

LIQUID FUEL FROM OIL SHALES BY
HYDROGENATION AND AQUEOUS CONVERSION

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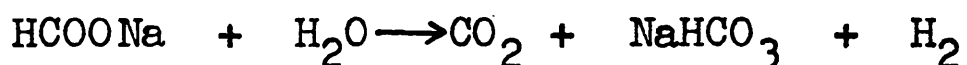
ABSTRACT

Oil shales from Lower Ordovician up to Eocene (organic content 15-60%) from different deposits of the USSR and other countries, were subjected to autoclaving by using hydrogenation and aqueous conversion. On hydrogenation the oil yield increases by a factor of 1,5-2 in comparison with semi-coking, by aqueous conversion different quantities of oil are obtained depending upon the nature of organic matter and mineral part. The study of high-sulfur shales (S content 5-11%), where nitrogen and oxygen content is high as well, showed that by hydrogenation the sulfur content decreases by a factor of about 2-3 in comparison with semi-coking oil. In the processes of thermal destruction under supercritical conditions ($>370^{\circ}$) water rapidly decomposes the organic matter of shales, the process being accelerated by addition of alkali to water. On conversion of some Lower Paleozoic shales substantial amounts of ketones are formed due to the decomposition of phenolic structures, particularly in the case of the Estonian kukersite shale.

Oil shales from different deposits and of different geological age differ in organic content and elemental composition, as well as heteroelement content, particular-

ly sulfur. In high-sulfur shales its concentration (S_t) amounts up to 9%. To all oil shale types is common the high hydrogen content (7-12%) of organic matter. Table 1 lists some of the shales investigated, presents their geological age, organic content and elemental composition.

The thermal destruction of mineral-rich oil shales yields volatile compounds easily separable from the solid residue. Semi-coking was carried out in a Fisher retort, but hydrogenation, conversion in water (in alkali medium) and liquefaction were performed in a 0,5l autoclave at 370° - 380° C for 3 hr. In hydrogenation ammonium molybdate served as catalyst, 1% Mo of organic matter, gaseous hydrogen had an initial pressure of 5 MPa. In some experiments hydrogen was obtained by decomposition of aqueous formate.



Autoclaving decreases the content of heteroelements and unstable components in shale oils, the former are removed in the order $\text{O} > \text{S} > \text{N}$. Nitrogen compounds are most stable, their content in shale oils being much higher than in petroleum. In all processes of thermal destruction also pyrite is decomposed to give mainly pyrrotine. The sulfur content of shale oil decreases also by conversion in water, particularly on addition of alkali to water. The use of catalysts in the processes of hydrogenation of high-sulfur shales is of low efficiency, since pyrrotine and hydrogen sulfide themselves act as catalyst. Thus, for example, in hydrogenation of Suzak oil shale the use of molybdenum as catalyst increased the oil yield only by 2%.

Table 2 reports the yields of oil by using different methods of thermal destruction. Under supercritical conditions ($>370^{\circ}$) water rapidly decomposes the organic matter of solid minerals, the hydrogen formed by reaction of water with organic matter has an hydrogenating effect, and part of hydrogen formed goes into the composition of oil.

Table 1

Geological data and composition of oil shale samples

Shale sample	Age million years	Organic content	Kerogen elemental composition			
			C	H	N	S O
Balkhashite, Lake Balkhash Recent		94	75,5	10,9	0,9	12,7
Suzak, Uzbek SSR	40	54	62,1	7,5	3,0	7,7 19,7
Menilitic, Ukrainian SSR	60	20	61,8	7,2	1,0	2,6 27,4
Krassava, Bulgaria	60	45	66,9	8,2	1,6	3,2 20,1
Sysola, Komi ASSR	Upper Ju-					
	rassic	28	57,5	7,0	2,0	2,8 30,7
Yarenga, Komi ASSR	Upper Ju-					
	rassic	76	70,4	7,9	1,5	7,9 12,3
Chagansk, Russian SFSR	Jurassic	56	62,5	8,3	1,0	8,7 19,6
Kenderlyk, Kazakh SSR	Upper Car-					
	boferros	48	71,9	7,5	1,8	1,0 17,8
Turov, Byelorussian SSR	Upper De-					
	vonian	17	60,3	9,2	1,2	3,6 25,7
Kukersite, Estonian SSR	Middle Or-					
	dovician	65	79,0	9,7	0,3	1,8 9,2
Dictyonema, Estonian SSR	Lower Or-					
	dovician	20	70,5	8,3	2,5	4,2 14,5

Table 2

Dependence of oil yield on the thermal destruction method

Shale sample	Semi-coking	Autoclaved for 3 h, at 370°			In alkali solution
		Hydrogenation	Liquefaction in benzene	In water	
Balkhashite	80	69	-	65	75
Suzek shale	22	59	30	12	16
Menilitic shale	11	54	-	9	13
Krassava shale	35	56	29	18	25
Sysola shale	29	52	27	13	22
Yarenga shale	33	55	28	18	21
Chagansk shale	43	55	36	40	48
Kenderlyk shale	19	51	-	17	24
Turov shale	30	62	-	20	28
Kukersite shale	66	69	-	50	59
Dictyonema shale	14	40	-	9	49

Table 3 shows the decrease in sulfur content of oil depending upon the method of thermal decomposition used.

Table 3

Sulfur content of oils obtained by thermal destruction of high-sulfur oil shales, %

Shale sample	Method of destruction		
	Semi-coking	Hydrogenation	Conversion in alkali solution
Suzak shale	5,5	1,6	3,8
Yarenga shale	8,1	2,7	3,0
Chagansk shale	9,3	5,3	6,3
Dchamsk shale	8,4	2,4	3,8
Sysola shale	5,0	1,9	6,5

Table 4 reports the elemental composition of some shale oils, it depends on the initial nature of kerogen and the method of destruction. Unlike semi-coking oils, those from autoclaving contain in the fractions of aliphatic compounds only paraffins (C_{10} to C_{20}), unbranched and isoprenoid compounds (iC_{15} to iC_{20}), the double bonds of olefins are saturated with hydrogen in autoclave experiments. In the oils from autoclaving only a low prevalence of "odd" paraffins (CPI) is observed. The concentrating of alkyl benzenes is considerably lower than by semi-coking. The composition of alkyl benzenes and polycyclic aromatic compounds in autoclave oils is less complicated than semi-coking oils.

Neutral oxygen compounds of semi-coking oils considerably differ from those of autoclaving when using water conversion. The study of kukersite shale showed that 5-alkylresorcinols are present in the semi-coking products, but 2-alkanones are abundant in the thermal destruction products of kerogen when aqueous conversion is used.

It is supposed that the indicated resorcinols and

alkyl ketones are formed from the same structural elements of kukersite kerogen, exactly from aliphatic chains containing poly- β -carbonyl groups. By thermal destruction cyclization proceeds via aldol condensatsion, then tautomeric conversion into enol (phenol) form. Aqueous medium prevents the condensation reaction, alkaly catalysed ketone cleavage takes place leading to ketones $R-CO-CH_3$. The ketones obtained are characterized by a high CPI - particularly alkanones C_{17} and C_{19} .

Electron microscopic studies of the initial oil shale and solid residues of thermal destruction of shale demonstrated that by autoclaving in supercritical water the mineral part of shale undergoes considerable changes as well. The study of Bulgarian Mandra shale showed that at high temperature and pressure (370° , 25 MPa) in aqueous medium solubilization of the mineral matter takes place which on subsequent cooling was crystallized out. X-ray diffraction analysis of the initial shale and solid residues of thermal destruction indicated that pyrite is completely decomposed, whatever the method of destruction used, but on aqueous conversion the major mineral of the shale analcinite is converted into polymorphous form krankeinite. This is observed with other oil shales containing minerals of hydrothermal origin.

Conversion of organic matter of oil shales is an attractive method for their underground processing, but the water is active only at high pressure. Consequently, the method may be applied to processing deep-deposited oil shale beds where rock pressure exceeds >20 MPa, and also hydrogeological conditions are suitable.

Group composition (wt.%) of thermal destruction products

Shale sample	Thermal destruction method	Aliphatic hydrocarbon	Aromatic compounds	Low polar compounds	High polar compounds
Suzak shale	semi-coking	19	37	20	24
	hydrogenation conversion ^{x)}	17	27	14	42
Chagansk shale	semi-coking	15	23	18	44
	hydrogenation conversion ^{x)}	6	54	20	20
Krassava shale	semi-coking	18	37	16	29
	hydrogenation conversion ^{x)}	8	36	18	38
Kenderlyk shale	semi-coking	16	32	13	39
	hydrogenation conversion ^{x)}	15	19	17	49
Dictyonema shale	semi-coking	16	23	18	43
	hydrogenation conversion ^{x)}	25	14	30	31
Kenderlyk shale	semi-coking	24	36	12	28
	hydrogenation conversion ^{x)}	25	33	14	38
Dictyonema shale	semi-coking	8	46	16	30
	hydrogenation conversion ^{x)}	8	47	14	31
		10	33	24	33