Composition of Low-Temperature Thermal Extracts from Colorado Oil Shale

Three articles, also from the Symposium on Tars, Pitches, and Asphalts, Division of Gas and Fuel Chemistry, 135th Meeting, ACS, will appear in the February 1960 issue of *Industrial and Engineering Chemistry*: "Processing Low-Temperature Lignite Tar," H. R. Batchelder, R. B. Filbert, Jr., and W. H. Mink (p. 131); "Chemicals from Low-Temperature Carbonization of Coal," E. W. Lang and J. C. Lacey, Jr. (p. 137); "Solvent Refining of Low Temperature Tar with Paraffinic Solvent," M. D. Kulik and M. B. Neuworth (p. 141).

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INFORMATION CONCERNING the constitution of the kerogen present in oil shale, the processes by which it is degraded to useful products, and the composition of its degradation products is needed for developing new and more economical methods of processing this natural resource. Information concerning the nature of the low-temperature pyrolytic products from kerogen was obtained and related to the constitution of kerogen.

The oil shale used in this study is a sedimentary rock containing various amounts of organic material (commonly called kerogen), which was derived from aquatic organisms. Associated with the kerogen are quantities of calcite and dolomite, with smaller amounts of clay minerals, quartz, pyrite, etc. The kerogen is a light-brown mixture of solids having no appearance of oil and is only partly soluble in organic solvents at room temperature. At present, it has not been possible to separate the organic and inorganic phases completely; consequently, most kerogen constitutional studies have been conducted on degradation products.

One method of degradation consists of heating kerogen at various temperatures to obtain soluble products. When oil shale is retorted at about 500° C. (932° F.), its kerogen can be converted to crude shale oil, gases, and carbon residue. As approximately 35% of the kerogen is cracked to gases and carbon residue by retorting, this method of degradation is not suitable for constitution studies. Kerogen can also be converted to soluble products at temperatures from 200° to 350° C. (392° to 662° F.) however, at a much slower rate. Extensive cracking of kerogen does not occur at these temperatures; consequently, the soluble products obtained by this thermal degradation should contain many of the structures present in the original kerogen.

Samples of raw oil shale were extracted with Tetralin at 25° to 350° C. for 24 to 144 hours. As a result, kerogen was degraded to a soluble material, with production of no or very little pyrolytic gases at 300° C., and only about 6% of the kerogen was degraded to gases at 350° C. There was no evidence of the formation of carbon residue at any temperature. The crude extracts were fractionated into oils, waxes, resins, and pentane-insoluble material and were characterized by ultimate analyses, ring analyses, x-ray diffraction, mass and infrared spectra, and chemical treatment.

This study showed that the composition of the extracts depended upon the time and temperature of extraction. At constant time of extraction, the amount of wax and pentane-insoluble material increased and the percentage of resins decreased with increase in temperature of extraction over the range studied and the percentage of oil remained nearly the same. At constant temperature of extraction (350° C.), the percentage of pentane-insoluble material decreased while the oil, wax and resins content increased with increase in extraction period. Based upon the composition of the extracts, the kerogen structure appears to be predominantly of a saturated heterocyclic nature with smaller amounts of cyclic paraffins, straight-chain paraffins, and aromatic portions constituting the remainder of the structure. These conclusions supplement those reported earlier (*7, 8*) from oxidation studies.

EXPERIMENTAL PROCEDURE

Materials. Alumina XF21 grade, 80–200 mesh (Aluminum Co. of America), preheated at 700° C. (1292° F.) for 2 hours before use.

Silica gel, analytical grade, 28–200 mesh (Davidson).

Tetralin, $C_{10}H_{12}$, b. p. 205–08° C. (Matheson, Coleman, and Bell), contained 0.04% residue after steam distillation. When heated to 350° C. for 48 hours in absence of air, the purified Tetralin contained an additional 0.05% residue after steam distillation.

Apparatus. Reaction vessel, 2000-ml. pressure apparatus (Parr Instrument Co. Series 4500) equipped with stirring mechanism to stir contents 1 minute of each 30 minutes of extraction.

Chromatographic columns, glass columns having three sections (lower section 1.0 x 85 cm., middle section 1.5 x 42 cm., and top 3.5 x 22 cm.), water-jacketed, and fitted with adapter so 10- to 15-p.s.i.g. nitrogen pressure could be applied to the column.

Oil-Shale Sample. The oil shale was obtained from the Mahogany zone of the Green River formation at the Bureau of Mines experimental mine near Rifle, Colo. The sample contained approximately 35% organic material (28.5% organic carbon) and assayed 66 gallons of oil per ton of shale by the modified Fisher-retort method (*9*). For use in this study, the shale was crushed and screened to pass a sieve of 100 meshes per inch.

Preparation of Extracts. Successive batches of 350 grams of oil shale were placed in the reaction vessel with 810 ml. of Tetralin (2.3 ml. of Tetralin per gram of shale), and each batch was extracted 48 hours at temperatures from 25° to 350° C. (Two other series of extractions were made using Tetralin as solvent for 48 and 144 hours at 200° C., and 24, 48, 96, and 144 hours at 350° C.) After cooling to room temperature, the vessel was opened and the contents were removed. The shale residue was centrifuged from the extract and solvent, then was extracted with benzene until free of Tetralin and soluble material. The shale residue was air-dried and was retained for analysis. The Tetralin and benzene extracts were combined and then were steam-distilled to remove the solvents. After removal of the Tetralin, the extract was removed from the water phase by solution in benzene. Most of the water was removed from the benzene solution of the soluble extract by means of a separatory funnel and the last trace by azeotropic distillation. Benzene was removed from the extract by atomospheric distillation and the final traces by drying at 80° C. under reduced pressure. (All extracts were dried under these conditions.) By treating several batches of oil shale at different temperatures in the presence of Tetralin for 48 hours, the following total amounts of extracts were obtained: 77 grams of extract at 25° C., 18 grams at 200° C., 165 grams at 250° C., 165 grams at 300° C., and 106 grams at 350° C.

The percentage of kerogen not extracted from the raw shale was determined from comparison of the kerogen-to-ash ratios obtained before and after the oil shale was extracted. (All percentages are calculated on a weight basis except where indicated differently.) Following is an expression of this relationship:

$$\left[\frac{\text{Kerogen after extraction, \%}}{\text{Ash after extraction, \%}} \div \frac{\text{kerogen before extraction, \%}}{\text{ash before extraction, \%}}\right] \times 100 = \text{unextracted kerogen, \%}$$

The percentage of kerogen was determined from ash and mineral carbon dioxide analyses and equalled 100 minus the sum of the ash and mineral carbon dioxide. This method of computing the percentage of kerogen decomposed was based upon the assumption that the mineral portion of the raw oil shale was unaltered by the thermal solution treatment.

The extractions were made at the pressure generated by the solvent plus pyrolytic gases that formed at the temperature of extraction. Hot pressures ranged from 80 p.s.i.g. at 250° C. to 700 p.s.i.g. at 350° C., while cold pressures ranged from 40 p.s.i.g. for the 250° C. extraction to 200 p.s.i.g. for the 350° C. extraction (pyrolytic gases).

The dried extracts were fractionated by a procedure outlined in Figure 1. The purpose of these fractionations was to obtain materials of similar properties for further analyses and study. Because of the complex nature of the material, the method of fractionation employed was not expected to separate individual components.

Fractionation of Extracts into Oils, Waxes, Resins, and Pentane-Insoluble Material. Ten-gram batches of the crude extracts were dissolved in a 40 to 1 volume ratio of pentane and allowed to stand overnight at 0° C. and then filtered. The pentane-insoluble material was washed with a small quantity of cold pentane (0° C.) and then dried, weighed, and designated as pentane-insoluble material. The soluble material was stripped free of pentane, dried, and weighed. Five-gram batches of the pentane-soluble material were placed on a prewetted column of alumina (25 to 1 weight ratio of alumina to sample) and eluted with pentane followed by benzene-methanol mixtures and acetone. The pentane-eluted material (oil plus wax) was stripped free of pentane, dried, and weighed. The material remaining on the column was removed by benzene-methanol mixtures and acetone. This material, referred to as resins, was stripped free of solvent, dried, and weighed. Five-gram batches of the oil and wax fraction were dissolved in a 40 to 1 volume ratio of 2-butanone (methyl ethyl ketone) and allowed to stand at −5° C. for 1 hour. The wax was filtered from the 2-butanone-soluble material, dried, and weighed. The 2-butanone was removed from the oil by distillation, and the latter was dried and weighed.

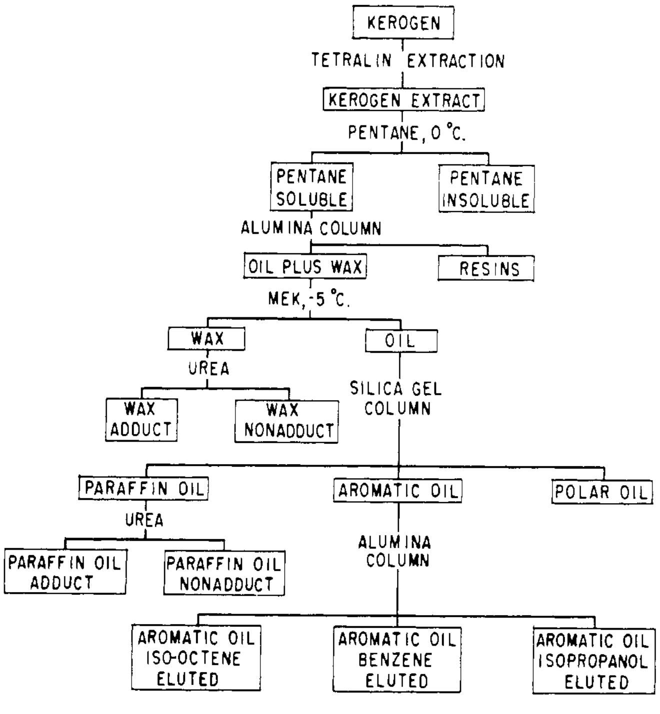

Figure 1. Flow diagram of fractionation procedure

Fractionation of Waxes. Urea adducts were prepared by reacting each gram of wax with 21 ml. of a saturated solution of urea in methanol. Excess urea amounting to 1.5 grams per gram of wax plus 6 or 7 drops of benzene was added. This mixture was stirred at room temperature for 14 to 24 hours. The adduct and nonadduct waxes were separated by filtration; the final traces of nonadduct material were removed by washing with 100 ml. each of pentane and iso-octane. The adduct was then decomposed with hot water and, after cooling, extracted from the water phase by ether. The adduct wax was freed from ether, dried, and weighed. The pentane–iso-octane–methanol solution of the nonadduct was freed from urea by washing with water. The nonadduct wax was freed of solvent by distillation, dried, and weighed.

Fractionation of Oils. The oil was fractionated by a method similar to that reported by Mair, Marculartis, and Rossini (*4*). Four-gram batches of the oil fraction were placed on a prewetted column of silica gel (25 to 1 weight ratio of silica gel to sample) and eluted successively with iso-octane, benzene, and 2-propanol. The three fractions were freed of solvent, dried, and weighed. The iso-octane–eluted material was called paraffin oil, the benzene-eluted material was called aromatic oil, and the 2-propanol–eluted material was called polar oil. The paraffin oil was further fractionated into paraffin-oil adduct and paraffin-oil nonadduct by the technique used for waxes. Additional fractionation of the aromatic oil was obtained on a prewetted column of alumina (25 to 1 weight ratio of alumina to sample) by using iso-octenes, benzene, and 2-propanol as eluting solvents. The solvent was removed from each of the fractions, and the oil was dried and weighed.

Physical Properties. The ultimate composition of the crude extracts and the various fractions was determined by conventional methods of analysis: Carbon and hydrogen were determined by a combustion train, nitrogen by Kjeldahl digestion, sulfur by ignition in a Parr oxygen bomb, and oxygen by difference. Densities were determined using pycnometers at 20° or at 40° C. and converting to d_4^{20}. Refractive indices were determined using the sodium *D* line (589 A.) and the mercury *g* line (436 A.) and were used to calculate specific dispersion for the aromatic fractions. Molecular weights were determined by the rise-in-boiling-point method using benzene as the solvent. Infrared, ultraviolet, and mass spectra, as well as x-ray diffraction, were used to characterize the various fractions.

Chemical Properties. The fractions were oxidized with an excess of aqueous alkaline potassium permanganate at reflux temperature for 100 hours by a method used previouly by Robinson and others (*8*). Concentrated hydriodic acid (70%) was used to reduce the resin and pentane-insoluble fractions by a method described by Raudsepp (*6*) in which the fraction plus hydriodic acid was sealed in a glass tube and heated 24 hours at 200° C. Basic nitrogen was determined for the resin and pentane-insoluble fractions by a method described by Deal and others (*2*), in which total basic nitrogen was determined by titration with perchloric acid. Neutral nitrogen compounds were determined as the difference between the basic nitrogen and the total nitrogen. Neutralization values were determined by the standard method (*1*) for petroleum products.

EXPERIMENTAL RESULTS AND DISCUSSION

Rate of Product Formation. The amount of kerogen converted to degradation products by thermal solution in Tetralin was dependent upon the temperature and time of extraction. For constant periods of extraction of 48 hours and varying the temperature from 25° to 350° C., the conversion of kerogen to degradation products increased (Table I). By maintaining the temperature constant at 200° C. and varying the time of extraction from 48 to 144 hours, the yield of products increased slightly. A comparable series of extractions at constant temperature of 350° C. and for extraction times from 24 to 144 hours, showed an increase in product yield; however, most of the product was obtained during the first part of the extraction, as 80% of the total (for 144 hours) was obtained after 24 hours. An additional 10% was formed in a subsequent 24-hour period with the final 10% requiring 96 more hours of extraction. This suggests that at lower temperatures, where low yields of product were obtained, it would be impossible in finite time to obtain 100% conversion of kerogen to souble products. Landau and Asbury (*3*) showed that a straight-line relationship existed between time of extraction and time of extraction divided by percentage yield of extract and that the slope of the line showed the ultimate yield of extract which could be obtained from coal. The calculated ultimate yield from a similar plot of data obtained from oil shale in this study was 9.6% at 200° C. and 100% at 350° C.

The influence of temperature on the conversion of kerogen to soluble material at constant heating time is shown in Table I. A gradual increase in yield of product per degree rise in temperature was obtained from 25° to 250° C., while from 300° to 350° C. a rapid increase in yield per degree rise in temperature was obtained. A plot of these data (not shown) suggested that a change in the thermal solution process took place at approximately 275° C.

Thompson and Prien (*10*) reported a similar relationship at 300° C. and suggested that the reaction taking place below 300° C. was the desorption of macromolecules of kerogen in which bond energies comparable to van der Waals forces were ruptures. Above 300° C. other secondary bonds were broken. Similar reasoning would indicate that the composition of the products obtained below 300° C. should differ from those obtained above 300° C. Likewise, the molecular weights of the crude extracts obtained at the two temperatures ranges probably would be different. Data presented later only partly confirm these statements.

Ultimate Composition of Crude Extracts. The sulfur and oxygen contents (Table II) of the extracts decrease with increase in temperature and time of extraction. This showed that structures which contained these elements were readily susceptible to thermal degradation. By contrast, the nitrogen structures in kerogen were difficult to degrade, and only a small amount of the kerogen nitrogen was evolved in the form of gases. In tests (Figure 2) where the time of extraction was constant at 48 hours and temperature increased, loss of oxygen (probably decarboxylation and dehydration) from the extracts occured between 200° and 250° C. and continued to 350° C., where only a small portion of the original kerogen oxygen remained in the extract. Sulfur contents remained high until a temperature of 350° C. was reached, when loss of sulfur (probably as H_2S) began. Hydrogen contents remained almost equal to that of the original kerogen over the temperature range. However, nitrogen contents of the extracts increased very rapidly at 300° C. with increase in temperature of extraction and nearly equaled that of kerogen in the 350° C. extract. In the tests where temperature remained constant at 350° C.

Table I. Yield of Extract

Time, Hr.	Temp., ° C.	Kerogen Extracted, %
48	25	4.4
48	200	8.8
48	250	10.2
48	300	28.7
48	350	84.9
144	200	9.3
24	350	75.8
96	350	87.9
144	350	94.5

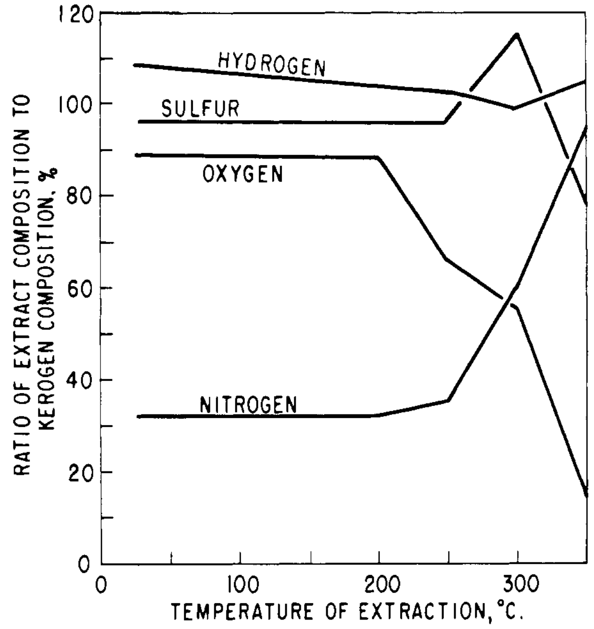

Figure 2. Relationship of extract composition to temperature of extraction for constant period of time

Table II. Ultimate Composition and Molecular Weight of Crude Tetralin Extracts

Temp. ° C.	Time, Hr.	C	H	O[a]	N	S	Atomic Ratios × 10^2 H/C	O/C	N/C	S/C	Molecular Weight
25	48	80.4	11.1	6.5	0.9	1.1	166	6.1	0.9	0.5	580
200	48	80.8	10.7	6.6	0.9	1.0	159	6.1	0.9	0.5	595
250	48	82.2	10.9	4.9	1.0	1.0	159	4.5	1.0	0.5	555
300	48	82.4	10.5	4.2	1.6	1.3	153	3.8	1.7	0.6	580
350	24	82.7	10.8	3.5	2.4	0.6	157	3.2	2.5	0.3	625
350	48	84.1	11.3	1.0	2.6	1.0	161	0.9	2.7	0.4	535
350	96	85.1	11.0	1.0	2.6	0.3	155	0.9	2.6	0.1	405
350	144	84.7	10.6	1.7	2.6	0.4	150	1.5	2.6	0.2	410

[a] Oxygen determined by difference.

and the time of extraction varied, similar trends for oxygen and sulfur were obtained (Figure 3) as oxygen and sulfur contents decreased with time of extraction. Nitrogen contents remained nearly constant while the hydrogen contents decreased after 48 hours of extraction. No significant differences were found in the molecular weights of the crude extracts (Table II) which were prepared at 25° to 350° C. and 48 hours of extraction time. However, molecular weights of the extracts decreased with increase in time of extraction at constant temperature of 350° C.

Pyrolytic Gases. Approximately 60% of the pyrolytic gas was hydrogen, some of which may have resulted from the dehydrogenation of the Tetralin used as solvent. At 350° C. approximately 28% of the oxygen and 19% of the sulfur present in kerogen were removed as pyrolytic gases (Table III) compared to about 3% of the total carbon. This suggested that at this temperature oxygenated groups such as carboxyl or others were degraded to carbon dioxide and carbon monoxide, while sulfur groups such as sulfides or others were degraded to H_2S. By contrast, only a small portion of the kerogen was degraded to gases at 25° to 300° C. Based on the total kerogen, approximately 6% of the kerogen was degraded to gases at 350° C., 0.2% at 300° C., and 0.09% at 250° C. This shows that little of the kerogen was cracked to final degradation products at 300° C. (and below) with only a small amount of kerogen being converted to gas at 350° C. Also, there was no evidence of the formation of carbon residue at any temperature. Consequently, extracts prepared at these temperatures should contain many of the structures present in the original kerogen.

Table III. Gases Produced by Degradation of 1 Kg. of Kerogen

	Degradation Temp., ° C.		
	250	300	350
	Gas Produced, Moles		
Methane	0.003	0.005	0.578
Ethane	...	...	0.163
Propane	0.004	0.008	0.078
n-Butane plus isobutane	...	...	0.020
n-Pentane plus isopentane	...	...	0.007
Carbon dioxide	0.007	0.013	0.637
Carbon monoxide	0.011	0.021	0.013
Hydrogen	0.040	0.081	2.677
Hydrogen sulfide	...	...	0.065
Nitrogen	...	...	0.208
Total	0.065	0.128	4.446

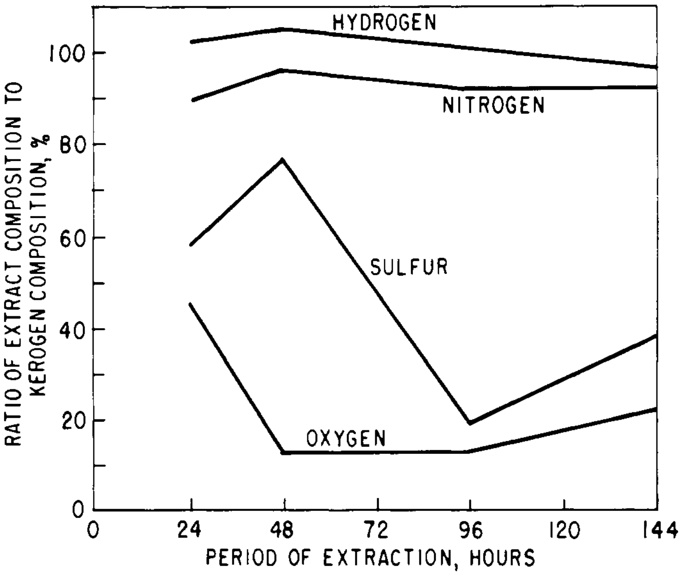

Figure 3. Relationship of extract composition to period of extraction at constant temperature

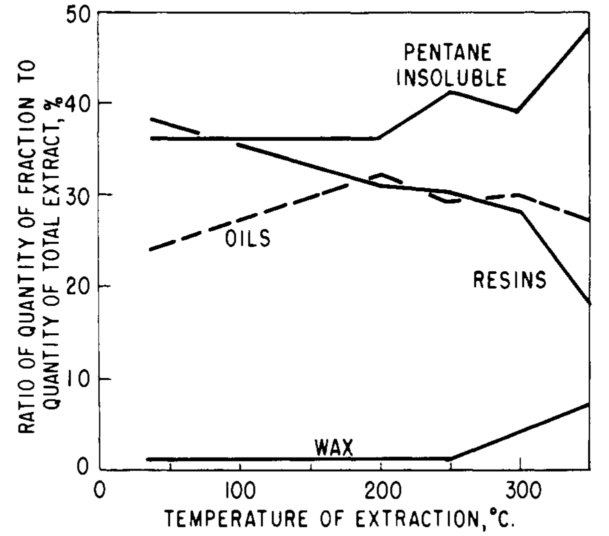

Figure 4. Relationship of fraction distribution to temperature of extraction

Product Distribution. The percentage of pentane-insoluble material in the extracts increased with increase in temperature of extraction at 250° to 350° C. (Figure 4), while the

Table IV. Ultimate Composition and Molecular Weights of the Major Fractions

	C	H	O[a]	N	S	Molecular Weight
	25° C. Extract					
Pentane-insoluble material	80.1	11.3	7.4	0.2	1.0	1320
Resin	78.9	11.0	7.8	0.9	1.4	625
Wax	83.6	13.8	2.3	0.2	0.1	415
Oil	86.7	12.2	0.7	0.1	0.3	350
	200° C. Extract					
Pentane-insoluble material	78.3	10.5	8.6	1.7	0.9	1250
Resin	80.3	10.8	6.5	1.1	1.3	605
Wax	84.8	13.8	0.8	0.2	0.4	480
Oil	86.5	12.4	0.5	0.1	0.5	350
	250° C. Extract					
Pentane-insoluble material	81.4	10.6	4.8	2.2	1.0	1290
Resin	79.9	10.4	7.0	1.5	1.2	570
Wax	84.6	14.3	0.9	0.1	0.1	440
Oil	87.2	11.7	0.7	0.1	0.3	365
	300° C. Extract					
Pentane-insoluble material	81.4	10.3	4.0	3.0	1.3	1210
Resin	78.3	10.4	8.6	1.8	0.9	650
Wax	84.8	13.9	1.0	0.1	0.2	415
Oil	87.5	11.7	0.2	0.1	0.5	340
	350° C. Extract					
Pentane-insoluble material	81.2	9.9	4.1	3.8	1.0	1280
Resin	83.3	10.9	2.4	2.9	0.5	575
Wax	86.1	13.3	0.2	0.2	0.2	355
Oil	86.8	12.2	0.3	0.4	0.3	375

[a] Determined by difference.

wax content of the extracts increased at 300° and 350° C., where time of extraction was constant at 48 hours. By contrast, resin contents decreased continuously with increase in temperature over the temperature range. Oil content increased at 200° C. and decreased slightly at 350° C. This showed that the composition of the extracts was dependent upon the temperature of extraction. Ultimate compositions and molecular weights of these fractions are shown in Table IV.

In the series of tests at 350° C., where time of extraction was varied from 24 to 144 hours, pentane-insoluble material decreased from 48 to 21% with increase in time of extraction. On the other hand, resins increased from 18 to 29%, oils from 27 to 37%, and wax from 7 to 13%. Approximately one half of the pentane-insoluble material was degraded into oil, wax, and resin at 350° C. after 144 hours of extraction.

Constitution of Waxes. The constitution of the wax fractions produced at the temperatures studied showed limited variation. The percentage of adduct (predominantly straight-chain structures) obtained from the wax tended to decrease with increase in temperature of extraction (see Table V). Also, the nonadduct wax was predominantly naphthenic. Mass spectra showed that the straight-chain portion of the waxes tended to decrease in carbon-chain length as the temperature of extraction increased—for example, the average chain length was 30 for the 25° C. wax adduct, 28 for 250° C. wax adduct, and 25 for 350° C. wax adduct. X-ray diffraction showed that the nonadduct wax fractions had an average chain length less than 16 carbon atoms. The wax fractions contained an average of 2.0 to 2.4 methyl groups per molecule, which indicated little or no branching. The cyclic portion of the wax contained 1 to 6 rings with 3 to 4 rings predominating. The average molecular weight of the crude-wax fraction (before fractionation by the formation of urea adducts) ranged from 355 to 480 (Table IV) and tended to decrease with increase in temperature of extraction from 25° to 350° C. Ultimate composition of the unfractionated wax showed only minor variations.

Constitution of Oils. The composition of the oil fractions tended to become more aromatic and less paraffinic with increase in temperature of extraction (Figure 5). In general, the percentage of paraffin oil nonadduct decreased with increase in temperature of extraction, the aromatic and polar oil fractions increased with increase in temperature, while the paraffin oil adduct remained nearly the same. Utilizing physical property data, ring analyses were determined for the paraffin oil nonadduct fraction by the n-d-M method (*11*) and for the aromatic oil by the Martin method (*5*). Mass spectra were used to determine the amount of straight-chain and cyclic paraffins present in the paraffin oil adduct and nonadduct fractions. The results of these analyses are shown in Table VI. Based on these data, approximately 33% of the 25° C. oil consisted of paraffinic, 48% naphthenic, 16% aromatic, and 3% polar oil. The 350° C. oil was more aromatic because it contained 18% paraffinic, 26% naphthenic, 36% aromatic, and 20% polar oil.

Table V. Carbon Distribution of Wax Fractions

Temp., ° C.	Carbon-Type Composition % C_P	% C_N	Percentage of Total Wax
	Wax (adduct)[a]		
25	91	9	72
250	88	12	56
350	88	12	51
	Wax (nonadduct)[a]		
25	22	78	28
250	34	66	44
350	22	78	49

[a] Determined from mass spectra.

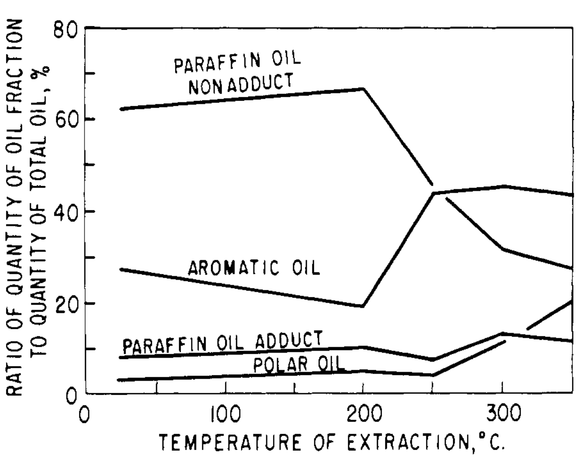

Figure 5. Relationship of the distribution of oil fractions to temperature of extraction

The percentage of aromatic compounds in the 350° C. may be erroneously high because of extraneous materials that were obtained from the Tetralin used as solvent. Based upon the amount of extract produced and the amount of Tetralin residue obtained at 350° C., approximately 0.7% of the total extract may have been derived from the Tetralin. Because of small yields, as much as 5% of the total 25° C. extract may have come from this source. The composition of the 350° C. oil was corrected for a maximum amount of 5% (based on total oil) of aromatic oil which may have been derived from the solvent. After this correction, the 350° C. oil contained approximately 19% paraffinic, 27% naphthenic, 33% aromatic, and 21% polar oil.

The paraffin-oil adduct fraction had an average of 2.6 to 3.4 rings per molecular, the paraffin-oil nonadduct had 2.8 to 5.1 rings per molecule, and the aromatic oil eluted with iso-octenes had an average of 3.0 to 4.0 rings per molecule. (The latter fraction represented 95% of the aromatic oil.) The aromatic-oil fraction (iso-octene eluted) had an average of 22 carbon atoms per molecule and a determined molecular weight of 305. Mass spectra of this fraction showed that it contained mostly indanes, Tetralins, benzenes, and indenes with smaller amounts of naphthalenes, acenaphthenes, acenaphthylenes, phenanthrenes, and anthracenes.

The molecular weight of the oil fraction before fractionation ranged from 340 to 375 (Table IV) and showed no correlation to temperature of extraction. Also, the elemental composition of the oil fractions showed very little variation.

Constitution of Resins. Significant differences in the elemental composition of the resin fractions were found (Figure 6). In general, oxygen, hydrogen, and sulfur contents of the resin fractions decrease with increase in temperature of extraction. The oxygen content of the resins decreased at temperatures from 25° to 200° C., reached a maximum at 300° C., and decreased very rapidly at 350° C. This showed that rapid degradation of oxygenated structures occured between 300° and 350° C., probably resulting in the formation of carbon monoxide and carbon dioxide. Hydrogen-to-carbon ratios gradually decreased over the temperature range indicating the presence of an easily dehydrogenated material, while sulfur contents tended to decrease only at the higher temperatures. By contrast, nitrogen-to-carbon ratios increased with increase in temperature over the temperature range.

Table VI. Ring Analysis and Molecular Weight of Oil Fractions

Temp., ° C.	% C_P	% C_N	% C_A	Molecular Weight
	Paraffin Oil (Adduct)[a]			
25	28	72	0	405
250	20	80	0	380
350	18	82	0	285
	Paraffin Oil (Nonadduct)[a]			
25	4	96	0	430
250	6	94	0	415
350	19	81	0	370
	Paraffin Oil (Nonadduct)[b]			
25	37	57	6	430
250	25	75	0	415
300	41	58	1	345
350	50	47	3	370
	Aromatic Oil (Iso-octene Eluted)[c]			
25	30	25	45	300
250	17	37	46	290
350	7	12	81	305

[a] Determined from mass spectra.
[b] Determined by n-d-M method. (*11*).
[c] Determined by Martin method (*5*).

The resin fraction obtained from the 350° C. extract was subjected to oxidation by an aqueous solution of alkaline potassium permanganate and approximately 75% of the resin was unoxidized. Comparable tests on the oil fraction from this extract showed that 71% of the oil remained unoxidized, also, comparable ratios of potassium permanganate to carbon were consumed in both tests. This shows that approximately the same proportion of structures, which are resistant to oxidation, are present in the resins as are present in the oils. The resin contained 3.0% nitrogen; however, this did not alter the oxidation appreciably from that of the oil which contained only 0.4% nitrogen. This suggested the presence of cyclic nitrogen structures which may be stable to potassium permanganate oxidation.

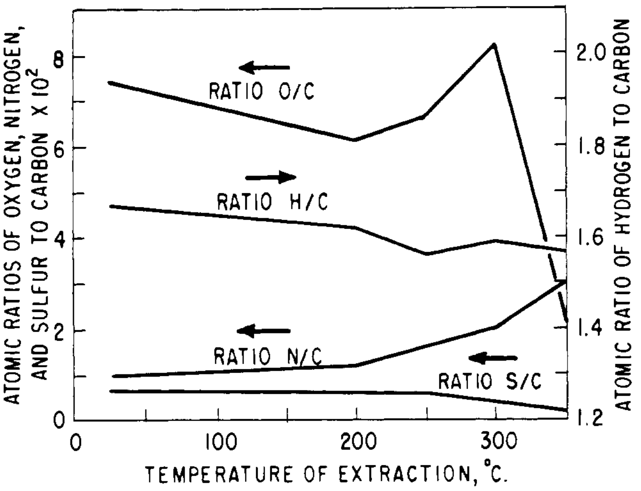

Figure 6. Composition of resin fraction at various temperatures

The 350° C. resin fraction was subjected to reduction by hydriodic acid; approximately 38% of the resin was reduced to oil, 2% to wax, and 60% remained unchanged. This indicated that approximately 40% of the resin had structures similar to that present in the oil and wax fractions.

Infrared spectra of the resin fractions indicated the presence of hydroxyl and carbonyl groups and that the amount of hydroxyl groups tended to increase with increase in temperature of extraction. The band indicating the presence of four or more methylene groups appeared to be weak which showed the presence of only small amounts of large side chains. Carboxyl groups, in addition to hydroxyl groups, appeared to present in the extracts prepared at higher temperatures.

Determination of basic nitrogen and neutralization numbers for the resin fractions (Table VII) showed that there appeared to be no relationship between these values and the temperature of extraction.

Molecular weights of the resin fractions ranged from 570 to 650 (Table IV) and did not appear to be related to temperature of extraction.

Constitution of Pentane-Insoluble Material. Elemental composition of the pentane-insoluble fractions (Figure 7) showed trends similar to those of the resin fractions. In general, oxygen, hydrogen, and sulfur contents decreased with increase in temperature of extraction, while nitrogen contents increased with temperature of extraction. Analyses

Table VII. Basic and Acidic Constituents

Temp., ° C.	Basic N, %	Neutralization Number	Acid Groups Per Mole
	Resin Fraction		
25	30.0	6.8	0.8
200	34.5	8.5	0.9
250	29.7	6.5	0.7
300	33.6	4.9	0.6
350	30.0	6.6	0.7
	Pentane-Insoluble Fraction		
25	40.9	59.4	1.4
200	42.6	61.7	1.4
250	25.2	43.6	1.0
300	34.8	42.6	0.9
350	35.8	40.9	0.9

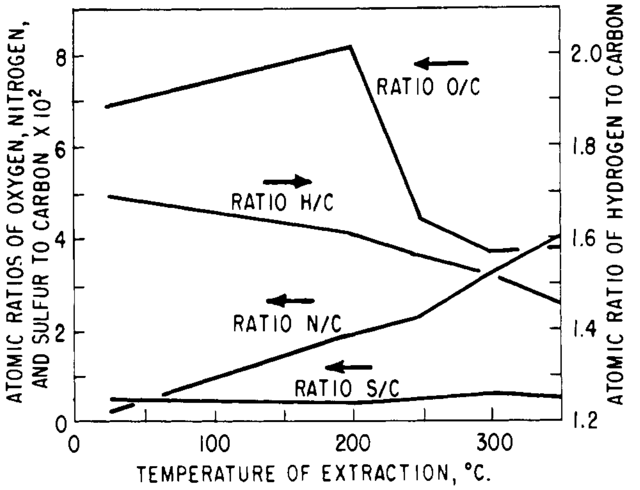

Figure 7. Composition of pentane-insoluble fractions

of the resin and pentane-insolubles suggested the following: (1) The decrease in oxygen to carbon and increase in nitrogen to carbon ratios obtained in the crude extracts was attributed to differences in the elemental composition of the resin and pentane-insoluble fractions present in the crude extracts. (2) A large portion of the oxygen structures present in the pentane-insoluble and resin fractions appeared to be unstable at temperatures above 200° and 300° C., respectively, and may indicate the presence of different type oxygen structures. (3) Nitrogen structures appeared to be more stable than oxygen structures and were more difficult to make soluble. Based upon bond energies, this suggested that more nitrogen is present in kerogen in the form of C═N than C—N. (4) A large portion of nitrogen-containing structures, which normally degrades to coke and gas during retorting, was converted into resins and pentane insolubles by low-temperature thermal solution. (5) Loss of hydrogen indicated the presence of easily dehydrogenated cyclic structures. (6) Sulfur structures were evenly distributed in the soluble products and were stable to 300° C. where loss of resin sulfur occured. (7) The pentane-insoluble material produced at higher temperatures contained less hydrogen and more nitrogen than the resins.

Oxidation of the 350° C. pentane-insoluble material in a manner similar to that used for resins showed that 25% of this fraction was resistant to oxidation compared to 70 to 90% for resins, oils, and waxes and only 5% for kerogen. This showed that the pentane-insoluble fraction contained fewer structures which were resistant to oxidation than the oil, wax, or resin fractions. About 40% of the pentane-insoluble material was oxidized to nonvolatile nonoxalic acid compared to 1% for kerogen, 9% for resins, 17% for oil, and 0% for waxes. This suggested the presence of benzenoid acids that may have been derived from benzenoid structures present in the pentane-insoluble material. These structures may have not been present in the kerogen as such but were formed during the thermal solution by dehydrogenation of partly unsaturated cyclic structures.

A comparable reduction test to that used for the resin fraction was made on the pentane-insoluble material. Approximately 25% of the material was reduced to oil, wax, and resins and 75% remained unchanged. These data showed that approximately 25% of the pentane-insoluble material contained structures similar to oils, waxes, and resins.

Infrared spectra of the pentane-insoluble fraction indicated the presence of hydroxyl, carboxyl, and aromatic groups. The structure appeared to be predominantly cyclic but may contain considerable chain branching and substitution at the higher temperatures of extraction.

Basic nitrogen and neutralization numbers for the pentane-insoluble fractions (Table VII) indicated that the amount of basic and acidic constituents in these fractions decreased with increase in temperature of extraction. Also, the pentane-insolubles in most cases contained more basic nitrogen and had more acid groups per mole than corresponding resin fractions.

Molecular weights of the pentane-insoluble material ranged from 1210 to 1320 and showed no relationship to temperature of extraction.

SUMMARY AND CONCLUSIONS

The elemental composition of the oil and wax produced over the temperature range remained nearly the same. By contrast, the composition of the resin and pentane-insoluble fractions depended upon temperature of extraction; however, no correlation was established between the composition of extracts and the increased rate of conversion to degradation products obtained at about 275° C. Oxygen content of the resin and pentane-insoluble fractions decreased with increase in temperature of extraction and indicated that oxygen structures present in kerogen are readily degraded. Nitrogen content of the resin and pentane-insoluble fractions increased with increase in temperature of extraction and indicated that nitrogen structures present in kerogen are stable and are not readily made soluble. Although differences were found in the composition of the extract fractions, the average molecular weights of the oil, wax, resin, and pentane-insoluble fractions did not change appreciably with increase in temperature of extraction.

The large yield of extract obtained at 350° and the increase in nitrogen content of the resin and pentane-insoluble fractions suggested that the thermal solution process solubilized structures having high nitrogen content which are normally degraded to gases and carbon residue during retorting. This suggests the presence of two different forms of kerogen, one with a low nitrogen content and another with a high nitrogen content and that the latter is more difficult to make soluble.

At temperatures from 25° to 350° C., kerogen was degraded to approximately 4 to 6% paraffinic carbon, 13 to 18% naphthenic carbon, 3 to 10% aromatic carbon, and 71 to 75% hetero material. Based upon the composition of the extracts and the fact that the hetero material contained some hydrocarbon structures, the kerogen structure may consist of approximately 5 to 10% straight- and branched-chain paraffins containing 25 to 30 carbon atoms, 20 to 25% naphthenic and 10 to 15% aromatic structures having an average of 3 to 5 rings per molecule, and 45 to 60% hetero material which is predominantly cyclic. This suggests that Colorado oil-shale kerogen is predominantly a heterocyclic material connected to or associated with smaller amounts of hydrocarbon material consisting of straight- and branched-chain paraffin, cyclic paraffin, and aromatic groups.

ACKNOWLEDGMENT

This work was done under a cooperative agreement between the Bureau of Mines, United States Department of the Interior and the University of Wyoming. The authors express their appreciation to G. L. Cook, D. G. Earnshaw, and F. R. McDonald for mass, infrared, and ultraviolet spectra analyses; to H. N. Smith and W. A. Robb for x-ray diffraction analyses; and to J. A. Lanum, Jr., and W. J. Lanum for other analyses presented in this report.

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RECEIVED for review August 19, 1959. Accepted October 19, 1959.

Division of Gas and Fuel Chemistry, Symposium on Tars, Pitches, and Asphalts, 135th Meeting, ACS, Boston, Mass., April 1959.