	82.3	75.2	74.4	60.5	78.9	62.4	81.4	73.2
Organic matter*	14.4	39.5	17.4	18.2	21.8	29.0	19.3	32.2	14.7	25.8
Total sulphur S^d_t	0.65	1.28	1.60	2.78	0.67	0.87	1.0	1.2	0.78	1.22
Including:										
Sulphate	0.02	0.16	0.17	0.05	–	0.03	–	–	0.11	0.16
Pyrite	0.35	0.55	0.54	2.50	0.51	0.56	–	–	0.55	0.98
Organic (by difference)	0.28	0.57	0.89	0.23	0.16	0.28	–	–	0.12	0.08
Heating value (bomb calorimeter), MJ/kg	5.36	13.27	3.68	6.32	5.32	11.26	5.48	11.64	3.68	7.68
Fischer assay product yield (standard retort), %:										
Shale oil	9.7	21.1	4.0	8.4*	4.8	18.5	6.9	15.9	3.8	10.3
Pyrogenetic water	1.2	4.2	3.9	2.7	0.7	2.3	3.3	3.7	1.8	2.8
Semicoke	86.7	71.7	89.4	85.2	88.0	74.7	85.6	74.6	89.9	83.5
Gas and losses (by difference)	2.4	3.0	2.7	3.7	6.5	4.5	4.2	5.8	4.5	3.4
Fischer assay oil of organic matter, %	67.4	53.5	23.0	46.2	22.0	63.8	35.7	49.4	25.8	39.9

Table 2. Properties of Low-Sulphur Oil Shales from Various Deposits of the World (Shale Samples *10-19*) (end)

Indices	USA, Green River	Brazil, Paraiba valley oil shale		Yugoslavia, Aleksinac	Roumania, Anin	Thailand, Mae Sot	Australia, Stuart	China		
		papery	lump sized					Hua-dian	Fu-shun	Mao-ming
	Investigated shale sample number									
	10	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
Ash composition, %:										
SiO_2	44.3	55.0	58.0	53.9	50.8	46.2	65.8	53.1	60.5	58.1
Fe_2O_3	5.5	10.2	}32.5	9.5	4.3	8.2	8.0	7.8	12.0	9.8
Al_2O_3	12.8	26.6		13.4	32.1	12.7	14.7	16.8	18.1	22.6
K_2O	2.8	}3.2	}2.9	1.5	–	}7.3	–	1.6	3.0	}5.4
Na_2O	3.5			1.3	–		–	0.3	2.3	
MgO	7.4	2.9	3.2	2.3	1.2	7.8	2.8	2.0	1.8	2.0
CaO	20.5	0.9	1.6	9.4	1.3	15.4	1.7	12.9	1.7	1.4
SO_3	2.4	1.1	1.3	7.9	–	2.4	0.8	3.8	0.6	0.3
Total	99.2	99.9	99.5	99.2	89.7**	100.0	93.8	98.3	100.0	99.6

* Fischer assay product yield (shale sample 200 g), %: shale oil - 8.1; pyrogenetic water - 2.8; semicoke - 85.0; gas and losses (by difference) - 4.1.

** Additionally, 8.2 % of FeO has been determined in the ash.

Table 3. **Properties of Fischer Assay Products from Low-Sulphur Oil Shales of Various Deposits of the World (Shale Samples *1-9*)**

Indices	Investigated shale sample number (see Table 1)								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
To obtain the semicoking products the Fischer retort was applied with oil shale sample, g	20	20	200	20	20	20	20	200	20
Shale Oil									
Density at 20 °C, kg/m^3	968	975	915	923	906	898	925	878	934
Molecular mass	276	–	188	–	–	–	294	–	–
Heating value (bomb calorimeter), MJ/kg	40.19	39.35	42.08	41.66	42.83	42.70	41.45	43.54	42.83
Elemental composition (dry basis), %:									
C	83.12	83.1	85.30	85.0	84.5	84.66	84.4	86.78	84.57
H	10.13	9.9	11.34	11.3	12.0	11.95	11.2	12.20	11.09
S	0.84	0.6	0.44	1.0	0.8	0.82	2.0	0.46	1.35
N	0.20	1.8	0.63	0.5	1.6	0.64	0.6	}0.56	1.75
O (by difference)	5.71	4.6	2.29	2.2	1.1	1.93	1.8		1.24
Semicoke									
Content (dry basis), %:									
Carbon dioxide $(CO_2)^d_M$	28.1	13.6	0.9	6.9	2.8	0.3	19.4	4.7	17.1
Ash A^d	64.8	82.6	79.6	80.1	89.3	81.6	76.4	88.7	76.2
Carbon C^d	7.6	3.5	14.3	10.2	6.4	10.5	4.2	4.0	6.5
Total sulphur S^d_t	1.5	0.3	1.34	2.35	1.0	1.3	1.1	0.4	1.7
Heating value (bomb calorimeter), MJ/kg	2.64	1.34	5.32	4.60	2.72	4.98	1.46	1.38	2.60

Table 4. **Properties of Fischer Assay Products from Low-Sulphur Oil Shales of Various Deposits of the World (Shale Samples *10-19*)**

Indices	Investigated shale sample number (see Table 2)									
	10	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
To obtain the semicoking products the Fischer retort was applied with oil shale sample, g	20	20	20	200	20	50	50	50	50	50
Shale Oil										
Density at 20 °C, kg/m^3	927	910	920	908	913	889	897	899	893	909
Molecular mass	233	–	–	230	–	278	234	236	–	–
Heating value (bomb calorimeter), MJ/kg	42.58	43.21	41.66	42.91	43.84	44.00	42.91	42.83	43.75	45.80
Elemental composition (dry basis), %:										
C	83.89	85.7	85.5	83.15	87.0	84.14	83.2	80.19	85.37	83.04
H	11.87	11.9	11.6	11.31	12.3	12.04	11.5	11.42	12.20	12.01
S	0.84	1.1	2.3	1.75	0.5	0.60	0.6	0.43	0.48	0.31
N	1.30	}1.3 (N + O)	}0.6 (N + O)	1.21	}0.2 (N + O)	1.81	0.7	0.10	1.32	0.61
O (by difference)	2.10			2.58		1.41	4.0	7.86	0.63	4.03
Semicoke										
Content (dry basis), %:										
Carbon dioxide $(CO_2)^d_M$	19.5	0.3	0.1	7.1	1.1	13.8	1.1	7.9	2.2	1.4
Ash A^d	78.2	84.3	90.8	86.9	84.4	79.9	91.3	80.6	88.9	85.3
Carbon C^d	2.7	9.8	4.5	5.3	8.2	6.0	7.6	9.6	4.9	6.8
Total sulphur S^d_t	0.4	1.3	1.3	2.29	0.75	0.69	1.0	1.1	0.74	1.28
Heating value (bomb calorimeter), MJ/kg	0.92	3.56	1.46	2.43	3.18	1.97	2.34	3.81	1.67	2.39

Table 5. **Yield and Characteristics of Gas* Obtained in the Fischer Retort from Low-Sulphur Oil Shales of Various Deposits of the World (Shale Samples *1-9*)**

Indices	Investigated shale sample number (see Table 1)								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Specific gas yield, m^3/t	38.2	17.0	38.1	35.2	33.1	51.0	22.0	22.7	30.0
Content of components, vol.%:									
CO_2	23.7	24.2	50.5	19.5	18.8	25.3	26.7	17.5	13.5
H_2S	14.6	5.0	0.0	2.8	0.8	4.3	9.3	0.4	25.7
H_2	5.3	34.9	12.1	25.0	44.5	24.4	23.2	40.7	20.5
CO	4.2	5.0	2.1	7.7	6.6	8.9	2.2	2.5	3.4
C_nH_{2n+2}	35.6	26.6	28.5	34.3	21.0	28.4	26.3	24.3	29.3
Including:									
CH_4	14.7	17.2	18.1	17.2	9.7	13.3	11.2	10.5	15.9
C_2H_6	8.6	6.4	5.9	9.4	6.4	10.1	7.3	7.4	6.4
C_3H_8	5.6	2.2	2.4	4.7	2.8	3.0	4.7	3.5	4.9
C_4H_{10}:									
n-butane	2.0	0.6	0.9	2.0	1.4	1.3	1.9	1.3	1.4
iso-butane	0.9	0.1	0.1	0.1	0.1	—	—	0.3	—
C_5H_{12}:									
n-pentane	3.0	0.1	0.6	0.9	0.6	0.7	1.2	1.0	0.7
iso-pentane	0.8	—	0.1	—	—	—	—	0.3	—
C_6H_{14}:									
n-hexane	—	—	0.4	—	—	—	—	—	—

* Here and later on all characteristics of gas are given at 20 °C and 760 mm Hg.

Table 5. Yield and Characteristics of Gas* Obtained in the Fischer Retort from Low-Sulphur Oil Shales of Various Deposits of the World (Shale Samples *1-9*) (end)

Indices	Investigated shale sample number (see Table 1)								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
C_nH_m	16.6	4.3	6.5	10.7	8.3	8.7	12.3	14.6	7.6
Including:									
C_2H_4	3.3	1.5	1.8	2.9	2.4	2.9	4.4	4.8	1.7
C_3H_6	6.1	1.8	2.2	4.2	2.9	3.7	3.9	4.6	3.1
C_4H_8:									
butene-1, *iso*-butene	3.3	0.6	0.9	1.8	1.5	1.0	2.1	1.9	2.5
trans-butene-2	0.8	0.1	0.4	0.4	0.3	0.3	0.4	0.7	—
cis-butene-2	0.5	0.2	0.3	0.4	0.3	0.6	0.2	0.3	—
C_5H_{10}:									
pentene-1	2.6	0.1	0.3	0.7	0.6	0.2	1.3	0.9	0.3
trans-pentene-2	—	—	0.1	}0.3	}0.3	—	—	0.1	—
cis-pentene-2	—	—	—			—	—	1.0	—
C_6H_{12}:									
2-methylbutene-1	—	—	0.1	—	—	—	—	0.2	—
3-methylbutene-1	—	—	0.1	—	—	—	—	0.1	—
hexene-1	—	—	0.3	—	—	—	—	—	—
Not identified	—	—	0.3	—	—	—	—	—	—
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Calculated heating value, MJ/m^3:									
high	46.51	24.58	24.07	35.37	27.34	29.26	33.75	35.08	33.50
low	42.92	21.22	22.06	32.36	24.83	26.75	30.90	32.02	30.60
Density, kg/m^3	1.481	0.945	1.394	1.099	0.891	1.117	1.205	0.909	1.140
Content of H_2S, g/m^3	206	71	—	41	12	61	131	5.7	363

Table 6. **Yield and Characteristics of Gas Obtained in the Fischer Retort from Low-Sulphur Oil Shales of Various Deposits of the World (Shale Samples *10-19*)**

Indices	Investigated shale sample number (see Table 2)									
	10	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
Specific gas yield, m^3/t	19.0	31.0	20.2	32.9	42.0	34.1	28.4	43.9	30.5	36.2
Content of components, vol.%:										
CO_2	27.3	16.0	18.0	26.7	52.3	19.9	45.5	28.6	32.0	32.7
H_2S	5.3	0.9	8.7	9.4	0.0	5.5	0.7	4.4	0.7	0.7
H_2	24.3	38.1	40.7	25.7	27.4	14.5	11.4	12.3	44.6	29.4
CO	2.6	8.1	6.1	3.8	6.3	4.5	7.0	6.4	4.4	5.4
C_nH_{2n+2}	31.0	26.2	19.3	25.0	10.0	37.2	26.7	34.7	12.4	24.2
Including:										
CH_4	18.2	14.9	11.0	12.2	6.6	18.8	15.6	18.2	5.8	12.3
C_2H_6	7.2	6.9	4.7	7.0	1.8	10.5	6.5	9.1	3.4	6.3
C_3H_8	3.5	2.6	2.2	3.4	0.9	4.9	2.4	3.9	1.7	3.0
C_4H_{10}:										
n-butane	1.1	1.1	0.7	1.3	0.5	1.7	1.0	1.6	0.7	1.2
iso-butane	0.3	0.2	0.4	0.1	—	0.2	0.1	0.2	0.1	0.3
C_5H_{12}:										
n-pentane	0.6	0.5	0.3	0.9	0.2	1.1	0.7	1.0	0.5	0.7
iso-pentane	0.1	—	—	0.1	—	—	0.1	0.1	0.1	0.1
C_6H_{14}:										
n-hexane	—	—	—	—	—	—	0.3	0.6	0.1	0.3

Table 6. Yield and Characteristics of Gas Obtained in the Fischer Retort from Low-Sulphur Oil Shales of Various Deposits of the World (Shale Samples *10-19*) (end)

Indices	Investigated shale sample number (see Table 2)									
	10	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
C_nH_m	9.5	10.7	7.2	9.4	4.0	17.9	8.5	13.1	5.7	7.3
Including:										
C_2H_4	4.1	2.7	1.8	3.1	1.8	4.9	2.7	3.7	1.5	2.0
C_3H_6	2.6	3.1	3.1	3.1	1.0	5.4	2.9	4.4	1.8	2.6
C_4H_8:										
butene-1, *iso*-butene	1.7	1.8	1.3	1.6	1.0	3.8	1.2	2.2	1.1	1.3
trans-butene-2	0.2	0.5	0.5	0.4	—	0.5	0.4	0.6	0.3	0.3
cis-butene-2	0.2	1.7	0.5	0.3	—	0.3	0.3	0.5	0.2	0.2
C_5H_{10}:										
pentene-1	0.3	0.4	—	0.5	0.2	1.1	0.4	0.7	0.3	0.4
trans-pentene-2	}0.2	}0.5	—	0.2		}1.9	0.2	0.3	0.2	0.2
cis-pentene-2			—	—	—		0.1	0.1	—	—
C_6H_{12}:										
2-methylbutene-1	0.1	—	—	0.1	—	—	0.1	0.2	0.1	0.1
3-methylbutene-1	—	—	—	0.1	—		—	—	—	—
hexene-1	—	—	—	—	—	—	0.2	0.4	0.2	0.2
Not identified	0.1	—	—	—	—	0.5	0.2	0.5	0.2	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Calculated heating value, MJ/m^3:										
high	30.35	30.87	25.28	29.85	12.89	44.34	25.54	37.72	19.82	26.71
low	27.67	28.13	22.92	27.26	11.68	40.91	23.70	34.83	17.98	24.45
Density, kg/m^3	1.127	0.925	0.912	1.149	1.228	1.292	1.391	1.344	0.960	1.135
Content of H_2S, g/m^3	75	13	123	133	—	78	10	62	10	10

Table 7. **Heat Balance of Retorting Low-Sulphur Oil Shales from Various Deposits of the World in the Fischer Retort, %, and Sulphur Distribution between Retorting Products, % (Shale Samples *1-9*)**

Indices	Investigated shale sample number (see Table 1)								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Chemical heat of shale									
Shale oil	70.5	50.9	28.9	63.8	59.0	58.7	64.5	37.3	58.4
Gas	14.3	11.7	12.1	9.6	11.4	11.7	13.1	24.4	14.1
Gasoline, unregarded losses and analytical errors (by difference)	0.3	2.3	-2.6	1.0	1.0	1.1	-0.1	-0.3	-2.9
Semicoke	14.9	35.1	61.6	25.6	28.6	28.5	22.5	38.6	30.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total sulphur of shale									
Shale oil	9.6	7.1	1.7	9.4	8.7	10.2	11.0	3.4	5.3
Gas (in the form of H_2S)	39.0	28.0	—	6.2	3.5	20.8	17.0	3.2	41.5
Semicoke	55.4	64.5	89.1	80.5	87.5	67.7	59.5	84.2	57.5
Other species of sulphur in gas and analytical errors (by difference)	-4.0	0.4	9.2	3.9	0.3	1.3	12.5	9.2	-4.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 8. **Heat Balance of Retorting Low-Sulphur Oil Shales from Various Deposits of the World in the Fischer Retort, %, and Sulphur Distribution between Retorting Products, % (Shale Samples *10-19*)**

Indices	Investigated shale sample number (see Table 2)									
	10	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
Chemical heat of shale										
Shale oil	77.1	68.7	45.2	55.0	39.6	72.3	54.0	58.5	45.1	61.6
Gas	8.7	7.2	13.9	15.5	10.2	13.4	13.2	14.2	16.4	12.6
Gasoline, unregarded losses and analytical errors (by difference)	-0.7	4.9	5.3	-3.1	-2.5	1.3	-3.8	2.9	-2.4	0.7
Semicoke	14.9	19.2	35.6	32.6	52.7	13.0	36.6	24.4	40.9	25.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total sulphur of shale										
Shale oil	12.5	17.8	5.7	5.1	3.6	12.6	4.1	5.7	2.3	2.6
Gas (in the form of H_2S)	20.6	2.9	14.6	14.8	—	28.6	2.6	21.4	3.6	2.8
Semicoke	53.3	72.8	72.6	70.0	98.5	59.2	85.6	68.4	85.3	87.6
Other species of sulphur in gas and analytical errors (by difference)	13.6	6.5	7.1	10.1	-2.1	-0.4	7.7	4.5	8.8	7.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 9. **Yield and Characteristics of Shale Oils Obtained in the Experimental Retort from Low-Sulphur Oil Shales of Various Deposits of the World**

Indices	Investigated shale sample number (see Tables 1 and 2)										
	1	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*11-12*	*13*	*14*
Yield of shale oil, %:											
Plant yield (raw shale basis)	20.6	2.4	16.62	9.5	10.0	6.2	2.8	7.3	9.1	7.36	1.72
Yield of Fischer assay oil	99.5	50.0	86.4	88.0	60.0	71.0	59.2	71.2	78.3	90.3	36.5
Density at 20 °C, kg/m^3	988	936	916	936	908	931	913	952	910	897	891
Water, %	6.5	46.2	5.8	6.8	14.5	6.4	1.0	11.6	12.4	0.4	1.2
Entrained fines, %	0.50	2.98	0.92	0.85	0.80	0.49	0.46	0.65	0.27	0.06	0.04
Ash, %	0.24	0.72	0.11	0.50	0.10	0.13	0.10	0.06	0.14	0.04	0.003
Viscosity at 75 °C, $10^{-6} \cdot m^2/s$	11.4	5.3	19.6	8.1	5.2	5.6	6.06	9.96	7.07	5.91	3.64
Flash point, °C	65	77	52	60	84	32	112	44	101	125	52
Pour point, °C	-25	18	—	—	22	-8	30	28	27	30	25
Refraction index, n^{20}_D	1.549	1.483	1.512	1.470	1.517	1.518	1.516	1.501	1.512	1.510	1.496
Molecular mass	249	222	178	298	184	285	275	300	293	293	305
Phenolic compounds, %	26.1	3.5	1.9	2.1	3.7	4.3	1.9	0.5	0.8	1.4	1.6
Heating value (bomb calorimeter), MJ/kg	39.77	41.75	42.87	41.95	42.58	41.62	42.79	42.58	43.29	42.62	43.96
Initial boiling point, °C	116	185	153	158	135	100	199	165	200	183	148

Table 9. Yield and Characteristics of Shale Oils Obtained in the Experimental Retort from Low-Sulphur Oil Shales of Various Deposits of the World (end)

Indices	Investigated shale sample number (see Tables 1 and 2)										
	1	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*11-12*	*13*	*14*
Distillation, vol.%, at:											
160 °C	3	—	2	—	—	6	—	—	—	—	1
180 °C	4	—	7	1	2	8	—	1	—	—	2
200 °C	8	1	9	3	4	13	—	2	—	2	3
220 °C	12	4	15	4	6	20	2	5	3	4	7
240 °C	14	10	19	8	12	30	5	8	7	8	13
260 °C	18	20	24	13	17	39	10	14	13	14	20
280 °C	22	26	28	22	23	44	18	21	19	21	31
300 °C	26	36	35	28	29	51	26	28	26	27	39
320 °C	30	48	42	36	35	61	36	34	34	35	49
340 °C	35	54	52	43	43	76	44	43	41	43	64
360 °C	45	72	68	58	55	—	56	54	50	65	83
Elemental composition (dry basis), %:											
C	81.8	84.33	84.0	84.2	84.45	82.3	84.60	84.75	84.2	84.28	87.0
H	10.1	10.88	10.8	10.4	11.63	11.7	12.01	11.12	11.9	11.84	12.3
S	0.9	1.51	0.4	1.3	0.76	1.4	0.73	1.13	0.6	1.16	0.5
N	0.2	0.65	}4.8	}4.1	0.81	}4.6	0.80	1.50	}3.3	1.25	}0.2
O (by difference)	7.0	2.63			2.35		1.86	1.50		1.47	

Table 10. **Chemical Group Composition of Light-Middle Fractions of Shale Oil Obtained in the Experimental Retort from Low-Sulphur Oil Shales of Various Deposits, wt.%**

Compounds	Investigated shale sample number (see Tables 1 and 2)								
	1	*4*	*5*	*6*	*7*	*8*	*9*	*11-12*	*14*
Fraction IBP-200 °C									
Alkanes and cycloalkanes	23	31	25	22	32	23	28	18	40
Alkenes	48	37	27	32	36	33	40	35	28
Aromatic hydrocarbons	20	19	23	27	16	28	19	28	19
Neutral heteroatomic compounds	5	13	22	16	15	10	11	16	4
Phenols	4	—	3	3	1	6	2	3	9
Fraction yield	7.6	13.43	6.5	8.7	10.7	2.6	5.5	6.53	4.7
Fraction 200-300 °C									
Alkanes and cycloalkanes	13	32	24	24	26	28	26	25	43
Alkenes	27	19	17	20	30	24	20	21	17
Aromatic hydrocarbons	28	27	34	33	26	28	33	37	29
Neutral heteroatomic compounds	17	22	20	15	13	17	17	13	8
Phenols	15	—	5	8	5	3	4	4	3
Fraction yield	16.5	17.9	21.37	19.9	27.4	26.8	19.2	23.7	28.8
Fraction 300-350 °C									
Alkanes and cycloalkanes	3	27	26	36	8	27	25	35	45
Alkenes	7	8	7	7	8	13	9	5	9
Aromatic hydrocarbons	27	30	29	31	43	29	36	36	30
Neutral heteroatomic compounds	36	35	31	21	26	25	25	18	14
Phenols	27	—	7	5	15	6	5	6	2
Fraction yield	11.8	12.84	12.13	15.6	9.9	13.6	12.5	17.84	16.9
Fraction IBP-350 °C									
Alkanes and cycloalkanes	12	30	25	28	23	27	26	27	43
Alkenes	25	21	16	18	27	21	19	17	15
Aromatic hydrocarbons	26	26	30	31	27	28	32	36	28
Neutral heteroatomic compounds	21	23	24	17	17	19	19	15	10
Phenols	16	—	5	6	6	4	4	5	4
Fraction yield	35.9	44.17	40.0	44.2	48.0	43.0	37.2	48.07	50.4

Table 11. **Distribution of Sulphur between Products during Retorting Low-Sulphur Oil Shales from Various Deposits of the World, %**

Deposit (sample Nr.)	Shale oil		Percentage of sulphur transferred into			Content of total sulphur in shale, %	Share in total sulphur of shale, %		Sulphur in semi-coke, %	H_2S in gas, g/m³
	Density at 20 °C, kg/m³	Content of sulphur, %	semicoke	gas (H_2S)	oil		Organic S	Pyrite S		
The first group										
Anin (*14*)	913	0.50	98.5	—	3.6	0.67	23.9	76.1	0.75	—
Eckibastuse (*3*)	915	0.44	89.1	—	1.7	1.32	17.4	81.8	1.34	—
Maoming (*19*)	909	0.31	87.6	2.8	2.6	1.22	6.6	80.3	1.28	10
Ust-Kamenogorsk (*5*)	906	0.80	87.5	3.5	8.7	1.00	—	—	1.00	12
Stuart (*16*)	897	0.60	85.6	2.6	4.1	1.00	—	—	1.00	10
Fushun (*18*)	893	0.48	85.3	3.6	2.3	0.78	15.4	70.5	0.74	10
Gurkovo-Nikolayev (*8*)	878	0.46	84.2	3.2	3.4	0.38	18.4	81.6	0.40	6
Kenderlyck (*4*)	923	1.00	80.5	6.2	9.4	2.10	10.5	—	2.35	41
Paraiba valley oil shale (*11*)	910	1.00	72.8	2.9	17.8	1.28	44.5	43.0	1.30	43
The second group										
Paraiba valley oil shale (*12*)	920	2.30	72.6	14.6	5.7	1.60	55.6	33.7	1.30	123
Aleksinac (*13*)	908	1.75	70.0	14.8	5.1	2.78	8.3	89.9	2.29	133
Huadian (17)	899	0.43	68.4	21.4	5.7	1.20	—	—	1.10	62
Boltysh (*6*)	898	0.82	67.7	20.8	10.2	1.40	12.1	79.3	1.30	61
Ukhta (*2*)	975	0.60	64.5	28.0	7.1	0.39	—	—	0.30	71
Luban (*7*)	925	2.00	59.5	17.0	11.0	1.60	25.0	68.7	1.10	131
Mae Sot (*15*)	889	0.60	59.2	28.6	12.6	0.87	32.2	64.4	0.69	78
Breznik (*9*)	934	1.35	57.5	41.5	5.3	2.47	4.9	91.9	1.70	363
Green River (*10*)	927	0.84	53.3	20.6	12.5	0.65	43.1	53.8	0.40	75

Table 12. **Characteristics of Shale Oils Obtained by Semicoking Low-Sulphur Oil Shale from Various Deposits of the World under Different Conditions**

Indices	Heat carrier gas single flow through the retort bed		Contact of oil vapours with hot (500-600 °C) solid material		
	Experimental retort	Hot model of the retorting chamber of a heat carrier gas cross-flow retort [4]		Solid heat carrier units (SHC)	
				Bench-scale	SCH-500
Kukersite Estonian deposit					
Density at 20 °C, kg/m³	988	1000	1021	—	975
Molecular mass	249	278	251	—	220
Flash point, °C	65	—	—	—	9
Bulgaria Breznik deposit					
Density at 20 °C, kg/m³	952	960	980	—	—
Molecular mass	300	303	218	—	—
Pour point, °C	28	29	16	—	—
Bulgaria Gurkovo-Nikolayev deposit					
Density at 20 °C, kg/m³	913	—	—	—	877
Molecular mass	275	—	—	—	169
Pour point, °C	30	—	—	—	20
Flash point, °C	112	—	—	—	20
Yugoslavia Aleksinac deposit					
Density at 20 °C, kg/m³	897	—	—	899	—
Molecular mass	293	—	—	212	—
Pour point, °C	30	—	—	15	—
Morocco Timahdit deposit					
Density at 20 °C, kg/m³	981	—	—	959	—
Molecular mass	262	—	—	180	—
Pour point, °C	0	—	—	-21	—
Flash point, °C	88	—	—	6	—

Low-sulphur shales yield retort gas which contains only a little hydrogen sulphide - in most cases no more than 50-100 g/m^3 (Tables 5 and 6). The corresponding value for high-sulphur shales is 300-500 g/m^3 [1]. Considering the sulphur present in oil shale, up to 10 % (with some exceptions) is transferred to oil (Tables 7 and 8), and the main portion of it remains in the semicoke.

In order to make a more thorough study of the physical and chemical properties of retort oil (which is the main product of oil shale thermal destruction) some of the samples have been processed in an experimental retort with semicoke gasification. The retort had a throughput of 500-1000 kg/day [2, 3]. As seen from Table 9, processing of low-sulphur shales yields shale oil which comprises from 50-80 % of the Fischer assay oil, dropping to 36 % only in the case of Romanian shales from the Anin deposit (Banata province).

Retort oils obtained in such a fashion are characterized by relatively low density, high solidification temperature, and very low content of oxygen and, consequently, of phenols, too. Compared to high-sulphur oils, low-sulphur ones contain more paraffins and olefins and less aromatic hydrocarbons (Table 10).

Low-sulphur oil shales which yield paraffinic retort oil, as investigated by the authors, may be divided into two groups (Table 11) rather precisely. All paraffinic oils are characterized by low density as already mentioned above (about 900 kg/m^3). The first group comprises the oil shales for which retorting results in having 70-100 % of the sulphur remain in the semicoke, and only 5-6 % is transferred into the gas (the H_2S content of gas is low and does not exceed 40 g/m^3). The second group comprises the oil shales for which 50-70 % of the original sulphur remains in the semicoke and the portion converted into gaseous components is significantly higher (14-40 %). The H_2S content of this gas is up to 60-135 g/m^3.

Neither the form of the sulphur nor the proportion of the different forms seem to influence its distribution between retorting products (see data in Table 11). Some other factors are probably impacting on those processes.

Solidification of paraffinic oils (i.e. products of thermal processing of oil shale samples under study) causes serious troubles during retorting. Therefore, it is extremely expedient to find possible routes for obtaining oils with lower values for oil solidification point. As seen from Table 12, this is attainable when processing oil shale in units with a solid heat carrier or using the reverse process in vertical retorts, i.e. repeated contact of vapour and gas mixture with heated semicoke (up to 500-600 °C) [4].

Conclusions

Oil shales which form low-sulphur paraffinic oil upon retorting have been studied. The total sulphur content of the studied samples is within the range 0.38-2.78 % and the organic sulphur content varies between 0.07 and 0.89 %. During the oil shale processing in Fischer retorts, sulphur is transferred to the products in the following proportions: 1.7-17.8 % to the oil, traces-41.5 % to the gas (as H_2S), and 53.3-98.5 % to the semicoke. The oils obtained from the studied oil shales have decreased values for density (about 900 kg/m^3). The tested shales produce light-middle fractions which contain less aromatic hydrocarbons and more paraffins and olefins than oils obtained during the retorting of high-sulphur oil shales. Paraffinic oils contain only small amounts of phenolic compounds - 2-4 %.

It is suitable to conditionally divide the oil shales studied into two groups. The first group is comprised of the oil shales for which 70-100 % of the total sulphur remains in the semicoke during retorting, and the portion of sulphur transferred into the gas (as H_2S) is very negligible - below 5-6 % (the H_2S content of this gas does not exceed 40 g/m^3).

The second group is comprised of the oil shales for which 50-70 % of the total sulphur remains in the semicoke upon retorting, and 14-40 % is transferred into the gas (the H_2S content of this gas rises up to 60-135 g/m^3). The form of sulphur present in oil shale and the proportion of different forms do not affect its distribution between the products; some other factors seem to be responsible for this separation.

The world-wide experience of thermal processing of low-sulphur shales which yield paraffinic oil upon retorting is very large. High values for solidification point (25-30 °C) of the produced oils very often complicate their transport and further chemical treatment. To avoid these problems, one should process those shales in retorting units with a solid heat carrier or in vertical retorts with repeated contact of oil vapours with the semicoke.

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REFERENCES

1. *Yefimov V. M., Doilov S. K., Pulemyotov I.* Research and experimental processing of high-sulphur oil shales // Oil Shale. 1995. V. 12, No. 4. P. 317-340.

2. *Yefimov V. M., Piik E. E.* About the characteristics of oil shales from some deposits // Khimiya tvyordogo topliva (Chemistry of solid fuel). 1967. No. 6. P. 65-72 [in Russian].

3. *Lööper R. A., Velbaum M. A., Paaps G. A.* The retorting of Volga-basin shales - special features of the process and primary products. Liquid products of oil shale processing as raw for chemical industry // Transactions of Oil Shale Research Institute. 1986. No. 24. P. 78-90 [in Russian].

4. *Yefimov V. M., Kundel H. A., Doilov S. K.* Effect of the composition of gaseous heat carrier on the yield of benzopyren at oil shale retorting // Khimiya tvyordogo topliva (Chemistry of solid fuel). 1993. No. 6. P. 60-65 [in Russian].

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