Nature of Oil-Shale Kerogen

Oxidations with Potassium Permanganate in Acetone Solution

GJORGJE STEFANOVIĆ and DRAGOMIR VITOROVIĆ
Institute of Chemistry, Faculty of Science, University of Belgrade, Yugoslavia

The oxidation with alkaline potassium permanganate has been used in many cases for investigating the chemical structure of various coals (*2–4,11,13,16,18,19,31*). Thus, Bone and collaborators (*3,4*) oxidized lignin and coals of different maturity and found that the coals could be totally oxidized relatively easily with alkaline potassium permanganate; only in the case of anthracite, 8% of carbon was left unoxidized after a reaction period of 60 hours. Among the oxidation products there was found 36 to 61% of carbon in the form of carbon dioxide, 7 to 28% in the form of oxalic acid, 2 to 7.5% in the form of acetic acid, and 10 to 50% in the form of "benzene carboxylic" acids. The percentage of the latter compounds increases with the maturity of the coal. From these results, Bone and collaborators came to the conclusion that the coals they investigated were of benzenoid structure and that there existed a definite continuity in structural change in coals of different maturity.

In analogy with coals, this oxidative method has often been applied in the course of the investigation of oil-shale kerogens (*8–10,12,17,20–22,29,30.33*).

Down and Himus (*9*) oxidized different types of oil shales with an alkaline solution of potassium permanganate and reported that these were more resistant to oxidation than coals, and that carbon could be found in the oxidation products in the form of carbon dioxide, oxalic acid, acetic acid, and nonvolatile nonoxalic acids. In the case of some types of oil shales, one part of the carbon remained unoxidized. The reaction times varied between 56 and 145 hours. They did not draw conclusions as to the chemical constitution of kerogens, but stated that the structure of some kerogens should broadly resemble that of coals, because of the high yield, in both cases, of nonvolatile acids; that in other kerogens, however, there was no evidence for the benzenoid structure, and that these, therefore, differed in constitution from coals; and that some kerogens contained two types of material, one comparatively easily oxidized with an alkaline solution of potassium permanganate, the other resistant to the action of this reagent.

Robinson, Heady, and Hubbard (*30*) have used alkaline potassium permanganate in the oxidation of Colorado oil shale (Green River formation). By applying the "carbon-balance" technique, 96 to 99% of the total organic carbon could be oxidized to water-soluble products, which consisted mainly of carbon dioxide and oxalic acid, and, in much smaller amounts, of steam-volatile and nonvolatile (nonoxalic) acids. For that reason, they presume that Colorado oil-shale kerogen is essentially nonbenzenoid in structure and may be similar to the organic material in Estonian algal limestone and Gdov oil shale, which on oxidation also afford only small amounts of nonvolatile acids and no benzenoid acids.

From all these results, obtained by oxidizing various oil shales with an excess of alkaline potassium permanganate (and by using the carbon-balance technique), the main and common feature is the relatively high yield of carbon dioxide and oxalic acid in the oxidation products. The same products, however, are also preponderantly formed under these conditions by potassium permanganate oxidation of many organic compounds, and it is, therefore understandable that on the basis of only such results no definite conclusion can be drawn about the structure of oil-shale kerogens. The most which can be concluded from the yields and types of nonvolatile acids obtained is the benzenoid or nonbenzenoid character of the examined kerogens.

Down and Himus (*9*), and later other authors, found that in the first stages of the oxidation of some kerogens various acids were formed which were not resistant to further action of alkaline potassium permanganate, and were subsequently oxidized to a large extent to carbon dioxide and oxalic acid. To prevent total oxidation, some authors have recently carried out a stepwise oxidation by adding permanganate in small portions at a time and isolating the oxidation products prior to each new addition of the oxidizing agent. In that way there have been obtained, in various yields depending upon the conditions used, various acids as well as intermediate "regenerated humic acids."

By applying this partial oxidation to Colorado oil shale, Robinson, Heady, and Hubbard (*30*) converted about 80% of the kerogen to high molecular weight acids, in contrast to the usual oxidation with an excess of alkaline permanganate which gave only 1% of nonvolatile acids. The U. S. Bureau of Mines (*33*) has reported that, depending on the oxidation conditions, different products could be obtained. An excess of permanganate oxidizes Colorado oil-shale kerogen in the first stages quickly and later more slowly, because the intermediate compounds and some parts of the kerogen are progressively oxidized to acids of lower molecular weight. Robinson, Cummins, and Stanfield (*29*) have oxidized Colorado oil-shale kerogen in only two steps and obtained principally dicarboxylic acids of two types: 59% of oxalic, succinic, glutaric, and adipic acid, and 41% of dicarboxylic acids with higher molecular weights up to about 800, which have not been identified. Fomina and Pobul (*10*) carried out a partial oxidation of Kukersite kerogen. The oxidation of 50% of carbon present results in the formation of steam-volatile monobasic acids, nonvolatile oxalic acid, other dibasic acids up to azelaic acid, and some viscous acids of unknown composition. By oxidizing this shale with an excess of alkaline permanganate, mainly carbon dioxide, acetic, and oxalic acid were obtained (*9*).

Although the intermediate compounds can be valuable for further constitutional studies, the "regenerated humic acids" are very complex in nature and are difficult to separate, isolate, and identify. Besides, one should be very careful in drawing conclusions based on intermediate products, because these consist of various compounds, whose yield and type depend on a considerable number of factors.

An analysis of the results hitherto obtained in the study of the structure of kerogen, and particularly of the results of the alkaline oxidation with potassium permanganate, pointed to the necessity, for structural determination of kerogens, of using milder and more specific agents which would oxidize the organic substances of oil shales only in definite positions, thus enabling the isolation of primary degradation products which would give more useful information about the structure of the starting material.

Potassium permanganate in alkaline solution was frequently used in the determination of structures of natural unsaturated triglycerides and unsaturated fatty acids. However, Armstrong and Hilditch (*1*), in 1925, described a novel and superior procedure for studying the constitution of these compounds, which consisted of the oxidation, with a neutral acetone solution, of potassium permanganate. In contrast to the alkaline solution, this combination gives fewer oxidation products in better yields. Thus, for example, from methyl oleate, they obtained as major products pelargonic acid and the half-ester of azelaic acid, and also found that under similar experimental conditions, esters of saturated fatty acids remained unchanged. Since then, this oxidizing agent has been applied to many structure determinations of unsaturated compounds. It is specific for the double bond, whereas tertiary and quaternary carbon atoms are oxidized to a lesser degree. Stefanović and Pejković (*32*) have recently demonstrated this specificity by oxidizing esters of chaulmoogric and hydnocarpic acids to the corresponding tricarboxylic acids, in 65% yield; the amounts of dicarboxylic acids were much smaller and did not exceed 28%.

It was believed that the oxidation with potassium permanganate in acetone solution would be a convenient method for investigating the constitution of oil-shale kerogens, mainly for the following reasons:

If kerogen is polymerized and of unsaturated character (as supposed by many authors), its total or partial oxidation with an excess of an acetone solution of permanganate would produce acids, which, taking into account the more specific action of the oxidizing agent, would allow the drawing of more definite conclusions about the structure of the native substance.

As the character of the shale oil was proved dependent on the nature of kerogen, parallel oxidations of shale oil and kerogen under similar conditions would probably furnish information on the structure of kerogen itself, naturally based on a knowledge of the mechanism of pyrolysis of kerogen.

By applying this oxidative method it should be possible to elucidate the nature of "bitumen" (*5-7,26,28*), an intermediate product of the thermal decomposition of kerogen, which is considered by some authors to be of unsaturated character (*23-25*). By comparing its structure with that of kerogen and its degradation products (shale oil), useful information could be obtained.

Finally, by investigating the action of potassium permanganate in acetone solution on other fuels (wood, coals, petroleum) data would be available for comparing these natural products with oil shales.

This work was undertaken in order to investigate *qualitatively* the possibility of using potassium permanganate in acetone in the study of the structural elucidation of oil shales and to acquire preliminary facts which could be of use for further investigations in this field.

Parallel oxidations were first carried out with alkaline and acetone solutions of potassium permanganate (in excess) on a specimen of oil shale from Aleksinac (Yugoslavia). The results of these preliminary experiments show that the oxidation in acetone gave considerably more ether-soluble products than the alkaline oxidation (39.6% as compared to 8.8%, based on kerogen and not taking into account the increase of oxygen).

By oxidizing a larger quantity of the same oil shale with an excess of permanganate in acetone, a series of products was obtained not hitherto found in the oxidation products of oil shales. The yield of the acid compounds was considerable (38.5% based on kerogen), whereas the yield of neutral products was very low (2.0%).

By applying this method to the shale oil of the same oil shale, a smaller amount of acids with a lower average molecular weight was formed, as compared with acids from the oil shale (18.5%, based on kerogen and not taking into account the increase of oxygen). However, the yield of neutral products was much higher (18.7%, based on kerogen).

The oxidation products obtained in all these experiments were investigated only in part. The results of the oxidations are reproducible.

After the orientation experiments, the authors are making a systematic study of various types of oil shales by the same method, in order to determine the exact balance of the organic carbon in the oxidation process and to investigate in greater detail the nature of degradation products. Oil shales from the following sources are being studied: Aleksinac (Yugoslavia), Colorado (Mahogany Ledge, Green River formation), England (Kimmeridge, Dorset).

Two samples of Yugoslav coals (from Kolubara and Aleksinac) have also been subjected to an oxidation with potassium permanganate in acetone under similar experimental conditions, and it was found, in contrast to the results reported by Bone and others (*3,4*) in their study of alkaline permanganate oxidation of coals, that the coals examined were only partly oxidized, mainly to acetic acid, and that most of the coal remained unchanged.

EXPERIMENTAL PROCEDURE AND RESULTS

The oil shale was obtained from Aleksinac (Yugoslavia). The sample contained 45.4% of organic material [as determined by the method of Jovanović and Vitorović (*15*) and without corrections for the change of pyrite], and gave 27.8% of oil by the Fischer retort method.

The oil shale was finely ground (-100-mesh, Tyler, 0.149 mm.), treated with hydrochloric acid (1 to 1), washed until the washings were chlorine-free, and dried at 105° C. to constant weight. The oil-shale concentrate contained 57.1% of organic material.

The preliminary experiments in alkaline and acetone solutions were carried out by adding an excess of potassium permanganate to the corresponding boiling solutions and, after the addition was complete, refluxing for another 16 hours. In acetone solution, powdered permanganate was added; in alkaline aqueous solution, part of the agent was first dissolved and then added, and the rest was added as solid. After the reduction of excess permanganate and manganese dioxide, the oxidation products were extracted from the acidified mixture with ether (carbon dioxide was not determined), and the acidic products were separated from neutral ones by means of 5% aqueous potassium hydroxide. The results of these oxidations are shown in Table I.

Based on these preliminary experiments, oxidations in acetone solution were carried out with larger amounts of the same oil-shale concentrate as well as with the oil obtained from it, and the oxidation products have been partly investigated.

Table I. Results of Oxidations with Excess Potassium Permanganate in Alkaline and Acetone Solution

	Alkaline Solution	Acetone Solution
Oil-shale concentrate, grams	60	60
Potassium permanganate, grams	600	300
Neutral products, based on organic material, %	0.6	3.2
Acidic products, based on organic material, not taking into account increase of oxygen, %	8.2	36.4

The same experimental conditions were applied in all cases. To a boiling mixture of material in acetone, powdered permanganate in excess was added in portions, after which refluxing was continued for 16 hours. In the first experiments, acetone was removed at once after the oxidation and the residue was then diluted with water. At that stage, violent explosions probably caused by peroxides occurred in several instances, so that in subsequent experiments acetone was not evaporated. The cooled mixture was directly treated with ice water, the excess reagent and manganese dioxide were reduced with sulfur dioxide, and the acidified mixture (hydrochloric acid) was extracted with ether. The acids were separated from the neutral products by shaking the ethereal layer with 5% aqueous potassium hydroxide, acidifying the alkaline solution with hydrochloric acid, and extracting with ether. The neutral products have not yet been investigated, whereas the acids were separated in three fractions: A most soluble in water, B steam-volatile, and C nonvolatile.

Oxidation of Oil Shale. After several preliminary experiments which were carried out to find the optimal conditions and best isolation procedure, 600 grams of oil-shale concentrate in 5000 ml. of purified acetone were oxidized with 3000 grams of potassium permanganate, and added to the boiling mixture in the course of 5 hours.

The yield, based on organic material and not taking into account the increase of oxygen, amounted to 2% for the neutral products, and to 38.5% for the acidic products. The neutral part was solid, brown in color, with a pleasant odor (composition: carbon, 76.53%; hydrogen, 11.98%); it was not further investigated.

Twice, in the course of separating the acid fractions, a yellowish precipitate (acidic) appeared which was sparingly soluble in ether. Both precipitates were collected and investigated separately. The yields of the acid fractions are shown in Table II, and the properties of the precipitates in Table III.

Table II. Yields of Acidic Products from Oxidation of Oil Shale

Type of Acids	Yield, Grams	% Total Acids	% Based on Organic Material and Not Taking into Account Increase of Oxygen
Water-soluble	18.93	14.4	5.5
Volatile	9.48	7.2	2.8
Nonvolatile	72.87	55.3	21.3
Sparingly soluble I[a]	19.80	15.0	5.8
Sparingly soluble II[a]	10.70	8.1	3.1
Total amount	131.78	100.0	38.5

[a] In ether.

Table III. Some Properties of Acids Sparingly Soluble in Ether which Precipitated in Course of Separation of Acidic Fractions

	Melting Point, °C.	Acidic Value	Equivalent
Sparingly soluble I	84-7	218.2	257.1
Sparingly soluble II	84-4.5	258.2	217.3

A. Water-soluble acids were extracted from the ethereal solution (4000 ml.) which contained all the acids, with 750 ml. of water (10 X 75 ml.). The aqueous layer was neutralized and evaporated to dryness; the residue was acidified with hydrochloric acid (1 to 1) and extracted with ether. The acids thus obtained were distilled at atmospheric pressure (Table IV).

The solid residue was esterified with an excess of absolute alcohol in the presence of dry hydrochloric acid and the esters were submitted to fractional distillation under reduced pressure (Table V).

B. The steam-volatile fraction consisted of a mixture of liquid yellowish acids. They were fractionated at atmospheric pressure (Table VI).

C. The nonvolatile fraction contained 55% of all the acids isolated. They were esterified with an excess of absolute alcohol in the presence of dry hydrochloric acid and the resulting esters were submitted to fractional distillation under reduced pressure (Widmer fractionating column, active part 10 cm. high). The results of the distillation, saponification values, and percentage compositions of the fractions are shown in Table VII.

Table IV. Distillation of Water-Soluble Acids Obtained by Oxidation of Oil Shale

Fraction	Boiling Range, °C.	Yield, Grams	M.P. of Anilide, °C.	Remarks
1	110-114 (*p* = 762 mm.)	14.40	114.5	M.P. of acetanilide 114° C.
Residue	. . .	5.70	. . .	Solid

Table V. Distillation of Esters of Water-Soluble Acids Which Did Not Distill at Atmospheric Pressure

Fraction	Boiling Range, *t*° C./*p* Mm.	Saponification Value	Yield, Grams	Remarks
1	112.5-125/14	589.7	0.91	Liquid
2	131.5-138/14	556.7	0.47	Liquid
3	149 -173/14	492.4	0.65	Liquid
Residue	. . .	319.1	1.85	Solid

Table VI. Distillation of Steam-Volatile Acids from Oxidation of Oil Shale

Fraction	Boiling Range	Yield, Grams	Remarks
1	105-114.5° C. (*p* = 762 mm.)	6.58	M.P. of anilide 113.8° C.
Residue	. . .	4.03	Equivalent 132.1

Table VII. Distillation of Ethyl Esters of Nonvolatile Acids from Oxidation of Oil Shale

Fraction	Boiling Range, *t*° C./*p* Mm.	Saponification Value	Yield, Grams	Yield of Acids, Grams	Composition C, %	Composition H, %	Remarks
I	85- 87/14	523.3	0.54	0.40	. . .	. . .	Liquid
II	110-121/14	502.2	2.30	1.72	60.58	9.12	Liquid
III	122-129/14	481.8	1.75	1.34	62.23	9.50	Liquid
IV	91-103/0.34	461.7	1.51	1.16	63.35	9.55	Liquid
V	104-113/0.34	438.5	2.75	2.15	65.03	9.77	Liquid
VI	118-127/0.83	392.6	3.23	2.60	66.16	10.07	Liquid
VII	137-149/0.83	361.2	2.97	2.43	67.05	9.97	Liquid
VIII	150-159/0.83	357.6	3.15	2.59	68.01	10.04	Viscous
IX	171-185/0.34	335.1	3.70	3.08	69.15	10.46	Semisolid
Residue	. . .	247.8	61.70	54.05	. . .	. . .	Solid

The color of the fractions varied from pale yellow to yellow-brown; the residue was dark brown. Under the conditions used, the major part of the esters of the nonvolatile acids did not distill. As the saponification value of the residue is still comparatively high, it is believed that under better conditions, a further amount of esters from the residue could distill over.

If results of the percentage analyses of esters (Table VII) are plotted in a diagram of carbon-hydrogen compositions of neutral ethyl esters of mono-, di-, tri-, and tetracarboxylic aliphatic acids, a curve is obtained, as illustrated in Figure 1, which lies in the region of curves of all these esters. These data, therefore, do not give any definite information about the composition and structures of the acids obtained, although it can be presumed that the nonvolatile fraction is composed of a mixture of di- or polycarboxylic acids.

To investigate that part of the organic material which remained unchanged or undissolved during the oxidation, the filtered residue, after the extraction of oxidation products with ether, was washed with water until the washings were chlorine-free and dried at 105° C.;yield, 360.1 grams. Sixty grams of the residue were then reoxidized with 300 grams of potassium permanganate in 500 ml. of acetone to afford 2.6 grams of neutral and 6.3 grams of acidic material (4.6 and 11%, respectively, based on oil-shale kerogen and not taking into account the increase of oxygen). From that experiment it follows that the kerogen residue can be further oxidized, which means that either the quantity of permanganate or the reaction period in the first oxidation was not sufficient, or that a change in physical structure of the original oil shale took place during the first treatment with permanganate, thus allowing the residue to be more easily oxidized on subsequent treatment with the same reagent.

In both steps, therefore, a total of about 50% of oil shale organic material underwent change during oxidation.

Oxidation of Shale Oil. The shale oil was obtained by distillation of oil shale from an aluminum retort (Fischer), capacity 300 grams; rate of distillation: first 30 minutes up to 400° C.;

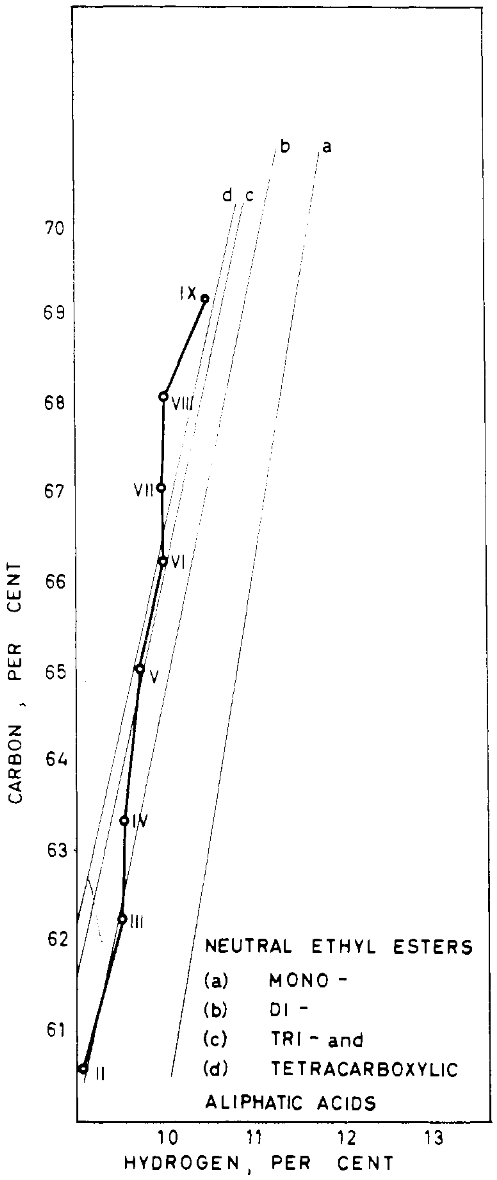

Figure 1. Compositions of ethyl esters of nonvolatile acids (fractions II to IX, Table VII) from oxidation of oil shale

second 30 minutes 400° to 520° C.; final 30 minutes from 520° to 550° C. The oil was purified by dissolving it in gasoline and treating the solution with 32% of aqueous sodium hydroxide. The losses during purification amounted to 32.6% including water. The purified oil had an average iodine value [determined by Hanus method (*27*)] of 42.56.

After preliminary experiments, 500 grams of purified shale oil in 5000 ml. of acetone were oxidized with 6500 grams of potassium permanganate, added during a period of 5 hours. Heating under reflux was continued for 16 hours and the mixture was then treated as described.

Yield of Oxidation Products

	% Based on Purified Oil	% Based on Kerogen, Not Taking into Account Increase of Oxygen
Neutral products	42.4	18.7
Acids	41.9	18.5

The neutral part was solid, yellow in color (composition: carbon, 84.12%; hydrogen, 13.60%). It was not further investigated. The yields of the acid fractions are shown in Table VIII.

(A.) Water-soluble acids were extracted from the ethereal solution (4000 ml.), which contained all the acids, with 1500 ml. of water (20 X 75 ml.). A larger quantity of water was used than in fraction A of oxidation products of oil shale, in order to extract acetic acid as completely as possible. The aqueous solution was neutralized, concentrated to a small volume, and acidified with hydrochloric acid; the residue was extracted with ether. The acids obtained by removal of the organic solvent were fractionated at atmospheric pressure (Table IX).

The solid, brown residue was esterified with an excess of absolute methanol in the presence of dry hydrochloric acid, and the esters were fractionated under reduced pressure. Because this residue was expected to consist mainly of oxalic acid, methanol was used. The identification of methyloxalate, a solid, is simpler. One fraction amounting to 1.29 grams was obtained, which boiled at 85° to 110° C., under 13.5 mm. of mercury; saponification value 540.2. The solid residue was recrystallized from 96% ethanol; saponification value 487.0.

(B.) The acids from the steam-volatile fraction were converted to their ethyl esters using an excess of absolute alcohol in the presence of dry hydrochloric acid. These were fractionated (Widmer column, active part 10 cm.) under reduced pressure. The results of the distillation and some properties of the fractions obtained are shown in Table X.

The first eight fractions were analyzed and the results are plotted in the diagram of carbon-hydrogen composition of neutral ethyl esters of aliphatic mono-, di-, tri- and tetracarboxylic acids (Figure 2). As shown, the analyses of the lower fractions correspond to the composition of esters of monocarboxylic acids, whereas for the higher fractions, the curve is shifted to the region of esters of dicarboxylic acids. From these results it appears that the fraction containing volatile acids obtained by oxidation of shale oil, consists mainly of monocarboxylic acids. The boiling points at atmospheric pressure [determined by the method of Emich (*14*)] and the saponification values indicate the presence of essentially monocarboxylic acids.

(C.) The fraction which consisted of nonvolatile acids, as in the case of oxidation of oil shale, was the largest and contained 42% of the oxidation products. The acids were esterified with an excess of absolute alcohol in the presence of dry hydrochloric acid, and the esters were fractionated under reduced pressure (see Table XI).

The saponification values of these esters are comparatively

Table VIII. Yield of Acidic Products from Oxidation of Shale Oil

Type of Acids	Yield, Grams	% of Total Acids	% Based on Kerogen
Water-soluble	97.64	46.6	8.6
Volatile	24.44	11.6	2.2
Nonvolatile	87.61	41.8	7.7
Total amount	209.69	100.0	18.5

Table IX. Distillation of Water-Soluble Acids from Oxidation of Shale Oil

Fraction	Boiling Range, °C., p = 748.7 Mm.	Yield, Grams	Melting Point of Anilide, °C.	Titration
1	101-110	23.28	114.8-115	77.8% of acetic acid
2	110-115	69.05	114.5-115	93.9% of acetic acid
Residue	. . .	14.67	. . .	. . .

Table X. Distillation of Ethyl Esters of Volatile Acids from Oxidation of Shale Oil

Fraction	Boiling Range, t °/p Mm.	Boiling Point at 1 Atm.	Saponification Value	Composition		Yield of Esters, Grams	Yield of Acids, Grams
				C, %	H, %		
1	up to 41/14	125-130	435.0	63.82	10.55	4.13	3.23
2	45- 56/13	148-152	395.2	66.06	11.05	2.55	2.01
3	58- 70/13	175-178	369.7	67.05	11.14	3.86	3.15
4	75- 87/13	192-194	344.2	69.09	11.20	3.80	3.15
5	89-102/13	210-212	325.8	70.41	11.17	4.57	3.83
6	104-107/13	225-228	303.4	70.56	11.36	2.88	2.44
7	112-120/13	241-244	290.2	71.24	11.55	2.71	2.32
8	151-158/19	above 255	264.0	72.06	11.68	2.25	1.95
Residue	. . .	. . .	. . .	. . .	. . .	1.22	. . .

high; it is believed that the nonvolatile acids from shale oil are in major part composed of di- or polycarboxylic acids. The results of analyses of most of the fractions, plotted in the diagram shown in Figure 2, also point to the presence of a mixture of esters of di- or polycarboxylic acids. However, some of the ester fractions (5,6 and 9,10) show an unusual increase in saponification value with increasing boiling point (Table XI). From the percentage composition of these same fractions it follows that they contain less hydrogen than the other fractions, which would point either to partial unsaturation of some esters (less probable) or to the presence of benzenoid (aromatic) structures.

DISCUSSION AND CONCLUSIONS

From the literature it can be seen that oxidations of oil shales with an excess of alkaline potassium permanganate afford essentially, and in high yields, carbon dioxide, oxalic and acetic acids, besides various quantities of nonvolatile acids, some of which have been isolated and identified. Thus, by subjecting oil shale to "bulk" oxidation (*8,9*), benzoic acid, *o*- and *p*-phthalic acids, benzenetetracarboxylic acid, benzenepentacarboxylic acid, and mellitic acid were obtained. Some authors have suggested (*12*) that the nature of these nonvolatile acids can be of help in comparing the chemical structures of coals and oil-shale kerogens. In a few cases the presence of succinic acid has been reported in the oxidation products.

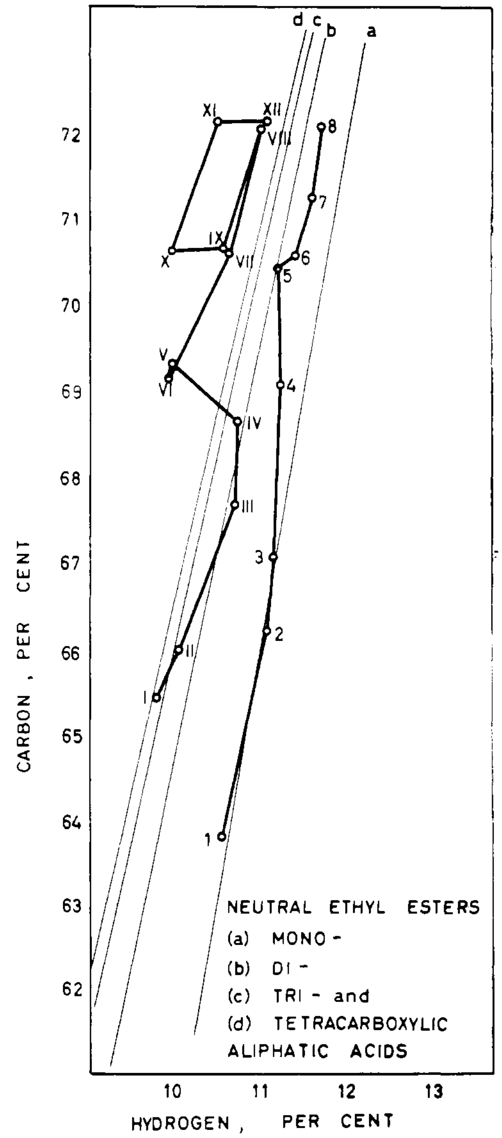

Figure 2. Compositions of ethyl esters of volatile (fractions 1 to 8, Table X) and nonvolatile (fractions I to XII, Table XI) acids from oxidation of shale oil

However, by performing the oxidation of oil shale in several steps, higher yields of intermediate acids were obtained: "regenerated humic acids" (*30*), a mixture of dicarboxylic acids ranging from oxalic to adipic acid, besides complex acids of higher molecular weight which were not identified (*29*) and volatile monocarboxylic acids, dicarboxylic acids ranging from oxalic to azelaic acid and some viscous acids of unknown composition (*10*).

In contrast to the results obtained by alkaline permanganate oxidation, the oxidation of Aleksinac oil shale with an excess of an acetone solution of potassium permanganate yielded acids which were not hitherto found in the oxidation products of oil shales. From these results and from the facts that permanganate in acetone solution is a more specific oxidizing agent and the oxidations are carried out with a large excess of reagent, more definite and reliable conclusions can be drawn about the structure of kerogen (or part of the kerogen). It is believed that this method could be successfully applied especially to those oil shales which are easily and completely oxidized by alkaline permanganate giving predominantly carbon dioxide and oxalic acid.

Table XI. Distillation of Ethyl Esters of Nonvolatile Acids from Oxidation of Shale Oil

Fraction	Boiling Range, *t* ° C./*p* Mm.	Saponification Value	Composition		Yield of Esters, Grams	Yield of Acids, Grams
			C, %	H, %		
I	91-101/13.5	389.1	65.43	9.83	3.18	2.56
II	103-115/13.5	367.8	65.99	10.05	2.70	2.20
III	116-128/13.5	346.1	67.70	10.68	4.89	4.04
IV	69- 88/0.09	329.1	68.65	10.71	6.74	5.63
V	88-103/0.09	351.0	69.30	9.99	9.25	7.63
VI	104-115/0.09	350.3	69.19	9.95	9.07	7.48
VII	118-132/0.09	298.4	70.56	10.62	6.54	5.56
VIII	133-139/0.09	294.6	72.09	10.95	5.49	4.68
IX	139-146/0.16	325.7	70.65	10.60	5.45	4.56
X	148-163/0.16	335.1	70.62	9.96	5.93	4.94
XI	165-178/0.27	283.7	72.15	10.45	5.95	5.11
XII	179-193/0.27	267.6	72.11	11.04	5.88	5.09
Residue	. . .	259.2	. . .	. . .	25.43	22.13

The oxidation products of the Aleksinac oil-shale kerogen have not yet been fully elucidated and neither is the exact balance of the organic carbon known. A complete analysis and identification of all the oxidation products call for a separate study and is now the subject of further investigation. For that reason, conclusions about a definite structure of the kerogen can not be advanced at present, but the following suggestions about the oxidized part of the Aleksinac oil-shale kerogen can be presented:

It consists of comparatively long aliphatic chains which are partly unsaturated (permanganate in acetone solution attacks the unsaturated bonds) and are probably interconnected by cross linkages (permanganate in acetone oxidizes, in part, tertiary and quaternary carbon atoms); the oxidation products are ether-soluble acids.

From the high yield of acids of higher molecular weight it can be concluded that the unsaturated bonds are mainly present as isolated double bonds.

The presence of polycarboxylic acids in the oxidation products can also be explained either by the fact that the aliphatic chains contain partially unsaturated hydroaromatic rings which would be oxidized at the double bonds to give two carboxyl groups or by the presence of shorter unsaturated side chains.

From what is known so far about the nature of the oxidation products of oil shale, it can be deduced that the acids obtained do not contain aromatic rings. This would point to the absence of benzenoid structures in that part of the kerogen which undergoes oxidation.

The hypothetic aliphatic chains in the oil-shale kerogen are cracked during the distillation of oil shale to give products of lower molecular weight. This would explain the fact that in the oxidation of shale oil, acids of similar nature are obtained, but with a lower average molecular weight.

If it is proved that the nonvolatile acids obtained by oxidation of shale oil contain aromatic rings, it can be presumed that these are formed during the distillation of oil shale or else that they are present in that part of the kerogen which is not oxidized, under the authors' experimental conditions, when the oil-shale concentrate is subjected to the action of potassium permanganate.

LITERATURE CITED

(1) Armstrong, E. F., Hilditch, T. P., *Chem. & Ind.* (*London*) **44,** 43-7T (1925).
(2) Bailey, A. E. W., Kimberley, I. E., Ward, S. G., *Fuel* **33,** 209-21 (1954).
(3) Bone, W. A., Horton, L., Ward, S. G., *Proc. Roy. Soc.* (*London*) **127A,** 480-510 (1930).
(4) Bone, W. A., Parsons, L. G. B., Sapiro, R. H., Groocock, G. M., *Ibid.*, **148A,** 492-522 (1935).
(5) Cane, R. F., *Australian Chem. Inst. J. & Proc.* **15,** 62-8 (1948).
(6) Cane, R. F., *J. Proc. Roy. Soc. N. S. Wales* **76,** 190-202 (1942).
(7) Cane, R. F., Oil Shale Cannel Coal, 2nd Conf., Glasgow, 1950, p. 592, Institute of Petroleum, 1951.
(8) Dancy, T. E., Giedroyc, V., *J. Inst. Petrol.* **36,** 607-23 (1950).
(9) Down, A. L., Himus, G. W., *Ibid.*, **27,** 426-45 (1941).
(10) Fomina, A. S., Pobul, L. Ya., *Izvest. Akad. Nauk Eston. S. S. R.* **4,** 48-56 (1955).
(11) Francis, W., *Fuel* **12,** 128-38 (1933).
(12) Himus, G. W., Oil Shale Cannel Coal, 2nd Conf., Glasgow, 1950, p. 112, Institute of Petroleum, 1951.
(13) Horton, L., *Fuel* **34,** 14-21 (1955).
(14) Houben-Weyl, "Methoden der Organischen Chemie," Bd. 2, p. 820, Stuttgart, 1953.
(15) Jovanović, S. Lj., Vitorović, D. K., *Glasnik Khem. Drushtva, Beograd* **17,** 347-60 (1952).
(16) Juettner, B., Smith, R. C., Howard, H. C., *J. Am. Chem. Soc.* **59,** 236-41 (1937).
(17) Karavaev, N. M., Vener, I. M., *Khimiya i Genezis Tverd. Goryuch. Iskopaemykh, Trudy I Vsesoyuz., Soveschaniya, Moskva,* **1950,** 367-85.
(18) Kent, C. R., *Australian Chem. Inst. J. & Proc.* **6,** 207-23 (1939).
(19) Khrisanfova, A. I., *Izvest. Akad Nauk S. S. S. R., Otdel Tekh. Nauk* **1949,** 1116-21.
(20) Kogerman, P. K., *Izvest. Akad. Nauk Eston. S. S. R.* **1,** 108-16 (1952).
(21) Kogerman, P. N., Inst. Petroleum Conf. June **1938,** p. 115, Institute of Petroleum, London.
(22) Lanin, V. A., Pronina, M. V., *Bull. acad. sci. U. R. S. S., Classe sci. tech.* **1944,** 745-51.
(23) Lyder, E. E., "Shale Oil," ACS Monograph Series, p. 106, Chemical Catalog Co., New York, 1925.
(24) McKee, R. H., Goodwin, R. T., *Ind. Eng. Chem.* **15,** 343-9 (1923).
(25) McKee, R. H., Goodwin, R. T., "Shale Oil," ACS Monograph Series, p. 74, Chemical Catalog Co., New York, 1925.
(26) McKee, R. H., Lyder, E. E., *Ind. Eng. Chem.* **13,** 613-8, 678-84 (1921).
(27) Marcusson, J. (Pueschel, F., Dierichs, A.), "Die Untersuchung der Fette und Oele," pp. 60, 78, Halle, 1952.
(28) Prien, C. H., Oil Shale Cannel Coal, 2nd Conf., Glasgow, 1950, p. 76, Institute of Petroleum, 1951.
(29) Robinson, W. E., Cummins, J. J., Stanfield, K. E., *Ind. Eng. Chem.* **48,** 1134-8 (1956).
(30) Robinson, W. E., Heady, H. H., Hubbard, A. B., *Ibid.*, **45,** 788-91 (1953).
(31) Smith, J. W., Mapstone, G. E., *Fuel* **36,** 191-204 (1957).
(32) Stefanović, Gj., Pejković, I., *Compt. rend.* **238,** 697-9 (1954).
(33) U. S. Bur. Mines, Rept. Invest. **5119,** Part II, 93 (1954).

RECEIVED for review April 22, 1958. Accepted September 15, 1958.

Nitrogen in Petroleum Asphalt

JOHN S. BALL, D. R. LATHAM, and R. V. HELM
Petroleum and Oil-Shale Experiment Station,
Bureau of Mines, U. S. Department of the Interior, Laramie, Wyo.

Nitrogen content is a property of asphalts that has not received the attention that its importance merits. Asphalt chemistry often is considered an extension of hydrocarbon chemistry, and the characteristics that are associated with the low-boiling fractions of petroleum are assumed to be slightly modified for asphalt. Asphalt, however, is composed essentially of nonhydrocarbon compounds containing sulfur, oxygen, and nitrogen.

This paper shows the importance of the nitrogen content through development of three concepts:

1. Most of the nitrogen in petroleum is found in the asphaltic fractions. Some asphaltenes contain as much as an average of two atoms of nitrogen per molecule.
2. Nitrogen not only forms an integral part of the high molecular weight compounds, but is so firmly combined that, upon pyrolysis, most of the nitrogen remains in the coke.
3. Nitrogen, and consequently asphalt, has significance geochemically as an indication of the degree of maturation or age of an oil.

These concepts have been developed from the results of the work of American Petroleum Institute Research Project 52b on the Nitrogen Constituents of Petroleum, as well as other Bureau of Mines projects. Project 52 is concerned chiefly with the distillable portions of the oil (*2, 4*); however, some information that applies to the asphaltic portions of the oil has been obtained. The project is studying intensively an oil from the Wilmington, Calif., field. A description of this oil has been published (*4*).

NITROGEN CONTAINED IN ASPHALT

A high percentage of the nitrogen content of a crude oil is normally found in its asphaltic fractions. For the purposes of this article, it is convenient to consider the residuum produced from the Bureau of Mines routine crude-oil analysis (*8*) as asphalt. This residuum (which is left after distillation to 300° C. at a pressure of 40 mm. of mercury) often is close to 100 penetration asphalt. Some comparisons taken from the data of Stanfield (*10*) are shown in Table I and indicate how well this relationship may be expected to hold. The nitrogen in a crude-oil residuum amounts to more than 85% of that in the crude oil, according to a study of 15 crude oils (*3*). For the Wilmington crude oil, the residuum amounts to 46.4 weight % and contains 1.20 weight % of nitrogen. Based on the crude oil nitrogen value of 0.65%, 85.7% of the nitrogen in the crude oil is found in the residuum.

A more detailed examination of the Wilmington residuum