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Composition of Low-Temperature Thermal Extracts Obtained from Colorado Oil-Shale Kerogen

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The oil shale used in this study is a sedimentary rock containing various amounts of organic material (commonly called kerogen), which was derived from decomposition of aquatic organisms. Associated with the kerogen are large 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 retorted at about 500° C. (932° F.), kerogen can be converted to crude shale oil, gases and carbon residue. As approximately 35 percent 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 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 pentane-insoluble material increased with increase in temperature of extraction, while the percentage of resins decreased with increase in temperature over the range studied. The percentage of oil remained nearly the same, while the wax content increased slightly at the higher temperatures. The composition of the extracts indicated that kerogen is composed predominantly of saturated heterocyclic structures and smaller amounts of straight-chain paraffins, cyclic paraffins, and aromatic structures. These conclusions agree with and supplement those reported earlier (6,7) from oxidation studies.

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. It was the purpose of this study to obtain information concerning the nature of kerogen and the low-temperature pyrolytic products obtained from it.

EXPERIMENTAL PROCEDURE

Materials. Alumina XF21 grade, 80-200 mesh (Alumina Company of America), preheated at 700° C. (1292° F.) for two hours before use.

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

Tetralin, $C_{10}H_{12}$, B. p. (205° - 208° 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 Company Series 4500) equipped with stirring mechanism to stir contents one minute of each 30 minutes of extraction.

Chromatographic columns, glass columns having three sections (lower section 1.0 cm. x 85 cm., middle section 1.5 cm. x 42 cm., and top section 3.5 cm. 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-Fischer-retort method (8). For use in this study the oil 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. tetralin per gram of shale), and each batch was extracted 48 hours at 25° to 350° C. (Two series of extractions were made using tetralin as solvent for 48 to 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 removed. The shale residue was centrifuged from the extract and solvent, then extracted with benzene until free of tetralin and soluble material. The shale residue was air-dried and retained for analysis. The tetralin and benzene extracts were combined and then steam-distilled to remove the solvents. After removal of the tetralin, the extract was recovered 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 atmospheric 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 extracted from the raw shale was determined from comparison of the kerogen-to-ash ratios obtained before and after the oil shale was extracted. 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 an ash and mineral CO_2 analyses and equaled 100 minus the sum of the ash and mineral CO_2. 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 : 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 : 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 : 1 volume ratio of methyl ethyl ketone (MEK) to extract and allowed to stand at -5° C. for 1 hour. The wax was filtered from the MEK-soluble material, dried, and weighed. The MEK was removed from the oil by distillation and the latter was dried and weighed.

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 non-adduct waxes were separated by filtration; the final traces of non-adduct material were removed by washing with 100 ml. each of pentane and isooctane. 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-isooctane-methanol solution of the non-adduct was freed from urea by washing with water. The non-adduct 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 et al. (3). Four-gram batches of the oil fraction were placed on a prewetted column of silica gel (25 : 1 weight ratio of silica gel to sample) and eluted successively with isooctane, benzene, and 2-propanol. The three fractions were freed of solvent, dried, and weighed. The isooctane-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 non-adduct by the technique used for waxes. Additional fractionation of the aromatic oil was obtained on a prewetted column of alumina (25 : 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 by a method described by Robinson et al. (7) with an excess of alkaline potassium permanganate at the boiling temperature of the solution for 100 hours. Concentrated hydriodic acid (70%) was used to reduce the resin and pentane-insoluble fractions by a method described by Raudsepp (5) in which the fraction plus HI 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 et al. (1), 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.

EXPERIMENTAL RESULTS AND DISCUSSION

Rate of Product Formation. The amount of conversion of kerogen 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, the conversion of kerogen to degradation products ranged from 4.4% at 25° C. to 84.9% at 350° C. (table 1). By maintaining the temperature constant at 200° C. and varying the time of extraction, the yield of products ranged from 8.8% for 48 hours to 9.3% for 144 hours of extraction. A comparable series of extractions at a constant temperature of 350° C. showed an increase in product yield of 75.8% for 24 hours of extraction to 94.5% for 144 hours of extraction. This showed that 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 soluble products. Landau and Asbury (2) 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.

TABLE 1. - Tetralin extraction of kerogen from raw shale

Time of extraction, hours	Temperature of extraction, °C.	Kerogen extracted, %
48	25	4.4
48	200	8.8
144	200	9.3
48	250	10.2
48	300	28.7
24	350	75.8
48	350	84.9
96	350	87.9
144	350	94.5

The influence of temperature on the conversion of kerogen to soluble material is shown in figure 2. 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. The break in the curve suggested that a change in the thermal solution process took place at approximately 275° C.

Thompson and Prien (9) 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 ruptured. 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 temperature ranges probably would be different. Data presented later in this paper only partly confirm these findings.

Ultimate Composition of Crude Extracts. The sulfur and oxygen contents (table 2) of the extracts decreased 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 (fig. 3) where the time of extraction was constant at 48 hours and temperature increased, loss of oxygen (probably decarboxylation and dehydration) from the extracts occurred between 200° and 250° C. and continued to 350° C., where only a small portion of the 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) became rapid. 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. and the time of extraction varied, similar trends for oxygen and sulfur were obtained (fig. 4). Overall oxygen and sulfur contents decreased with time of extraction, nitrogen contents remained nearly constant, and the hydrogen contents decreased after 48 hours of extraction. No significant differences were found in the molecular weights of the crude extracts which were prepared at 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.

TABLE 2. - Ultimate composition and molecular weight of crude tetralin extracts

Temperature of extraction, °C.	Time of extraction, hours	C	H	O[1/]	N	S	Atomic ratios x 10^2 H/C	O/C	N/C	S/C	Molecular weight
25	48	80.4	11.1	6.5	0.9	1.1	159	5.8	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	10.3	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

1/ Oxygen was determined by difference.

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 was removed as pyrolytic gases (table 3) compared to about 3% of the total carbon. This suggested that at this temperature oxygenated groups such as carboxyl or others were degraded to CO_2 and Co, 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 very little of the kerogen was cracked to final degradation products at 300° C. and below, 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 3. - Gases produced by degradation of one kilogram of kerogen

	Gas produced, moles		
	Degradation temperature, °C.		
	250	300	350
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 gas produced	0.065	0.128	4.446

Product Distribution. The percentage of pentane-insoluble material present in the extracts increased with increase in temperature of extraction at 250° to 350° C. (fig. 5), while the 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 4.

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%. This showed that approximately half of the pentane-insoluble material was degraded into oil, wax, and resins 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 as the 25° C. wax produced 72% wax adduct compared to 51% for the 350° C. wax (see table 5). Also, the non-adduct 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 increase, 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 non-adduct wax fractions had an average chain length less than 16 carbon atoms. The wax adduct 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

TABLE 4. - Ultimate composition and molecular weights of the major fractions

	C	H	O[1]	N	S	Atomic ratios x 10^2 H/C	O/C	N/C	S/C	Molecular weight
				25° C. Extract						
Pentane-insoluble material	80.1	11.3	7.4	0.2	1.0	169	6.9	0.2	0.5	1320
Resin	78.9	11.0	7.8	0.9	1.4	167	7.4	1.0	0.7	625
Wax	83.6	13.8	2.3	0.2	0.1	198	2.1	0.2	0.04	415
Oil	86.7	12.2	0.7	0.1	0.3	169	0.6	0.1	0.1	350
				200° C. Extract						
Pentane-insoluble material	78.3	10.5	8.6	1.7	0.9	161	8.2	1.9	0.4	1250
Resin	80.3	10.8	6.5	1.1	1.3	162	6.1	1.2	0.6	605
Wax	84.8	13.8	0.8	0.2	0.4	195	0.7	0.2	0.2	480
Oil	86.5	12.4	0.5	0.1	0.5	172	0.4	0.1	0.2	350
				250° C. Extract						
Pentane-insoluble material	81.4	10.6	4.8	2.2	1.0	156	4.4	2.3	0.5	1290
Resin	79.9	10.4	7.0	1.5	1.2	156	6.6	1.6	0.6	570
Wax	84.6	14.3	0.9	0.1	0.1	203	0.8	0.1	0.04	440
Oil	87.2	11.7	0.7	0.1	0.3	161	0.6	0.1	0.1	365
				300° C. Extract						
Pentane-insoluble material	81.4	10.3	4.0	3.0	1.3	152	3.7	3.2	0.6	1210
Resin	78.3	10.4	8.6	1.8	0.9	159	8.2	2.0	0.4	650
Wax	84.8	13.9	1.0	0.1	0.2	197	0.9	0.1	0.09	415
Oil	87.5	11.7	0.2	0.1	0.5	160	0.2	0.1	0.2	340
				350° C. Extract						
Pentane-insoluble material	81.2	9.9	4.1	3.8	1.0	146	3.8	4.0	0.5	1280
Resin	83.3	10.9	2.4	2.9	0.5	157	2.2	3.0	0.2	575
Wax	86.1	13.3	0.2	0.2	0.2	185	0.2	0.2	0.09	355
Oil	86.8	12.2	0.3	0.4	0.3	169	0.3	0.4	0.1	375

1/ Determined by difference.

average molecular weight of the crude-wax fraction (before fractionation by the formation of urea adducts) ranged from 355 to 480 and tended to decrease with increase in temperature of extraction from 25° to 350° C. Ultimate composition of the unfractionated wax showed minor variations and averaged 84.8% carbon, 13.8% hydrogen, 1.0% oxygen (by difference), 0.2% nitrogen, and 0.2% sulfur.

TABLE 5. - Carbon distribution of wax fractions

Temperature of extraction, °C.	Carbon-type composition		Percentage of total wax
	% C_N	% C_P	
Wax (adduct)1/			
25	9	91	71.6
250	12	88	55.6
350	12	88	50.5
Wax (non-adduct)1/			
25	78	22	28.4
250	66	34	44.4
350	78	22	49.5

1/ Determined from mass spectra.

Constitution of Oils. The composition of the oil fractions tended to become more aromatic and less paraffinic with increase in temperature of extraction (see fig. 6). In general, the percentage of paraffin oil non-adduct 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 non-adduct fraction by the n-d-M method (10) and for the aromatic oil by the Martin method (4). Mass spectra were used to determine the amount of straight-chain and cyclic paraffins present in the paraffin oil adduct. The results of these analyses are shown in table 6. Based on these data approximately 33% of the 25° C. oil consisted of straight-chain paraffins, 48% cyclic paraffins, 16% aromatics, and 3% polar oil. The 350° C. oil was more aromatic as it contained 18% straight-chain paraffins, 26% cyclic paraffins, 36% aromatics, and 20% polar oil.

TABLE 6. - Ring analysis and molecular weight of oil fractions

Temperature of extraction, °C.	Carbon-type composition			Molecular weight
	% C_A	% C_N	% C_P	
Paraffin oil (adduct)1/				
25	0	72	28	405
250	0	80	20	380
350	0	82	18	285
Paraffin oil (non-adduct)2/				
25	6	57	37	430
250	0	75	25	415
300	1	58	41	345
350	3	47	50	370
Aromatic oil (0-2-1)3/				
25	45	25	30	300
250	46	37	17	290
350	81	12	7	305

1/ Determined from mass spectra.
2/ Determined by n-d-M method.
3/ Determined by Martin method.

The percentage of aromatic compounds in the 350° C. oil may be too 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 an assumed 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% straight-chain paraffins, 27% cyclic paraffins, 33% aromatics, and 21% polar oil.

The paraffin-oil adduct fraction had an average of 2.6 to 3.4 rings per molecule, the paraffin-oil non-adduct had 2.8 to 5.1 rings per molecule, and the aromatic oil eluted with isooctenes 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 (isooctene eluted) had an average of 22 carbon atoms per molecule and a determined molecular weight of 305. Mass spectra of this fraction showed that every homologous series was present in percentages ranging from 10 to 19%.

The molecular weights of the oil fraction before fractionation ranged from 340 to 375 and showed no correlation to temperature of extraction. Likewise, the elemental composition of the oil fractions showed very little variation and averaged 86.9% carbon, 12.0% hydrogen, 0.5% oxygen, 0.2% nitrogen, and 0.4% sulfur.

Constitution of Resins. Significant differences in the elemental composition of the resin fractions were found (fig. 7). 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 occurred between 300° and 350° C., probably resulting in the formation of CO and CO_2. 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. These results suggested the following: (1) Oxygen structures present in resins are readily made soluble and are easily degraded further to CO_2, CO, and perhaps water. (2) Nitrogen structures present in resins are difficult to make soluble and are quite stable to further degradation. From bond energies it appears that kerogen contains more C=N structures, which have higher bonding energies, than C-N structures. (3) Loss of hydrogen from the resins at all temperatures indicated that easily dehydrogenated structures such as partly unsaturated cyclic structures, isoprenoid, steroid, or similar structures are present in kerogen. (4) Loss of sulfur at 300° and 350° C. indicated the presence of some unstable sulfur compounds.

The molecular weights of the resin fractions ranged from 570 to 650 and did not appear to be related to the temperature of extraction.

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 $KMnO_4$ to carbon were consumed in both tests. This shows that approximately the same amount 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 $KMnO_4$ oxidation.

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 be present in the extracts prepared at higher temperatures.

Basic nitrogen determinations on the resin fractions showed that the ratio of basic nitrogen to total nitrogen ranged from 0.44 for the 25° C. resins to 0.34 for the 350° C. resins. Thus, the neutral nitrogen present in the resins tended to increase with increase in temperature of extraction and represented from 56 to 66% of the total nitrogen.

Constitution of Pentane-Insoluble Material. The composition of the pentane-insoluble fractions (fig. 8) 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. The same general conclusions concerning hetero structures can be made for the pentane-insoluble material as were made for the resin fractions in the preceding section. There was, however, one difference in that the loss of oxygen from the pentane-insoluble material occurred between 200° to 350° C. compared to 300° to 350° C. for the resin fraction. This suggested differences in the type of oxygenated structures present in the two materials. Also, the pentane-insoluble material produced at higher temperatures appeared to contain less hydrogen and more nitrogen than the resins. The molecular weights of the pentane-insoluble material ranged from 1210 to 1320 and showed no relationship to temperature of extraction.

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 less structures which were resistant to oxidation than the oil, wax, or resin fractions. About 40% of the pentane-insoluble material was oxidized to non-volatile non-oxalic 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 probably were not in the kerogen as such but were formed during the thermal solution by dehydrogenation of partly unsaturated cyclic structures present in kerogen.

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 the pentane-insoluble material contained approximately 25% 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 determinations on the pentane-insoluble fractions showed that the ratio of basic nitrogen to total nitrogen ranged from 0.29 to 0.36 and was not related to the temperature of extraction. Therefore, the amount of neutral nitrogen

ranged from 64 to 71% of the total nitrogen and was slightly higher than that present in the resin fractions.

SUMMARY AND CONCLUSIONS

Based upon the weight-percent of total extract obtained at constant periods of extraction time, the amount of wax and pentane-insoluble material increased with increase in temperature of extraction, the percentage of resins decreased with increase in temperature, and the percentage of oil remained nearly the same. At constant temperature of extraction (350° C.), the percentage of pentane-insoluble material decreased with increase in time of extraction and the percentage of oil, wax, and resins increased with increase in the period of extraction.

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 quite 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.

At 350° C. kerogen was degraded to approximately 10 to 15% straight-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% heterocyclic material. These materials are probably representative of structures present in the original kerogen and suggest that kerogen is predominantly a heterocyclic material connected to or associated with smaller amounts of hydrocarbon material consisting of straight-chain, cyclic paraffin, and aromatic groups.

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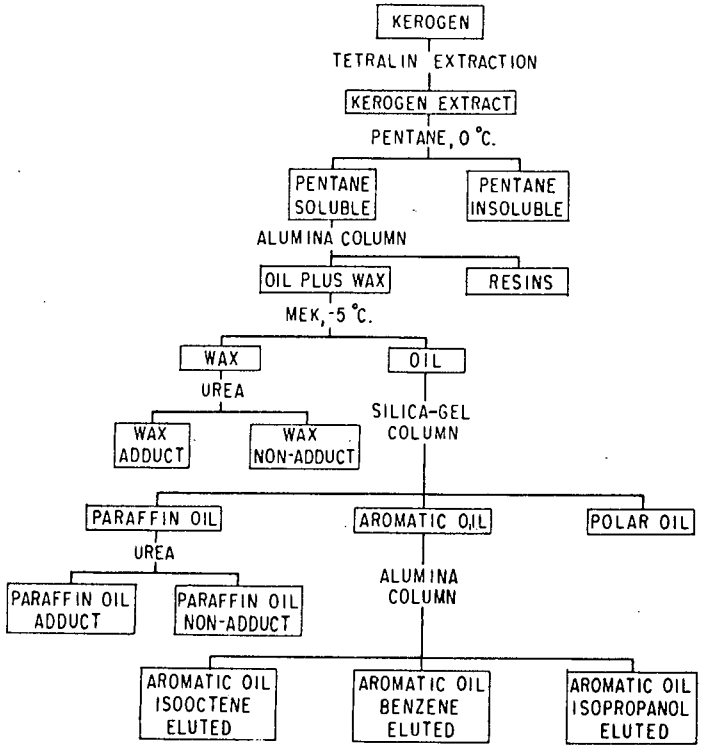

FIGURE 1.-FLOW DIAGRAM OF FRACTIONATION PROCEDURE.

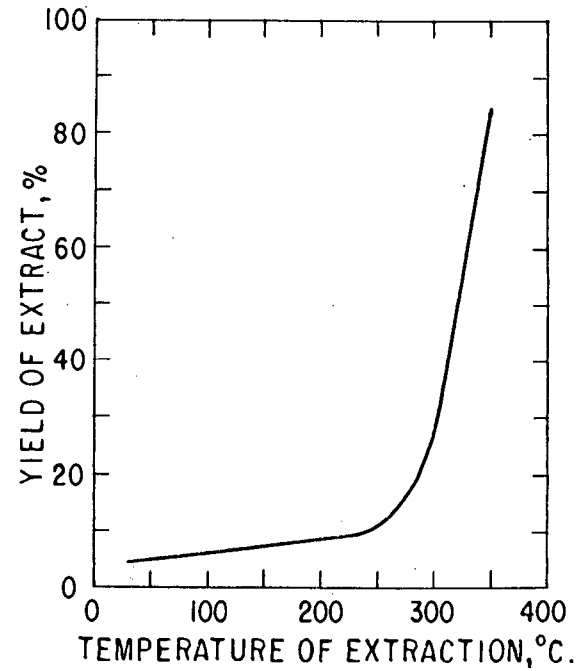

FIGURE 2.-INFLUENCE OF TEMPERATURE ON EXTRACTION OF KEROGEN FOR 48 HOURS.

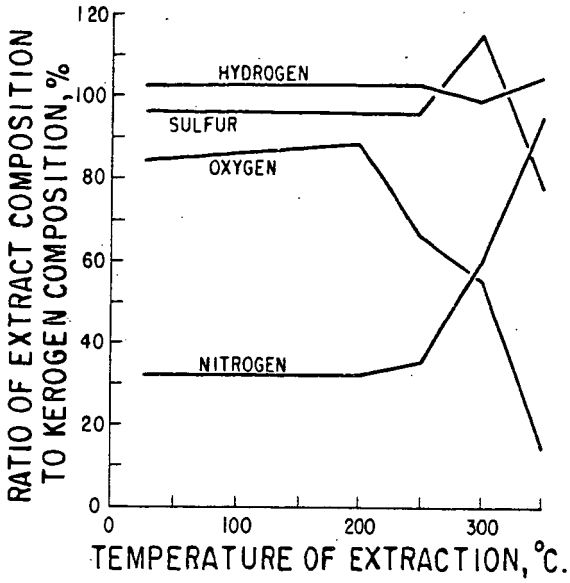

FIGURE 3.-RELATIONSHIP OF EXTRACT COMPOSITION TO TEMPERATURE OF EXTRACTION FOR CONSTANT PERIOD OF TIME.

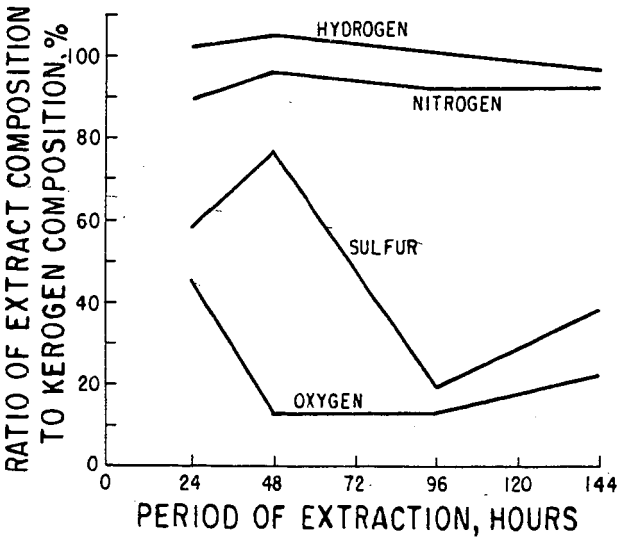

FIGURE 4.-RELATIONSHIP OF EXTRACT COMPOSITION TO PERIOD OF EXTRACTION AT CONSTANT TEMPERATURE.

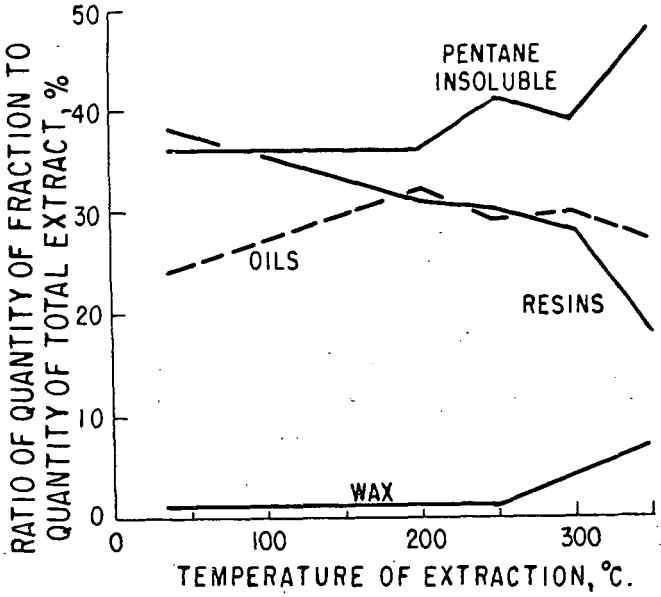

FIGURE 5.-RELATIONSHIP OF FRACTION DISTRIBUTION TO TEMPERATURE OF EXTRACTION.

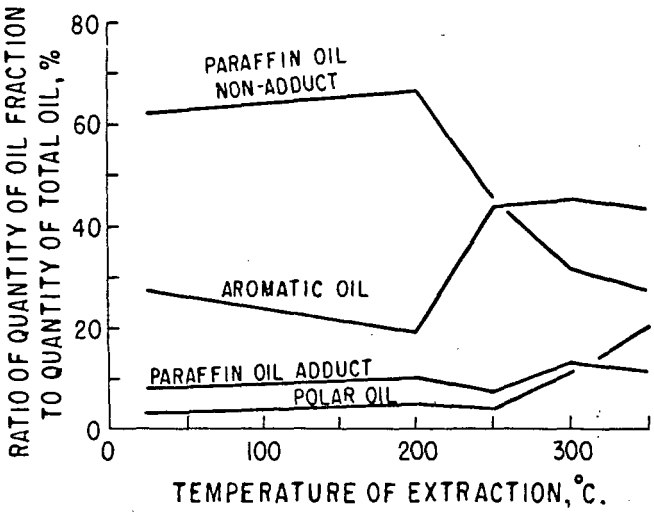

FIGURE 6.-RELATIONSHIP OF THE DISTRIBUTION OF OIL FRACTIONS TO TEMPERATURE OF EXTRACTION.

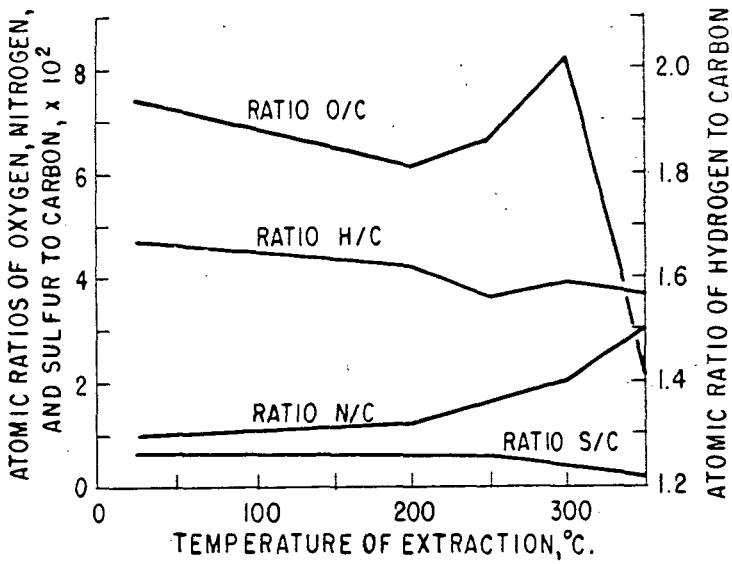

FIGURE 7.-COMPOSITION OF RESIN FRACTION AT VARIOUS TEMPERATURES.

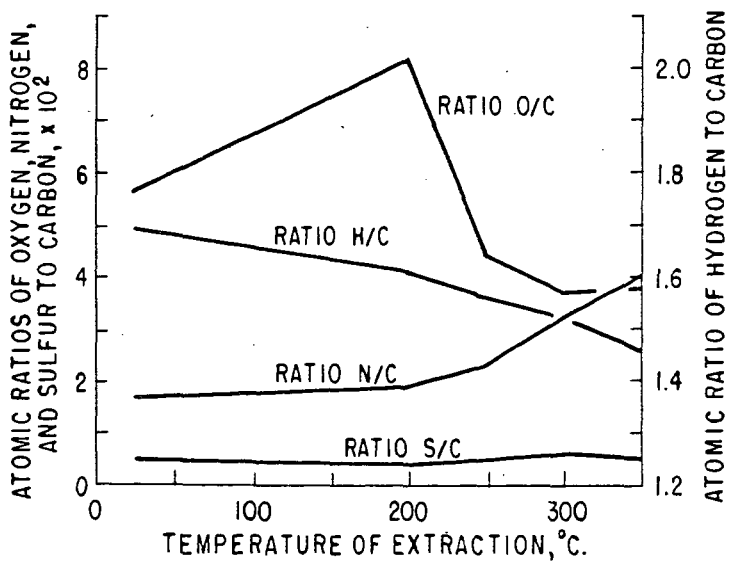

FIGURE 8.-COMPOSITION OF PENTANE-INSOLUBLE FRACTIONS AT VARIOUS TEMPERATURES.