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HIGH-SULPHUR SHALE OIL AS A PRIME MATTER FOR BITUMEN PRODUCTION

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The composition and properties of heavy residues of Israeli shale oil (S content 6.8 %) were investigated as a source for bitumens. Both principal methods of asphalt production - vacuum distillation and oxidizing with air - were studied. Straight-run bitumen had satisfactory characteristics. As to oxidized bitumen, the values of its penetration, ductility and softening point were also satisfactory. The drawback of shale oil bitumens is their high viscosity after the thin film oven test, which means their high sensitivity to aging. The shale oil composition changes significantly as a result of distillation and oxidation. The content of asphaltenes sharply increases: from 3.5 to 20-22 % in straight-run bitumen and to 30 % in oxidized bitumen. It is explained by the reactions of condensation and polymerization of the most unstable polar components during heating and oxidation. Unlike petroleum, shale oil is a product of pyrogenic origin, i.e., it is formed as a result of thermal decomposition of large molecules of kerogen and a part of this cracked material consists of unstable fragments of these molecules, which have a tendency to polymerization. The C/H ratio and nitrogen content increase significantly in the order "saturated hydrocarbons - naphthenoaromatics - aromatics - asphaltenes".

Introduction

Israel has considerable reserves of high-sulphur oil shales. Utilization of heavy oil fractions obtained from these shales is a serious problem, since heavy fractions cannot be used for the production of fuels or electrode coke because of a high sulphur content (up to 7 % in the total oil). Therefore, other possibilities of utilization of heavy oil fractions should be investigated. The use of oil for bitumen production may be one of these possibilities.

Effect of different variables on the process of bitumen production from the Baltic shale oil was thoroughly studied in the 1950's by Usk [1]. Shale oil bitumen is produced in large quantities in Estonia and Russia, where it is used not only for road pavement, but mainly for the production of roofing materials, anti-corrosive coatings, etc. [2]. As a local road paving material, shale oil bitumen covers about 50 % of the bituminous binders used in Estonia. Shale oil bitumen (softening point below 30 °C) is used also for surface dressing of asphaltic pavement. At present, practically all road surfacing in Estonia is carried out using shale oil bitumens to maintain satisfactory friction of the pavement surface for extended periods of time. No similar effect could be obtained by surface dressing with petroleum bitumens [3]. Attention to investigations in the field of production of shale oil bitumens is paid also in the USA [4].

Researches in asphalt chemistry and technology have been done for more than a century [5]. In recent years, significant progress was made in research of chemical composition of bitumens and heavy petroleum, coal tar, and shale oil residues. Effect of the bitumen composition on their properties is one of the central topics of many investigations [6-8], but no general relation between chemical composition of asphalts and their physical, rheological and technical properties has been established yet. There exist also no general rules to predict the yield of asphalt from one or another stock, bitumen properties and the conditions of its production. Therefore it is necessary to search conditions of asphalt production from each kind of petroleum or shale oil by empirical methods.

This research was aimed at investigating composition and properties of the shale oil heavy residues, to make them usable for obtaining bitumens.

Experimental

Determination of asphaltenes and separation of maltenes into group components by column adsorption chromatography

The so-called "saturated hydrocarbons - aromatics - resins - asphaltenes" (SARA) method (ASTM D 2006-80) or Corbett's procedure (ASTM D 4124-86) were used for determination of asphaltenes and chromatographic group analysis. However, some changes were made in the standard method in order to obtain group components in quantities sufficient for their further investigation.

Physico-chemical (density, viscosity, etc.) and rheological (penetration, ductility, etc.) properties

were characterized according to the ASTM standards. Elemental analysis was performed by the Perkin-Elmer CHN-S automatic analyzer, oxygen content was calculated by difference.

Molecular weight

Molecular weights were determined by the cryoscopic method. Diphenyl ether was used as a solvent for hydrocarbon components of shale oil

("saturated hydrocarbons" and "naphtheno-aromatics"), and *o*-chloro-nitrobenzene for aromatics and asphaltenes. *o*-Chloro-nitrobenzene was chosen for its high polarity (its dipole moment is 4.66 D as compared to 4.01 D of that of nitrobenzene); besides, it has a much higher crystallization temperature as compared to nitrobenzene (32 and 5.7 °C, respectively). This prevents the formation of molecular complexes during the determination and allows to get more correct results.

Obtaining bitumens

The residue of oil atmospheric distillation, obtained from oil shales of the Rotem Yamin deposit, Israel, was used as a source for the bitumen production. There are two principal methods of conventional asphalt production from heavy residues: vacuum distillation ("straight-run" asphalts) and oxidizing with air. Both methods were investigated. Shale oil is a thermolabile product; the first signs of its thermal decomposition are observed at temperatures of 200-220 °C. Therefore, cautious vacuum distillation is needed. On the other hand, unstable hetero-atomic compounds are more inclined to thermal polymerization. Hence, one can expect that shale oil can be easily reduced to the penetration grade of asphalt by vacuum distillation.

The term "oxidation" is applied to the method of bitumen manufacturing only by tradition. Blowing of air into petroleum residues has been used for about 100 years; however, the mechanism of this process is not clear up to now. It is supposed that the main trend is dehydrogenation with formation of free radicals and unsaturated linkages; the next step is polymerization (condensation) of unsaturated linkages. Mechanism and products of oxidation were investigated by various methods [9-11]. The main variables of the oxidation process of the residue are the temperature, air blow rate, and time. The higher the temperature, the higher the rate of oxidation. However, air blowing at too high temperatures usually results in a product of a lower quality. After preliminary investigations, the temperature of 230 °C was chosen. The unit shown in Fig. 1 was used for shale oil oxidation.

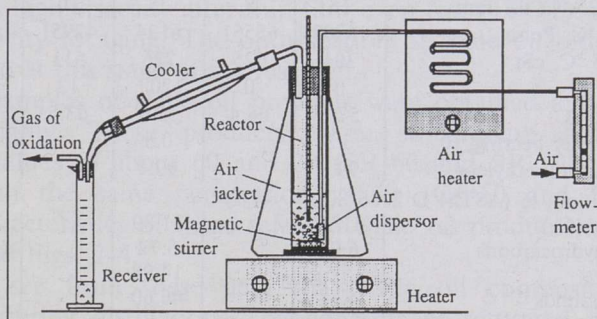


Fig. 1. Laboratory unit for shale oil oxidation

Results and Discussion

The yield and characteristics of the initial oil and the atmospheric residue are presented in Table 1. A large part of shale oil consists of sulphur, oxygen and nitrogen compounds.

The dependence of the properties of straight-run bitumen on the percentage of vacuum distillation of shale oil atmospheric residue is presented in Table 2. The higher the percentage of distillation, the lower the penetration value of the bitumen.

Table 1. Characteristics of the Initial Shale Oil and its Atmospheric Residue

Characteristics	Initial oil	Residue > 280 °C
Fraction yield, wt. %	100	55.2
Density at 15 °C	0.9827	0.998
Viscosity at 50 °C, cSt	11.57	16.6
Bromine number	76	58.5
Elemental analysis, %:		
C	79.53	81.67
H	9.74	9.91
O	2.20	1.41
N	1.52	1.53
S	6.81	5.48
Molecular mass	213	343
Insoluble in heptane, wt. %	1.78	—
Insoluble in toluene, wt. %	0.04	0.08

Table 2. Effect of the Percentage of Vacuum Distillation of Atmospheric Residue on the Properties of Shale-Oil Straight-Run Bitumen

Characteristics	Sample I		Sample II		Sample III	
	Time of the exposure*, hours					
	0	5	0	5	0	5
Bitumen yield, %	31		35		42	
Penetration at 25 °C, 0.1 mm	15	8	25	10	47	17
Viscosity at 60 °C, Poise	15308	65551	6124	42951	1446	8378
Viscosity at 135 °C, cSt	304	625	226	511	127	252
Ductility, cm	0	0	120+	12	120+	137
Softening point, °C	57.3	66.4	55.0	63.5	48	57.8
Loss in weight after heating, %	0.3		0.5		0.7	
Solubility in trichloroethylene, %	99.0		99.1		99.3	
Group composition, % (ASTM D 2006-80):						
Asphaltenes (C ₅)	31.97		31.89		29.30	32.43
Saturated hydrocarbons	6.96		5.72		5.76	6.50
Aromatics	15.58		14.98		16.54	16.02
Polar compounds	42.8		46.60		46.87	45.10
Index IC**	0.66		0.61		0.56	0.62

* Exposure at 163 °C ("thin film oven test").

** Gastel Index IC = (asphaltenes + saturated hydrocarbons) / (aromatics + resins).

Characteristics of the oxidized shale oil bitumens are presented in Table 3. The longer the time of oxidation, the lower the bitumen yield and its penetration value. One can see that oxidation is a flexible process which allows to obtain various modifications of very hard and very soft shale bitumens with a wide range of penetration values, viscosities and softening points. The best result from the point of view of the properties needed for paving asphalt is achieved at the middle degrees of oxidation.

Table 3. Effect of the Oxidation Time on the Yield and Properties of Shale Oil Bitumens

Characteristics	Sample I		Sample II		Sample III		Sample IV	Sample V
	Time of the exposure*, hours							
	0	5	0	5	0	5	0	0
Oxidation time, hr	6		8		9		12	2
Yield, %	82		78		75		72	70
Penetration, 0.1 mm	88	33	52	22	42	25	12	2
Viscosity:								
at 60 °C, Poise	547	-	2389	34506	4668	41530	33578	-
at 135 °C, cSt	101	-	172	468	225	520	1476	-
Ductility, cm	43	38	100	100	35	8	0.5	
Softening point, °C	41.3	53.1	53.1	60.5	57.7	60.8	71.3	93.7

* Exposure at 163 °C ("thin film oven test").

The characteristics of some samples of straight-run and oxidized shale oil bitumens as compared to the specifications of the ASTM D 3381 standard are presented in Table 4. Straight-run bitumen has satisfactory characteristics. The low viscosity at 135 °C has only functional effect since it can lead to the decrease of temperature during the production of bitumenous mixtures. As to the oxidized bitumen, values of its penetration, ductility and softening point are also satisfactory. The drawback of the bitumen is its high viscosity after thin film oven test (TFOT), which means a high sensitivity to aging. The optimization of shale oil bitumen quality was not aimed at this stage of the research.

Selected samples of shale oil products were obtained and investigated more thoroughly. These products were: straight-run bitumens with penetration values of about 60 and 20 (SR-60 and SR-20) and oxidized bitumens with the same penetration values (Ox-60 and Ox-20). The chemical characteristics of these selected shale oil products are presented in Table 5 and Figs. 2-4.

One can see from these data that shale oil composition changes significantly during distillation. The contents of saturated hydrocarbons and naphtheno-aromatics decrease (Fig. 2), while molecular weight of the oil increases. The changes in the content of asphaltenes are especially

significant. It is suggested that shale oils are not suitable for the production of bitumens because they contain no asphaltenes. Indeed, the initial shale oil practically does not contain substances insoluble in heptane (see Table 1). However, the content of asphaltenes increases sharply with the boiling point of the fraction: the atmospheric residue (280 °C + fraction) contains only 3.5 % asphaltenes, whereas the content of C₇-asphaltenes (insoluble in *n*-heptane) in the bitumen (i.e., 430 °C + fraction) is 20-22 %. It is much more than the content of asphaltenes in petroleum bitumens, which is usually within the range of 7-10 % for straight-run bitumens and 10-15 % for visbroken bitumens [12, 13]. Therefore, a high or a low quality of the bitumens is not determined only by asphaltenes.

The high content of asphaltenes in shale oil bitumens cannot be explained only by concentrating asphaltenes in the heavy fractions during distillation (in this case the content of asphaltenes in straight-run bitumens

Table 4. Comparative Characteristics of Straight-Run and Oxidized Shale Oil Bitumens

Characteristics	Straight-run		Oxidized		ASTM D 3381 requirements	
	Time of the exposure*, hours					
	0	5	0	5	0	5
Penetration, 0.1 mm	47	17	52	22	> 40-60	-
Viscosity at 60 °C, Poise	1446	8378	2389	34506	1600-2400	< 10,000
Viscosity at 135 °C, cSt	127	252	172	468	> 300	-
Ductility, cm	120+	137	100	100	-	> 50
Softening point, °C	48	57.8	55.3	60.5	-	-

Exposure at 163 °C ("thin film oven test").

Table 5. Chemical Characteristics of Shale Oil Bitumens

Characteristics	Atmospheric residue	SR-60	SR-20	Ox-60	Ox-20
Molecular weight	343	527	602		554
Group composition, % (ASTM D 4124-86):					
Saturated hydrocarbons	7.5	1.7	0.7	2.9	2.0
Naphtheno-aromatics	33.2	17.2	19.3	22.4	21.2
Aromatics	55.8	58.6	55.9	43.8	44.2
Asphaltenes	3.5	22.5	24.1	30.9	32.7
Elemental composition, %:					
C	81.67	82.08	82.19	82.35	82.14
H	9.91	9.24	9.16	9.07	9.00
N	1.53	2.11	2.12	1.46	1.47
S	5.48	4.95	4.90	5.17	5.43
O	1.41	1.62	1.63	1.95	1.96
Bromine value	58.5	46.3	-	51.2	-
Molecular weight of asphaltenes	2114	2527	2643	2231	2288

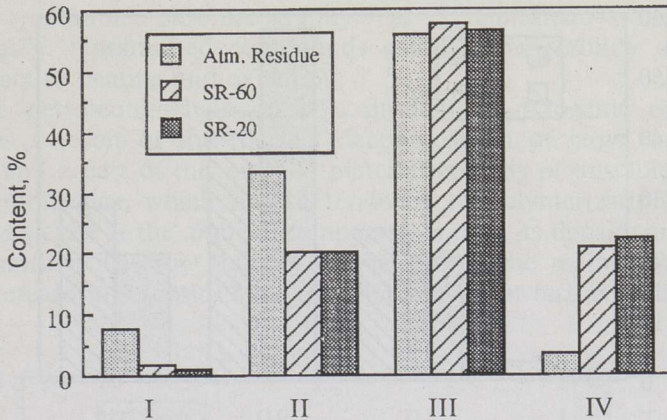


Fig. 2. Changes in the composition of shale oil produced by vacuum distillation: I - saturated hydrocarbons, II - naphtheno-aromatics, III - aromatics, IV - asphaltenes

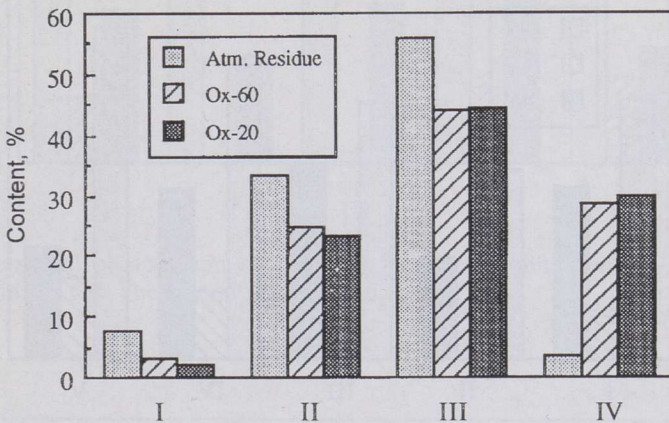


Fig. 3. Changes in the composition of shale oil produced by oxidation. The legend see in Fig. 2

would be only 11-12.5, and not 12-24 %, as it happens to be). Evidently, even during vacuum distillation, when real temperatures of the oil in the still (flask) reach 330 °C, reactions of condensation and polymerization of the most unstable components occur, which results in the formation of asphaltenes.

Even more significant increase in the asphaltene content is observed during oxidation (Fig. 3). The content of asphaltenes in bitumens reaches 30 %, in spite of the higher yield of the oxidized products as compared to the straight-run bitumen (i.e., the concentrating of asphaltenes during distillation does not take place in this case). The content of naphtheno-aromatics and aromatics decreases. Air blow almost does not change the elemental composition of the product; the oxygen content remains on the

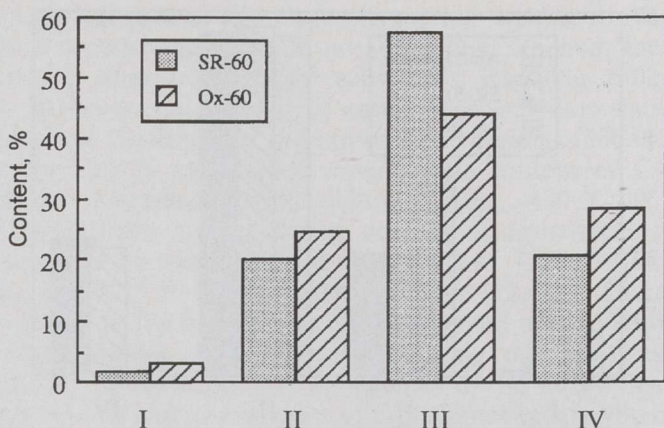


Fig. 4. Comparison of the group composition of shale oil straight-run and oxidized bitumens. The legend see in Fig. 2

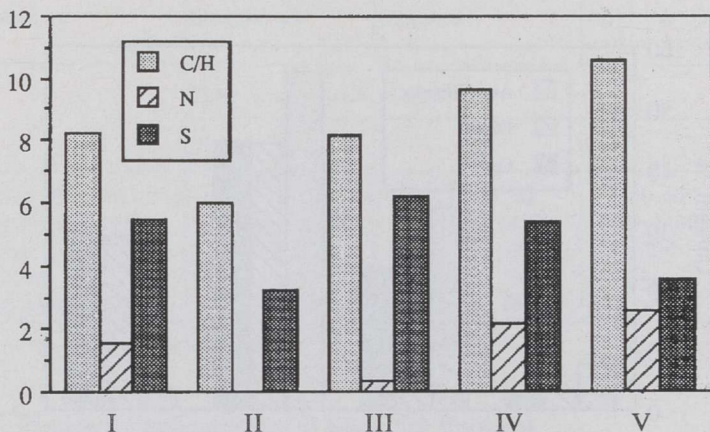


Fig. 5. Elemental composition of shale oil atmospheric residue (C/H - weight ratio, N and S - %): I - total product, II - saturated hydrocarbons, III - naphtheno-aromatics, IV - aromatics, V - asphaltenes

same level even at the highest degree of oxidation. A slight decrease in the hydrogen content indicates a process of dehydrogenation as a result of interaction of hydrocarbons with oxygen.

The comparison of straight-run and oxidized bitumens (Fig. 4) shows that the former contains less naphtheno-aromatics, and more aromatics and asphaltenes. Both kinds of bitumen have a low content of saturated compounds, but are rich in asphaltenes and sulfur. All shale oil products have a large content of aromatics - polar compounds, rich in heteroatoms, which are inclined to polycondensation and play therefore a role of the precursors of asphaltenes in thermal and thermo-oxidizing process. The high bromine values also indicate an unsaturated character of shale oil (unsaturated compounds have a polar nature, and therefore are determined

by the column chromatography as “naphtheno-aromatics” or “aromatics”). Unsaturated compounds cause a low stability of shale oil with respect to heating and oxidation.

Unlike petroleum, shale oil is a product of pyrogenic origin. It is formed as a result of the thermal decomposition of large molecules of kerogen, and a part of this cracked material consists of unstable fragments of these molecules, which have a tendency to polymerization. Shale oil polymerizes even at the ambient temperatures, and its density and viscosity grow at storing. The low stability of shale oil is the main reason for the drastic increase in viscosity after the thin film oven test as well as for the

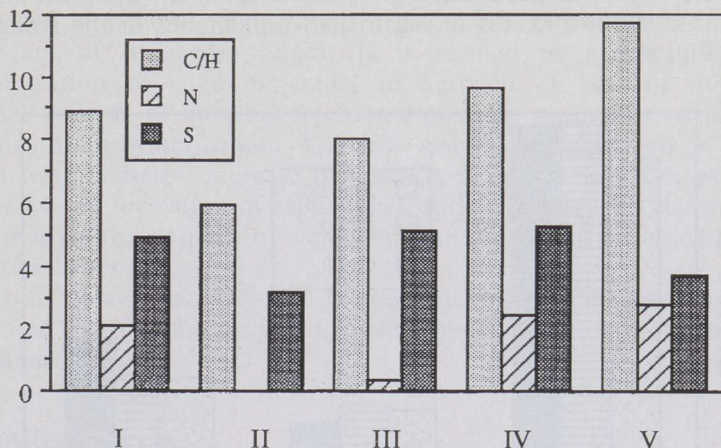


Fig. 6. Elemental composition of shale oil straight-run bitumen (C/H - weight ratio, N and S - %). The legend see in Fig. 5

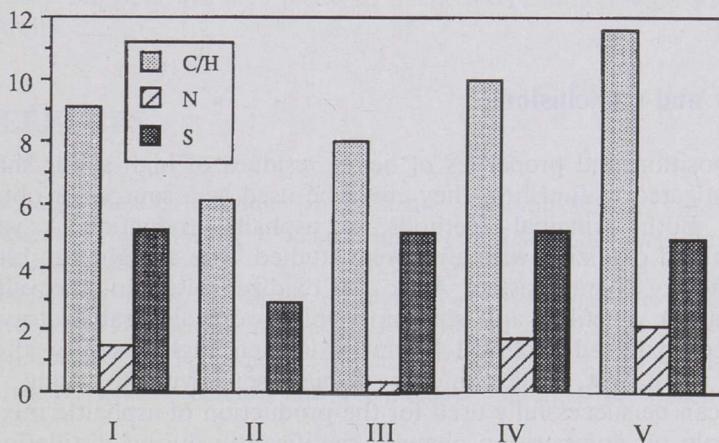


Fig. 7. Elemental composition of shale oil oxidized bitumen (C/H - weight ratio, N and S - %). The legend see in Fig. 5

asphaltene formation during vacuum distillation. For the same reason, the content of asphaltenes increases during the oxidation of the atmospheric residue.

The elemental composition of the principal chemical groups of shale oil bitumens are presented in Figs. 5-7. The C/H ratio and nitrogen content increase significantly in the order "saturated hydrocarbons - naphthenoaromatics - aromatics - asphaltenes". The sulphur content, as a rule, increases with the polarity of the groups; however, the sulfur content of aromatics is higher than that of asphaltenes. These phenomena are also noted for petroleum products [14].

There exist some differences in the elemental composition of the same components of various products, e.g., asphaltenes of the oxidized bitumens contain more sulfur and less nitrogen than asphaltenes of the straight-run product (Fig. 8).

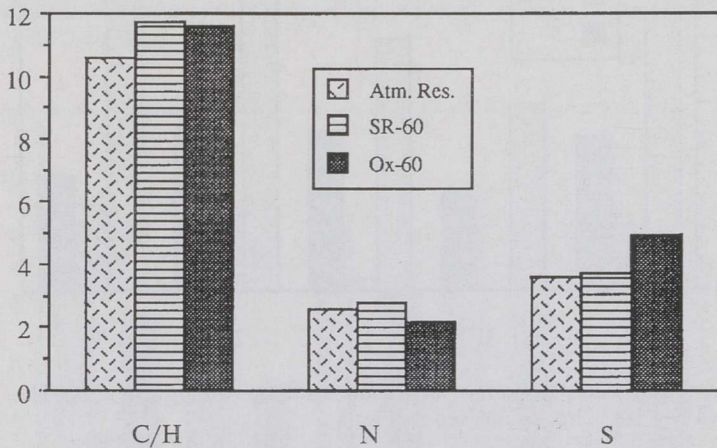


Fig. 8. Elemental composition of asphaltenes of shale oil bitumens (C/H - weight ratio, N and S - %)

Summary and Conclusions

The composition and properties of heavy residues of high-sulfur shale oil were investigated to find how they could be used as a source for obtaining bitumens. Both principal methods of asphalt production - vacuum distillation and oxidizing with air - were studied. The straight-run bitumen had satisfactory characteristics. As to the oxidized bitumen, the values of its penetration, ductility and softening point were also satisfactory. The drawback of oxidized shale oil bitumens is their high viscosity after the thin film oven test, which means a high sensitivity to aging. Shale bitumens can be successfully used for the production of asphaltic mixtures.

The shale oil composition changes significantly during distillation and oxidation. The content of saturated hydrocarbons and naphthenoaromatics decreases, while molecular weight of the oil increases. The

changes in the content of asphaltenes are especially significant. The initial shale oil practically does not contain substances insoluble in heptane; the atmospheric residue (280 °C + fraction) contains only 3.5 % asphaltenes, whereas the content of asphaltenes in the straight-run bitumen (430 °C + fraction) is 20-22 % and that in the oxidized bitumen even 30 %. The high content of asphaltenes in shale oil bitumens is explained as a result of condensation and polymerization reactions of the most unstable components during heating and oxidation.

Shale oil bitumens have a low content of saturated compounds, but are rich in asphaltenes and sulfur. They have a large content of aromatics - polar compounds, rich in heteroatoms, which are inclined to polycondensation and play therefore a role of the precursors of asphaltenes in thermal and thermo-oxidizing processes. Unlike petroleum, shale oil is a product of pyrogenic origin. It is formed as a result of thermal decomposition of large molecules of kerogen. A part of this cracked material consists of unstable fragments of these molecules, which have a tendency to polymerization. The low stability of shale oil is the main reason for the drastic increase in viscosity after the thin film oven test as well as for the formation of asphaltenes during vacuum distillation. For the same reason, the content of asphaltenes increases during oxidation of the atmospheric residue.

The C/H ratio and nitrogen content increase significantly in the order "saturated hydrocarbons - naphtheno-aromatics - aromatics - asphaltenes".

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