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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<sup>3</sup>. 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<sup>3</sup>) 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.

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Indices	Estonia,	Russia		Kazakhstan	off ) icat;	Ukraine,	Byelorus,	Bulgaria	
ante più let più let vià let vià ciativa ciativa dia più le ca he ca	Estonian (kukersite)	Ukhta	Eckibastuse	Eckibastuse Kenderlyck Ust-Kame	Ust-Kame- nogorsk	Boltysh	Luban	Gurkovo- Nikolayev	Breznik
	Investigated	Investigated shale sample number	e number		10 10 10 10 10 10				
reality and a second and a second a	I	2	3	4	5	6	7	80	6
Fischer assay product yield (shale sample	ple 200 g), %:								
Shale oil	1	1	3.9	1	1	1	1	2.8	1
Pyrogenetic water	I	1	1.8	1	l	1	1	3.2	I
Semicoke	1	1	86.5	1	1	1	1	91.4	1
Gas and losses (by difference)	100	I	7.8	I	1	1	1	2.6	1
Fischer assay oil of organic matter, %	1	I	15.5	1	T	1	1	20.7	1
Ash composition, %:			-		10				nii
SiO <sub>2</sub>	28.5	66.4	60.3	57.4	57.2	65.8	36.8	59.9	40.0
Fe <sub>2</sub> O <sub>3</sub>	5.5	1.5	14.0	6.3	1246	8.6	5.8	8.3	7.5
Al <sub>2</sub> O <sub>3</sub>	6.7	4.5	17.6	14.0	ر ۲۰۰۰	17.6	10.2	19.1	14.0
K <sub>2</sub> O	2.1	110	1.2	1.1	177	2.6	1	1	1.9
Na <sub>2</sub> O	0.4	71.0	0.6	1.6	7.1	1.7	I	1	6.0
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 <sub>3</sub>	6.5	1.6	0.2	3.3	2.5	Ĩ	5.0	1.6	8.8
Total	98.9	99.1	97.3	98.4	99.3	6.66	0.06	99.3	100.0

Indices	Estonia	Russia	5.0	Kazakhstan	10	Ilbraina	Dirolomo	Bulgaria	28
	Estonian (kukersite)	Ukhta	Eckibastuse	Kenderlyck		Boltysh	Luban Luban	Gurkovo-	Breznik
	Investigated	Investigated shale sample number	number	Quite 1	nogorsk	0 38		Nikolayev	0.0
	1	2	3	4	5	6	7	8	6
Moisture of oil shale tested in experimental retort, %	5.1	1 35 1	7.3	2.8	1.0	4.4	1.2	10.7	0.7
Carbon dioxide $(CO_2)^d$ Ash $A^d$	20.8	13.0	4.0	5.5 57.4	3.3	0.5	17.0	4.3	14.9
Organic matter*	33.0	11.5	25.1	37.1	22.0	42.0	16.0	13.5	00.00
Total sulphur $S_t^d$ Including	1.90	0.39	1.32	2.1	1.0	1.40	1.6	0.38	2.47
Sulphate	0.05	-	0.01	1	I	0.12	0.1	1	0.08
Pyrite	1.30	1	1.08		1	1.11	1.1	0.31	2.27
Urganic (by difference) Heating value (bomb calorimeter),	cc.0	sparte santh	0.23	0.64	1	0.17	0.4	0.07	0.12
	12.43	3.56	7.58	12.94	7.91	12.73	5.65	3.27	7.12
product yield (standard	retort), %:						neib l		
	21.8	4.6	5.2	19.8	10.9	17.5	8.8	5.3	9.7
c water	2.4	0.4	2.1	2.1	0.5	3.9	1.2	1.4	2.4
	70.2	93.3	87.8	71.9	83.3	72.9	86.6	90.7	83.5
-	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	495	417	55.0	393	571

Low-Sulphur Oil Shale Research and Experimental Processing

Indices	USA.	Brazil, Par	Brazil, Paraiba valley	Yugoslavia,	Roumania,	Thailand,	Australia.	China		
	Green	oil shale		Aleksinac	Anin	Mae Sot	Stuart			
	River	papery	lump sized	R. 10%				Hua- dian	Fu- shun	Mao- ming
	Investigate	Investigated shale sample number	ple number	0.0						
	10	11	12	13	14	15	16	17	18	19
Moisture of oil shale tested in evnerimental retort %	1991 1	3	3.7	35	15		1	1	1	-
Content (dry basis) %.	33.0		1.22		0.55		161		12	180
Carbon dioxide $(CO_2)^d_M$	17.3	0.2	0.3	9.9	3.8	10.5	1.8	5.4	3.9	1.0
Ash A <sup>d</sup>	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 $S_t^d$	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	1	0.03	1	1	0.11	0.16
Pyrite	0.35	0.55	0.54	2.50	0.51	0.56	1	1	0.55	0.98
Organic (by difference)	0.28	0.57	0.89	0.23	0.16	0.28	I	1	0.12	0.08
Heating value (bomb calorimeter),	17	N. S.		1.1.	1 million on				-	1
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 r	retort), %:									- A - C
	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 assav oil of organic matter, %	67.4	535	23.0	46.7	0.00	62.8	7 7 7	40.4	0 30	0.00

<i>Hable 2.</i> Froperties of Low-Supplier Oil Shares from Various Deposits of the World (Share Samples 19-12) (Shu)	r Oil Shale	es from Var	ious Depos	sits of the W	'orld (Shale	Samples 1	10-19) (end)	64	0.5-01	18 82
Indices	USA, Green	Brazil, Paraiba valley oil shale	aiba valley	Yugoslavia, Aleksinac	Roumania, Anin	Thailand, Mae Sot	Australia, Stuart	China	C R	N.S.
	River	papery	lump sized		116 22		1	Hua- dian	Fu- shun	Mao- ming
	Investigate	Investigated shale sample number	ple number	The second		0.44	1 82 1		NS 30-1-1	132
	10	11	12	13	14	15	16	17	18	19
Ash composition, %:									- ON STEN	12 N
SiO,	44.3	55.0	58.0	53.9	50.8	46.2	65.8	53.1	60.5	58.1
Fe <sub>2</sub> Õ <sub>3</sub>	5.5	10.2	1275	9.5	4.3	8.2	8.0	7.8	12.0	9.8
Al <sub>2</sub> O <sub>3</sub>	12.8	26.6	C.7C2	13.4	32.1	12.7	14.7	16.8	18.1	22.6
K20	2.8	13.7	129	1.5	1	173	1	1.6	3.0	154
Na20	3.5	7.7	] 4.7	1.3	-		1	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 <sub>3</sub>	2.4	1.1	1.3	7.9	+	2.4	0.8	3.8	9.0	0.3
	99.2	6.66	99.5	99.2	89.7**	100.0	93.8	98.3	100.0	9.66

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

Indices	Investigated	Investigated shale sample number (see Table 1)	e number (se	: Table 1)					
1410 T	I	2	3	4	5	9	7	~	6
To obtain the semicoking products the Fischer retort was applied with oil shale sample, g	20	20	200	20	20	20	20	200	20
			Shal	e 0					
Density at 20 °C, kg/m <sup>3</sup>	968	975	915	923	906	898	925	878	934
Molecular mass	276	- 0	188	-	1	1	294	1	4
Heating value (bomb calorimeter),									1 40.1
MJ/kg Flamental commosition (Arry horie) 02.	40.19	39.35	42.08	41.66	42.83	42.70	41.45	43.54	42.83
	83.12	83.1	85.30	85.0	84.5	84.66	84.4	86.78	84.57
H	10.13	9.6	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	וחבר	1.75
O (by difference)	5.71	4.6	2.29	2.2	1.1	1.93	1.8	٥٢.٥٤	1.24
During the filments of			Semi	icoke					
Content (dry basis), %:									
Carbon dioxide $(CO_2)^d_M$	28.1	13.6	6.0	6.9	2.8	0.3	19.4	4.7	17.1
Ash A <sup>d</sup>	64.8	82.6	79.6	80.1	89.3	81.6	76.4	88.7	76.2
Carbon C <sup>d</sup>	7.6	3.5	14.3	10.2	6.4	10.5	4.2	4.0	6.5
Total sulphur $S_t^d$	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	Investigate	d shale san	Investigated shale sample number (see Table 2)	(see Table	2)					
minution honores	10	11	12	13	14	15	16	17	18	19
To obtain the semicoking products the			NN DY	an an		9 3	27 11	1 5 1	1.0.1	1.0
Fischer retort was applied with oil shale sample, g	20	20	20	200	20	50	50	50	50	50
			S	Shale Oil			·····			·····
Density at 20 °C, kg/m <sup>3</sup>	927	910	920	908	913	889	897	899	893	606
Molecular mass	233	2	1	230	1	278	234	236	+	1
Heating value (bomb calorimeter),			1.1	9-T1 - 11-	0		5	112	103	621
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), %:								303	5.45	2.49
C	83.89	85.7	85.5	83.15	87.0	84.14	83.2	80.19	85.37	83.04
Η	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	09.0	0.6	0.43	0.48	0.31
N	1.30	313	306	· 1.21	102	1.81	0.7	0.10	1.32	0.61
O (by difference)	2.10	2t [	2.2	2.58	7.5	1.41	4.0	7.86	0.63	4.03
2 martin flammer 1			S	Semicoke						300
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 <sup>d</sup>	2.7	9.8	4.5	5.3	8.2	6.0	7.6	9.6	4.9	6.8
Total sulphur $S_t^d$	0.4	1.3	1.3	2.29	0.75	0.69	1.0	1.1	0.74	1.28
Heating value (bomb calorimeter),		MCGH051bon	History 1	Stori Rola		A HO THE	Riba di An	tions rich	Child -	
MJ/kg	0.92	3.56	1.46	2.43	3.18	1.97	2.34	3.81	1.67	2.39

of the World (Shale Samples 1-9)		13	C.# 1	13.30	1.2 M	0.99	1 1	PT O	
Indices	Investigated	shale sampl	Investigated shale sample number (see Table	e Table 1)		6 0.er	08	88.0	83.3
Countral (11) Judger 8.	I	2	3	4	5	6	7	8	6
Specific gas yield, m <sup>3</sup> /t	38.2	17.0	38.1	35.2	33.1	51.0	22.0	22.7	30.0
Content of components, vol. %:	0	11.2	Jabal	- 2.2802]	the set	A THE INC	10 - Person	6 1 - 1 0.63	\$0.00 - T
CO2	23.7	24.2	50.5	19.5	18.8	25.3	26.7	17.5	13.5
H <sub>2</sub> S	14.6	5.0	0.0	2.8	0.8	4.3	9.3	0.4	25.7
H <sub>2</sub>	5.3	34.9	12.1	25.0	44.5	24.4	23.2	40.7	20.5
CO min contraction for the manual	4.2	5.0	2.1	7.7	9.9	8.9	2.2	2.5	3.4
C <sub>n</sub> H <sub>2n+2</sub>	35.6	26.6	28.5	34.3	21.0	28.4	26.3	24.3	29.3
Including:									1 12:30
CH4	14.7	17.2	18.1	17.2	9.7	13.3	11.2	10.5	15.9
C <sub>2</sub> H <sub>6</sub>	8.6	6.4	5.9	9.4	6.4	10.1	7.3	7.4	6.4
C <sub>3</sub> H <sub>8</sub>	5.6	2.2	2.4	4.7	2.8	3.0	4.7	3.5	4.9
C4H <sub>10</sub> :									
<i>n</i> -butane	2.0	9.0	0.0	2.0	1.4	1.3	1.9	1.3	1.4
iso-butane	6.0	0.1	0.1	0.1	0.1	1	1	0.3	SI
C <sub>5</sub> H <sub>12</sub> : Common the monthle the									
<i>n</i> -pentane	3.0	0.1	0.6	0.0	0.6	0.7	1.2	1.0	0.7
iso-pentane	0.8	1	0.1		-	F	1	0.3	1
C <sub>6</sub> H <sub>14</sub> :						and the literation			
<i>n</i> -hexane	Singl-Synd	alal -sam	0.4	(S-lables)	1	1	1	1	

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Table 5 Yield and Characteristics of Gas\* Obtained in the Fischer Retort from Low-Sulphur Oil Shales of Various Denosits

Indices	Investigated	i shale samp	Investigated shale sample number (see Table 1	e Table 1)					
v-beuteus C <sup>2</sup> H <sup>13</sup>	10.6	2	3	4	5	6 20 02	7	8	9 00
C <sub>n</sub> H <sub>m</sub> Individua-	16.6	4.3	6.5	10.7	8.3	8.7	12.3	14.6	7.6
$C_{2}H_{4}$	3.3	1.5	1.8	2.9	2.4	2.9	4.4	4.8	1.7
C <sub>3</sub> H <sub>6</sub>	6.1	1.8	2.2	4.2	2.9	3.7	3.9	4.6	3.1
C <sub>4</sub> H <sub>8</sub> : hurtene-1 iso-hurtene	33	0.6	0.0	1 8		10 201	10	1 19	26
trans-butene-2	0.8	0.1	0.4		0.3	0.3	0.4	0.7	<u>]</u>
cis-butene-2	0.5	0.2	0.3	0.4	1	0.6	0.2	0.3	1
C <sub>5</sub> H <sub>10</sub> :									
pentene-1	2.6	0.1	0.3	0.7	0.6	0.2	1.3	6.0	0.3
trans-pentene-2	1	1	0.1			1 0012	I	0.1	Ĩ
cis-pentene-2	-2X	1				10001	10.91	1.0	The second
C <sub>6</sub> H <sub>12</sub> :									
2-methylbutene-1	1900 - 100e1	- 0.14	0.1 3	281 - 42	- 34.1	-5804	1	0.2	E
3-methylbutene-1	1	1	0.1	1	-	1	1	0.1	1
hexene-1	1	1	0.3	1	3	12-0.2	112-0.4	CU- 81	- 01
Not identified	1 martine	1	0.3	L	1	1 02	1	I	1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Calculated heating value, MJ/m <sup>3</sup> :									
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 <sup>3</sup>	1.481	0.945	1.394	1.099	0.891	1.117	1.205	606.0	1.140
Content of H <sub>3</sub> S. g/m <sup>3</sup>	206	11	1	41	17	61	131	57	262

	of the World (Shale Samples 10-19)									
Indices	Investigated	I shale sam	Investigated shale sample number (see Table	(see Table 2)		100.0	100.0	100.0	0.001	1000
	10	11	12	13	14	15	16	17	18	19
Specific gas yield, m <sup>3</sup> /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.%:	27.3	16.0	1 18.0	26.7	52.3	19.9	45.5	28.6	32.0	32.7
ScH Sch	5.3	6.0	8.7	9.4	0.0	5.5	0.7	4.4	0.7	0.7
H,	24.3	38.1	40.7	25.7	27.4	14.5	11.4	12.3	44.6	29.4
CÔ	2.6	8.1	6.1	3.8	6.3	4.5	7.0	6.4	4.4	5.4
$C_nH_{2n+2}$ Including:	31.0	26.2	19.3	25.0	10.0	37.2	26.7	34.7	12.4	24.2
CH4	18.2	14.9	11.0	12.2	6.6	18.8	15.6	18.2	5.8	12.3
C <sub>2</sub> H <sub>6</sub>	7.2	6.9	4.7	7.0	1.8	10.5	6.5	9.1	3.4	6.3
C <sub>3</sub> H <sub>8</sub>	3.5	2.6	2.2	3.4	6.0	4.9	2.4	3.9	1.7	3.0
C4H10:	. 33	_		1.8.1				1.5	1.8	Y.I.
n-butane	1.1	1.1	0.7	1.3	0.5	1.7	1.0	1.6	0.1	1.2
iso-butane	0.3	0.2	0.4	0.1	1	0.2	0.1	0.2	0.1	0.3
C <sub>5</sub> H <sub>12</sub> :			12			-	-		-	
<i>n</i> -pentane	9.0	0.5	0.3	6.0	0.2	1.1	0.7	1.0	0.5	0.7
iso-pentane	0.1		-	0.1	1	1	0.1	0.1	0.1	0.1
C <sub>6</sub> H <sub>14</sub> :										-
n-hevane	1	1	-				03	0 0	0	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	I shale samp	le number (	Investigated shale sample number (see Table 2)						
outer and the sources was a substration of the source of t	10	11	12	13	14	15	16	17	18	61
C <sub>n</sub> H <sub>m</sub>	9.5	10.7	7.2	9.4	4.0	17.9	8.5	13.1	5.7	7.3
Including: C <sub>2</sub> H <sub>4</sub> C <sub>5</sub> H <sub>2</sub>	4.1 2.6	2.7	1.8	3.1	1.8	4.9	2.7	3.7	1.5	2.0
CAHe:						-	-	-	2.4	
butene-1, <i>iso</i> -butene	1.7	1.8	1.3	1.6	1.0	3.8	1.2	2.2	1.1 00	1.3
trans-butene-2	0.2	0.5	0.5	0.4	1	0.5	0.4	0.6	0.3	0.3
cis-butene-2	0.2	1.7	0.5	0.3	1	0.3	0.3	0.5	0.2	0.2
C <sub>5</sub> H <sub>10</sub> :										
pentene-1	0.3	0.4	1	0.5	0.2	1.1	0.4	0.7	0.3	0.4
trans-pentene-2	10.2	305	1	0.2	1	319	0.2	0.3	0.2	0.2
cis-pentene-2	10.5	2.2		1	T	/··· [	0.1	0.1	1	
C <sub>6</sub> H <sub>12</sub> :			as Itro	p n ult o I	ab a u s					
2-methylbutene-1	0.1	1	1 3	0.1	1	1	0.1	0.2	0.1	0.1
3-methylbutene-1	1	1	1	0.1	1	1	E	1	1	1
hexene-1	1	1	oble Thomas	(see Table	1	1	0.2	0.4	0.2	0.2
Not identified	0.1			1	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/m3:										100.0
high	30.35	30.87	25.28	29.85	12.89	44.34	25.54	37.72	19.82	26.71
Iow	27.67	28.13	22.92	27.26	11.68	40.91	23.70	34.83	17.98	24.45
Density, kg/m <sup>3</sup>	1.127	0.925	0.912	1.149	1.228	1.292	1.391	1.344	0.960	1.135
Content of H <sub>2</sub> S g/m <sup>3</sup>	75	13	123	133	1	78	10	69	10	10

	Low-Sulp	hur Oil Sha	ules from Va	rious Deposit	s of the V	Vorld i	n the Fisc	her Retort	, %,	
and Sulphur Distribution between R	tetorting F	Retorting Products, % (Shale Samples 1-9)	(Shale Sam	ples 1-9)						
Indices	Investigate	Investigated shale sample number (see Table 1)	le number (se	e Table 1)	2		16 03	10 0.4	20 31	20 21
	1001	2	ŝ	4	5	9	100	7	8	6
Coordenada-2	22.3. H	Ch	emical h	Chemical heat of shale	le	2.0	1.01	1.0%	0707	rts li
Shale oil	70.5	50.9	28.9	63.8	59.0	-	58.7	64.5	37.3	58.4
Gasoline unregarded losses and	14.5	11./	1.2.1	0.6	11.4		11./	1.01	24.4	14.1
analytical errors (by difference)	0.3	2.3	-2.6	1.0	1.0	01	1.1 03	-0.1	-0.3	-2.9
Semicoke	0 14.9	35.1	61.6	25.6	28.6	2.0	28.5 0 4	22.5	38.6	30.4
Total	100.0	100.0	100.0	100.0	100.0	-	0.00	100.0	100.0	100.0
		Total	tal sulphur	ur of shale	e					
Shale oil	9.6	5 2.1	1.7	9.4	8.7	4.4	10.2	11.0	3.4	5.3
Gas (in the form of H <sub>2</sub> S)	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	123	67.7	59.5	84.2	57.5
Other species of sulphur in gas and	01	¥ U	0	2.0	0.2		1 2	2 61	0.0	5 Vi 1
					C.D		+			C++
Total	100.0	100.0	100.0	100.0	100.0	1	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)	tow-Sul	phur Oil S Products,	Shales from % (Shale S	Various De amples 10-	posits of t 19)	he World in	1 the Fisch	er Retort,	%	
Pathone contonner of in	artisethd a	sale salut	multiple (198	Tablet 1 st	d 21 45	C.1	0.0	0.0	0.1	0.1
Indices	Investigate	ed shale san	Investigated shale sample number (see Table 2)	(see Table 2	7.582	825	9,000	111.293	1,503	1 1202
Betration to tex war	10	11	12	13	14	<i>IS</i> - 30	16	17 50	18 30	19
Elast agginget.		0	Chemical	heat of	shale	00.0	- the contract	101	701	ica
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		-	0		200	2	0.11	1.4.4	10.0	
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
Xield of shake oil, %;			Total sulphur	of	shale					45
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 <sub>2</sub> S)	20.6	2.9	14.6	14.8	1	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		aldunia ata	Winnper (sog	(Tabled 1 stra	123 82	84.6	0 11 84.7	1 84.2	84.28	810
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
A DESCRIPTION OF A DESC	of Principa	Color Parkstern	Contractions and and and	Characteristics and the	Concerns of the	AND IN MARK SHARE	White white	C. C. Constanting		

Low-Sulphur Oil Shale Research and Experimental Processing

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Table 9. Yield and Ch	of Various Denosits of the World
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or various meposits of the world	DI										
Indices Investigated shale sample number (see Tables 1 and	Investigate	d shale sar	nple numbe	r (see Tabl	es 1 and 2)		10	-	2.04	6.6	
Cast (in the term of H <sup>3</sup> g)	I	3	4	5	9	7	8	9	11-12	13	14
Yield of shale oil, %:		2	10101	RELDER	TO TO TO	-					
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	60.09	71.0	59.2	71.2	78.3	90.3	36.5
Density at 20 °C, kg/m <sup>3</sup>	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 <sup>-6</sup> ·m <sup>2</sup> /s	11.4	5.3	19.6	8.1	5.2	5.6	6.06	96.6	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	+	T	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	Cat Thereat P	inft radau	and he find	into team	Action of	0.0				25	2.4.3
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

Indices Mere	Investigat	'estigated shale san	nple numb	er (see Tabi	sample number (see Tables 1 and 2)						
	1	3	4	5	6	7	80	6	11-12	13	14
Distillation, vol.%, at:		7	00	Theafter	A LOSE P		E1			01	10 1
160 °C	3	0.50	2	1	1	9	1	1	1	1	1
180 °C	4 (		2	1	2	8	1 12		1	1 '	5
200 °C	× 5	-	9		4 4	13	1 0	2 4	6	2 4	2) L
240 °C	71	+ -	01	* ~	10	30	1 5	n œ	0 5	+ ∝	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	1	56	54	50	65	83
Elemental composition (dry basis), %	is), %:	481-75	1 0050	2748		02	34				
C	81.8	84.33	84.0	84.2	84.45	82.3	84.60	84.75	84.2	84.28	87.0
Н	10.1	10.88	10.8	10.4	11.63	11.7	12.01	11.12	11.9	11.84	12.3
S	6.0	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
0 (by difference)	7.0	2.63	and ble unit	1 002 (200 I	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.%

4.7 28.8 6.91 17 45 9 30 19 19 19 43 15 28 10 50. 43 30 00 15 4 14 53 84 23.7 10 17. 18 35 28 16 3 225 221 337 337 13 36 17 36 15 48. 35 9 27 11-12 2.5 37.2 12.5 40 61 26 233 333 17 .61 25 6 36 25 26 19 19 4 0 26.8 43.0 2.6 13.6 28 24 17 21 21 28 19 233 28 10 10 27 13 29 25 9 4 00 43 26 15 32 36 16 10 26 26 13 27. 00 10 23 27 17 48. 0 50 Investigated shale sample number (see Tables I and 2) 300 350 P-200 300-350 15.6 19.9 44.2 00 24 220 233 333 15 36 28 18 31 9 21 17 31 200d IB B 9 raction action 12.13 Fraction ction 40.0 21.37 6.5 223 223 223 17 34 26 31 16 30 24 25 5 LL L 13.43 12.84 44.17 6.11 31 337 19 13 32 19 22 11 27 8 30 35 30 21 26 23 4 7.6 16.5 11.8 35.9 23 20 5 12 25 26 21 13 27 17 15 27 27 27 16 4 Neutral heteroatomic compounds Neutral heteroatomic compounds Neutral heteroatomic compounds Neutral heteroatomic compounds Alkanes and cycloalkanes Alkanes and cycloalkanes Alkanes and cycloalkanes Alkanes and cycloalkanes Aromatic hydrocarbons Aromatic hydrocarbons Aromatic hydrocarbons Aromatic hydrocarbons Fraction yield Fraction vield Fraction yield Fraction yield Compounds Alkenes Phenols Alkenes Phenols Alkenes Phenols Alkenes Phenols

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Deposit (sample Nr.)	Shale oil		Percentage into	Percentage of sulphur transferred into	ransferred	Content of total	Share in total sulphur of shale, %	tal sulphur	Sulphur in semi-	H <sub>2</sub> S in gas, g/m <sup>3</sup>
Worksonier u Deurgia ar y Nicita ar y Libert bonuci	Density at 20 °C, kg/m <sup>3</sup>	Content of sulphur, %	semicoke	gas (H <sub>2</sub> S)	oil	sulphur in shale, %	Organic S	Pyrite S	coke, %	- in mos onding v the sulp
Politzbolist	irat ler tek	of nce mi		The first	group		ly ce d	ine asi		
Anin (14)	913	0.50	98.5	1	3.6	0.67	23.9	76.1	0.75	- 00 P
Eckibastuse (3)	915	0.44	89.1		1.7	1.32	17.4	81.8	1.34	- 37.80
Maoming (19)	606	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	-16 - B	1	1.00	12
Stuart (16)	897	0.60	85.6	2.6	4.1	1.00	518 - 812	1	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	9
Kenderlyck (4)	923	1.00	80.5	6.2	9.4	2.10	10.5	1	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
			T	he secon	d group					
Paraiba vallev 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	A Doug	1	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	1	-	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	6.16	1.70	363
Green River (10)	729	0.84	53.3	20.6	12.5	0.65	43.1	53.8	0 40	75

Indices	Heat carrier gas single flow through the retort bed	gle flow through	Contact of o material	Contact of oil vapours with hot (500-600 °C) solid material	h hot (500-6	00 °C) solid	2.8
	Experimental	Hot model of the retorting chamber of Solid heat carrier units (SHC)	retorting chan	iber of Solid	heat carrier	units (SHC)	50
	2 22	a heat carrier gas cross-flow retort [4]	cross-flow reto	irt [4] Bencl	Bench-scale	SCH-500	
	Kukersite	site Estonian	an deposit	t	1 1 19		
Density at 20 °C, kg/m <sup>3</sup> Molecular mass	988 249 65	1000 278	251			975 220	
	Bulgaria	ria Breznik	deposit	24		-	
Density at 20 °C, kg/m <sup>3</sup> Molecular mass	952		980 218 218	2	11	+ 1	
Pour point, °C	28	29	16	-	1		
	Bulgari	а	Gurkovo-Nikolayev	ev deposit	it		
Density at 20 °C, kg/m <sup>3</sup> Molecular mass	913	1.1		23		877	
Pour point, °C	30	R toon to			1	20	
ash point, °C	112	-	-		1	20	
	Yugos	Yugoslavia Aleksinac	inac deposit	sit			
Density at 20 °C, kg/m <sup>3</sup> Molecular mass	897 293		13	trike 2 LAUR	899 212		
Pour point, °C	30				15	1	
	Morocco	cco Timahdit	it deposit				
Density at 20 °C, kg/m <sup>3</sup>	981			nine la brinning	959	1	
Molecular mass Pour point. °C	262 0		Í I		-21		
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V. Yefimov et al.

Low-sulphur shales yield retort gas which contains only a little hydrogen sulphide - in most cases no more than 50-100 g/m<sup>3</sup> (Tables 5 and 6). The corresponding value for high-sulphur shales is 300-500 g/m<sup>3</sup> [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<sup>3</sup>). 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<sub>2</sub>S content of gas is low and does not exceed 40 g/m<sup>3</sup>). 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<sub>2</sub>S content of this gas is up to 60-135 g/m<sup>3</sup>.

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  $^{\circ}$ 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<sub>2</sub>S), 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<sup>3</sup>). 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<sup>3</sup>).

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<sub>2</sub>S content of this gas rises up to 60-135 g/m<sup>3</sup>). 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  $^{\circ}$ 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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