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Thermal Degradation of Green River Kerogen at 150° to 350° C

Composition of Products

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7924

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UNITED STATES DEPARTMENT OF THE INTERIOR
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CONTENTS

ILLUSTRATIONS

TABLES

THERMAL DEGRADATION OF GREEN RIVER KEROGEN AT 150° TO 350° C

Composition of Products

by

J. J. Cummins,[1] F. G. Doolittle,[1] and W. E. Robinson[2]

ABSTRACT

The Bureau of Mines heated at 150° to 350° C for 0.5 to 360 days Green River oil shale that had been previously extracted by benzene to provide information on in situ processing conditions, to determine the effect of low-temperature heating on the unconverted kerogen, and to determine the composition of benzene-soluble thermal products. The methods used in determining the composition of the soluble thermal products consisted of fractionation of the soluble material, elemental analysis of the soluble products, fractionation of the polar resins by ion-exchange chromatography, gas chromatographic analysis of n-alkanes, and mass spectral analysis of the branched plus cyclic alkanes and aromatic oils. The methods used to determine the effect of low-temperature heating on the unconverted kerogen remaining in the oil shale heated residues consisted of carbon-hydrogen analysis, volatile material determination, carbon residue determination, and oxidation rate determination. In general, it was concluded that significant increases in the degradation of kerogen to oil occurred between the temperature range of 250° to 350° C; that the composition of the soluble products depends upon the temperature at which they are formed; and that the n-alkanes are pyrolytically degraded from the kerogen structure. In particular, the 250° C heating temperature is beneficial to the formation of branched plus cyclic alkanes. Also, the heated and unconverted oil shale kerogen and the soluble thermal products become more aromatic as the temperature increases from 150° to 350° C.

INTRODUCTION

The production of shale oil from oil shale without first removing the oil shale from the ground could be economically and environmentally advantageous. Research on the in situ, or in-place, retorting technique has indicated that some of the oil shale may be held at temperatures above the usual ground temperature but below the usual retorting temperature for extended periods of time. This heat soaking may alter both the composition and the quantity of the oil that is produced. In this supplemental laboratory research, oil shale samples were held at temperatures between 150° and 350° C for periods of time

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[1] Research chemist.

[2] Project leader.

from 0.5 to 360 days to evaluate differences in the product oils on subsequent extraction or on conversion of the organic material remaining in the shales to oil after the low-temperature heat-soaking period. An attempt was made to relate the results to the in situ processing of oil shales.

Several investigators have reported a variety of experimental conditions for the conversion of oil shale to pyrolytic products. Dinneen (10)[3] studied the effect of retorting temperature on the composition of shale oil and found that as the temperature increased the aromatic content of the shale oil increased. Robinson and Cummins (16) made a thermal solution study of the conversion of oil shale and found that the composition of the soluble products depended upon the time and temperature of extraction. Cummins and Robinson (9) studied the rate at which kerogen degrades to thermal products at 150° to 350° C. They found that kerogen degrades primarily to bitumen following an approximate first-order thermal reaction and that the kerogen decomposition rate increased more than 900 times as it was heated from 150° to 350° C. Burwell (6-7) studied the fracturing and production techniques needed to convert oil shale to shale oil in place. They obtained some success in shale buried 68 to 80 feet beneath the surface, but another experiment at double this depth was not successful, probably because sufficient surface for heat transfer was not created in a fracturing step.

In extending earlier studies, this paper discusses the effect of heat soaking oil shales for considerable lengths of time at temperatures of 150° to 350° C, which is below the usual retorting temperature. These conditions may occur during the in situ processing of oil shale.

EXPERIMENTAL PROCEDURES

Preparation of Oil Shale Samples

The oil shale sample was obtained from the Bureau of Mines oil shale mine near Rifle, Colo. This shale sample contained 30.2 percent ±0.1 organic carbon and assayed about 65 gallons of oil per ton of shale. Portions of this shale sample, each weighing approximately 4.7 kilograms and crushed to pass a 100-mesh screen, were extracted twice in a large glass bottle by stirring the shale in 6 liters of purified benzene overnight at room temperature (3). After each extraction, the shale was filtered from the benzene solution and washed with fresh benzene. Finally, the moist shale was placed in a Cole-Parmer ultrasonic[4] extractor and extracted the third time with benzene (1.3 ml per gram of shale) for 10 minutes. The shale was filtered from the benzene solution, washed with fresh benzene, and dried overnight under reduced pressure at 60° C. The extractions removed 7.5 weight-percent of the oil-shale organic material.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[4] Reference to specific equipment or trade names does not imply endorsement by the Bureau of Mines.

Simulation of In Situ Processing Conditions

Benzene-extracted oil shale samples were heated as described by Cummins and Robinson (9) at 150° to 350° C for 0.5 to 360 days to simulate potential in situ processing conditions. Oil shale samples weighing 1.5 to 2.0 kilograms were maintained at 150°±2° C or 200°±2° C for 90, 180, 270, and 360 days. Oil shale samples weighing 100 grams were held at 250°±3° C for 10, 12, 16, and 21 days and at 300°±3° C or 350°±3° C for 0.5, 1.0, 2.0, 3.0, and 4.0 days. The oil shale samples weighing 1.5 to 2.0 kilograms were heated in an electric oven in 1-gallon gastight metal containers; those weighing 100 grams were heated in an electric multiple-unit furnace containing a glass Pyrex combustion tube similar to that described by Hubbard and Robinson (14). All samples were blanketed with a helium atmosphere.

Characterization of the Reaction Products

Separation Techniques

The mixture of minerals, bitumen, kerogen, and kerogen residues resulting from the simulated in situ processing was separated to give the fractions indicated in figure 1. The separation procedures have been described (8). Extraction with benzene gave a soluble fraction and a fraction containing the minerals, unchanged kerogen, and residues of kerogen that may have been changed, but not sufficiently to become benzene-soluble. The soluble fraction was placed in pentane at 0° C to give a pentane-soluble and a pentane-insoluble fraction. Separation of the pentane soluble fraction over alumina gave a hydrocarbon fraction and a resin fraction. The hydrocarbons were separated into alkanes and aromatics by chromatography over silica gel. The n-alkanes were obtained by treating the alkane concentrate with 5A molecular sieves; the unadsorbed portion contained the branched plus cyclic alkanes.

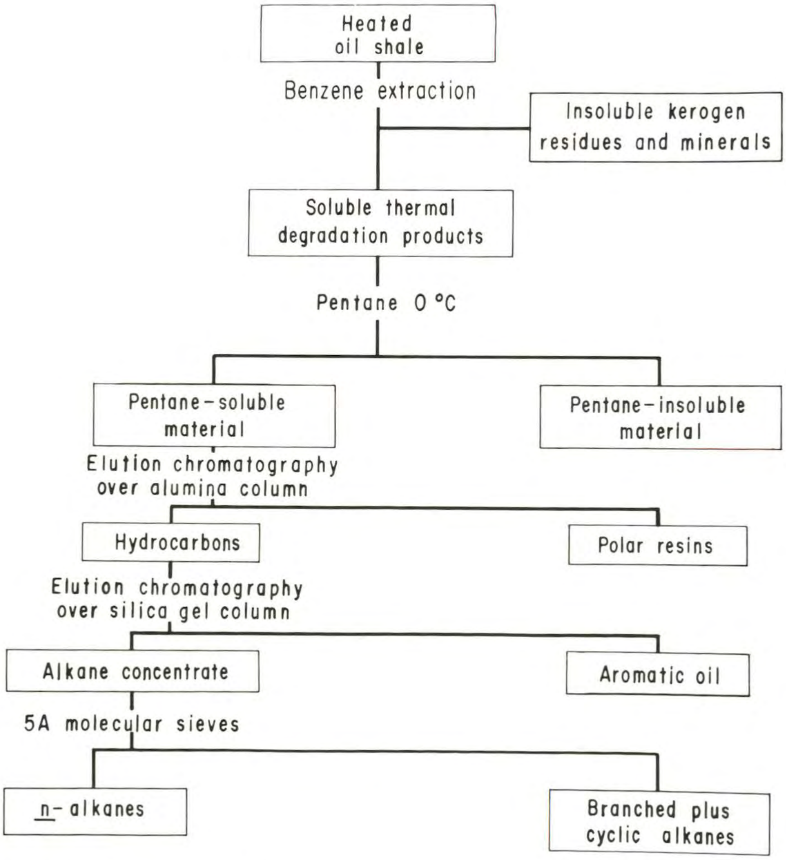

FIGURE 1. - Procedure for separation of reaction products.

Elemental Analysis

The elemental composition of the soluble thermal products was determined by conventional methods of analysis: Carbon and hydrogen were determined by a gas chromatographic carbon and hydrogen analyzer, nitrogen by Kjeldahl digestion, sulfur by ignition in a Parr oxygen bomb, and oxygen by difference. Total carbon of the heated residues was determined by the standard combustion method (12). Inorganic carbon was determined by measurement of the carbon dioxide evolved upon treatment of a portion of the sample with an excess of boiling 10-percent hydrochloric acid solution. Organic carbon was determined by difference. The atomic hydrogen/carbon (H/C) ratio is used as an indicator of the aromaticity of the heated and unconverted kerogen.

Gas-Liquid Chromatography (GLC)

The n-alkane samples were analyzed in a Micro Tek-2000-R gas chromatograph using a 50-foot SE-30 capillary column. Carbon-number distributions of the n-alkane compounds were determined by injecting n-C_{16} with each sample to serve as a marker. Area for each peak was determined by measuring each peak height and multiplying this value by the peak width at one-half the peak height. Component percentages were determined by use of the following equation:

$$\text{Pct } i^{th} \text{ component} = \frac{hiWi}{\sum_{i=1}^{N} hiWi} \times 100,$$

where hi is peak height and Wi is peak width at one-half peak height.

Mass Spectrometry

Mass spectra of the branched plus cyclic alkane samples and the aromatic oil samples were obtained using an AEI MA-12 medium-resolution mass specrometer at an ionization energy of 70 eV and an ion source temperature of 250° C. The type and amount of each type of compound present in the branched plus cyclic alkane samples were determined by the standard ASTM D2786-7 (2) method of analysis. A similar analysis was performed for the aromatic oil samples by the Hasting's (13) method. For comparative purposes, a Bendix Model 14-107 time-of-flight (TOF) mass spectrometer was used to determine the composition of the oil shale thermal decomposition products at temperatures from room temperature to 350° C. The TOF mass spectrometer was equipped with a direct-heated-inlet probe that allowed the oil shale sample to be heated in the ionization region of the instrument. The quantities of products were measured by setting the instrument gates to monitor continuously a predetermined molecular ion.

Ion-Exchange Separations

The resin fractions were separated into acidic, basic, and neutral subfractions on Amberlyst A-29 anion resin and Amberlyst 15 cation resin using a method developed by Jewell (15). This separation provided some information about the composition of the polar fractions of the thermal products.

Volatile Material and Carbon Residue Determinations

Volatile matter was defined as the loss in weight of a sample per unit of organic carbon when heated at 500° C in an inert atmosphere for 30 minutes (1). Carbon residue was the percent of the total organic carbon remaining in a sample after being heated at 500° C in an inert atmosphere for 30 minutes. The volatile material and carbon residue determinations provide structural information about the kerogen. Aliphatic structures are volatilized at 500° C, while aromatic structures produce carbon residue.

Oxidation Rates

The rate of oxidation of the organic carbon present in the heated residues was equal to the milliliters of 3-percent potassium permanganate solution consumed per gram of organic carbon per minute. The method was the same as described by Erdman and Ramsay (11). The rate of oxidation of kerogen by 3-percent permanganate solution provides structural information about the kerogen. Fatty materials are resistant to oxidation, whereas aromatic structures and oxygen-containing structures are oxidized.

RESULTS AND DISCUSSION

Because the naturally occurring benzene-soluble material was removed from the oil shale prior to the heat treatment, any benzene-soluble material formed after subjecting the samples to simulated in situ processing conditions represents kerogen that was sufficiently degraded to become soluble. The quantities and rates of formation of the extracts have been reported elsewhere (9). Table 1 indicates the elemental analyses obtained on the extracts after subjecting the shale to several temperatures for periods of time up to 1 year.

On an average basis for each temperature, the atomic H/C ratios tend to remain nearly the same up to 350° C, where a definite decrease from about 1.6 to 1.4 occurs. This decrease in H/C ratio of the extracts shows a loss of hydrogen relative to carbon and shows that a partial loss occurs at 350° C. The amount of oxygen in the soluble extracts increases significantly at 250° and 300° C, followed by a decrease at 350° C. This suggests that additional oxygen-containing structures are made soluble at 250° and 300° C. Upon heating to 350° C, these structures are degraded with loss of oxygen in the form of carbon dioxide as verified by the TOF mass spectrometer tests. On an average basis nitrogen and sulfur values remain nearly constant.

TABLE 1. - Elemental analyses of benzene-soluble products

Heating time, days	Kerogen converted, wt-pct	Wt-pct of total					H/C ratio
		C	H	O[1]	N	S	
	150° C						
90	2.0	84.8	10.9	2.5	1.5	0.3	1.54
180	3.6	85.3	12.1	.7	1.7	.2	1.70
270	6.1	84.3	11.1	2.3	1.5	.8	1.58
360	7.7	84.5	11.4	1.0	1.9	1.2	1.62
Average	-	84.7	11.4	1.6	1.7	.6	1.62
	200° C						
90	3.0	84.9	11.3	1.1	1.9	0.8	1.60
180	4.9	85.1	11.3	1.3	1.8	.5	1.59
270	7.5	83.9	11.3	2.1	1.8	.9	1.62
360	8.9	85.4	11.0	.6	1.9	1.1	1.54
Average	-	84.8	11.2	1.3	1.9	.8	1.58
	250° C						
10	9.1	83.5	11.0	2.9	1.9	0.7	1.58
12	9.8	82.8	11.1	3.5	1.8	.8	1.61
16	11.8	80.2	10.9	6.0	2.1	.8	1.63
21	14.4	80.9	11.0	5.2	1.9	1.0	1.63
Average	-	81.8	11.0	4.4	1.9	.8	1.61
	300° C						
0.5	3.3	80.1	10.9	6.4	1.6	1.0	1.63
1.0	3.8	81.7	10.1	6.0	1.4	.8	1.48
2.0	7.5	80.8	11.2	6.6	.7	.7	1.66
3.0	8.7	83.2	10.5	4.5	1.2	.6	1.50
4.0	12.8	83.1	10.4	4.7	1.2	.6	1.50
Average	-	81.8	10.6	5.6	1.2	.7	1.56
	350° C						
0.5	27.6	84.4	10.4	2.6	1.8	0.8	1.48
1.0	44.5	84.1	10.3	3.3	1.7	.6	1.47
2.0	53.9	85.4	9.9	2.6	1.7	.4	1.39
3.0	62.4	86.4	10.3	.8	2.1	.4	1.43
4.0	65.1	85.8	10.3	1.3	2.1	.5	1.44
Average	-	85.2	10.2	2.1	1.9	.5	1.44

[1] Oxygen determined by difference.

The elemental compositions of the soluble thermal products relative to the original unheated kerogen are shown in figure 2. The hydrogen and carbon contents of the thermal products are generally higher than those of the original kerogen, with the hydrogen showing a slight decrease over the temperature range. Nitrogen content of the thermal product tends to increase from values of 60 to 80 percent of that of the kerogen up to 250° C, then decreases to as low as 40 percent at 300° C, followed by an increase up to 80 percent at 350° C. This nitrogen decrease at 300° C is supported by the TOF mass spectrometer study and indicates the loss of nitrogen in the form of ammonia from relatively unstable but soluble nitrogen compounds. At 350° C, degradation of nitrogen-containing compounds continues, but they are retained in the thermal product and not released as volatile materials. Oxygen content of the thermal product ranges from a low of about 25 percent of that present in the kerogen

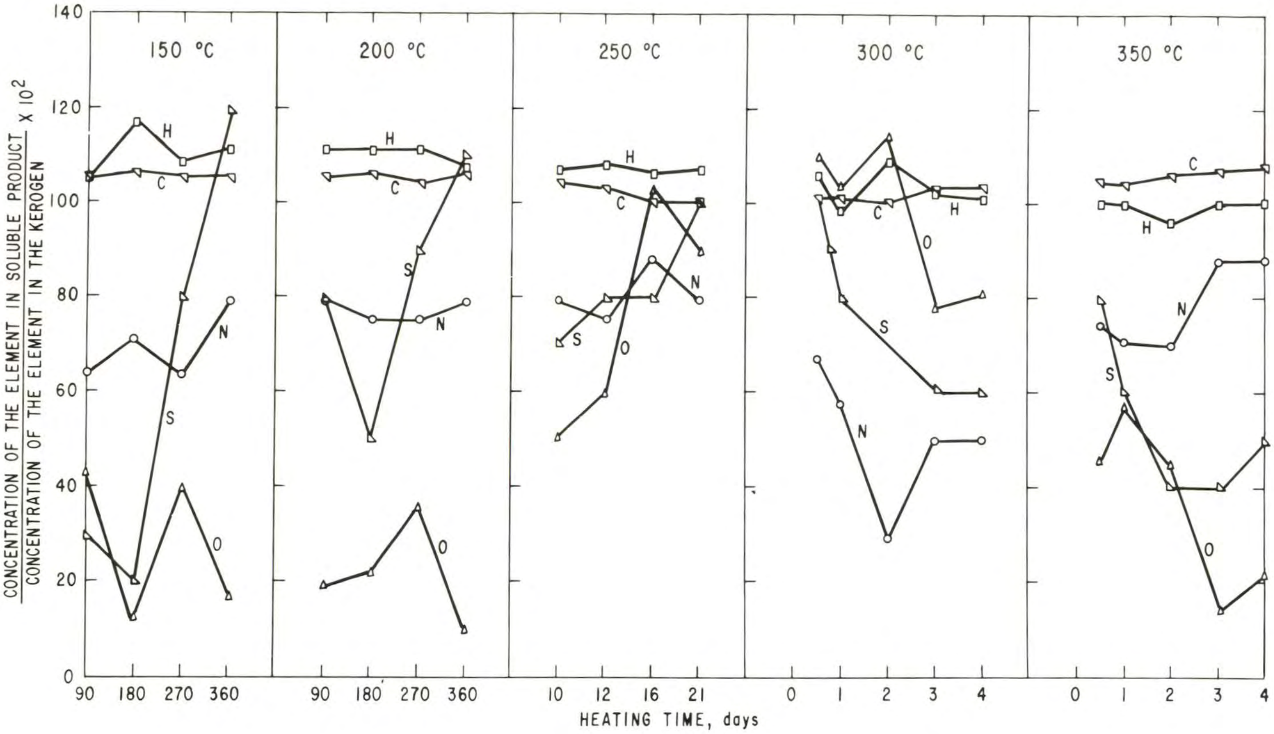

FIGURE 2. - Elemental composition of soluble thermal products relative to kerogen.

at 150° C to about 90 percent at 300° C, with a decrease to about 30 percent at 350° C. This suggests that degradation at 300° C produces products of comparable oxygen content to that of the original kerogen, but at 350° C these compounds are degraded further with a loss of oxygen in the form of carbon dioxide, as shown by TOF mass spectrometer study, and possibly as carbon monoxide, oxygen, or water. The sulfur content of the soluble extracts tends to reach a maximum of about 80 percent of that of the original kerogen at 250° C and decreases at 300° and 350° C. This also shows a degradation of sulfur-containing compounds at temperatures of 300° and 350° C, with the loss occurring in the form of hydrogen sulfide as indicated by the TOF mass spectrometer study on raw shale.

Soluble Product Components

Table 2 shows the type and amount of each component present in the soluble thermal products obtained during simulated in situ processing conditions. Some compositional trends are observed with increased temperature, but no compositional trends are observed with increased heating time at each temperature. The n-alkanes, branched plus cyclic alkanes, and aromatic oils comprise the hydrocarbon portion of the soluble products. The polar resins and pentane insolubles comprise the polar portion of the soluble products.

The thermal product containing the largest amount of pentane-insoluble material was formed at 150° C, and the thermal product containing the largest amount of resins was formed at 200° C. Likewise, the thermal product containing the largest amount of *n*-alkanes was formed at 350° C, and the largest amount of branched plus cyclic alkanes formed at 250° C. On an average basis, the thermal product containing the largest amount of total hydrocarbons was formed at 250° C. This suggests that at the higher temperatures polar constituents were degraded from the kerogen and made soluble at a faster rate than polar constituents were degraded to hydrocarbons. Also, it suggests that a significantly higher percentage of the hydrocarbon constituents are made soluble at 250° C than at other temperatures.

TABLE 2. - Distribution of components of the soluble pyrolytic products

Heating time, days	Soluble product components, wt-pct of total				
	n-Alkanes	Branched plus cyclic alkanes	Aromatic oil	Polar resins	Pentane insolubles
150° C					
90	3.6	3.6	6.7	54.9	31.2
180	3.2	8.3	1.1	66.3	21.1
270	4.3	9.7	1.6	71.7	12.7
360	4.3	8.0	1.8	66.4	19.5
200° C					
90	1.3	10.0	1.3	71.7	15.7
180	.8	8.5	.8	82.9	7.0
270	1.1	5.5	.3	82.9	10.2
360	.9	4.8	.4	84.8	9.1
250° C					
10	2.2	19.0	2.4	73.6	2.8
12	3.0	18.8	3.1	71.9	3.2
16	2.1	13.7	2.1	78.1	4.0
21	1.5	14.6	3.0	77.5	3.4
300° C					
0.5	2.1	5.6	2.1	76.7	13.5
1.0	1.6	9.7	2.1	81.1	5.5
2.0	1.5	9.1	5.1	81.7	2.6
3.0	1.6	9.4	5.6	77.5	5.9
4.0	2.3	9.4	9.4	74.3	4.6
350° C					
0.5	2.3	7.2	5.7	75.5	9.3
1.0	5.5	9.3	8.5	65.7	11.0
2.0	2.7	7.6	3.4	70.3	16.0
3.0	4.5	5.8	1.9	58.9	28.9
4.0	4.8	7.6	6.7	76.5	4.4

GLC Analysis of the *n*-Alkanes

The distributions by carbon numbers for the *n*-alkanes isolated from the thermal products obtained by heating bitumen-free oil shale under simulated in situ retorting conditions are shown in figure 3. The analyses for each product at each temperature were averaged and are presented here as representing an average value for each temperature. Also shown are the odd-even

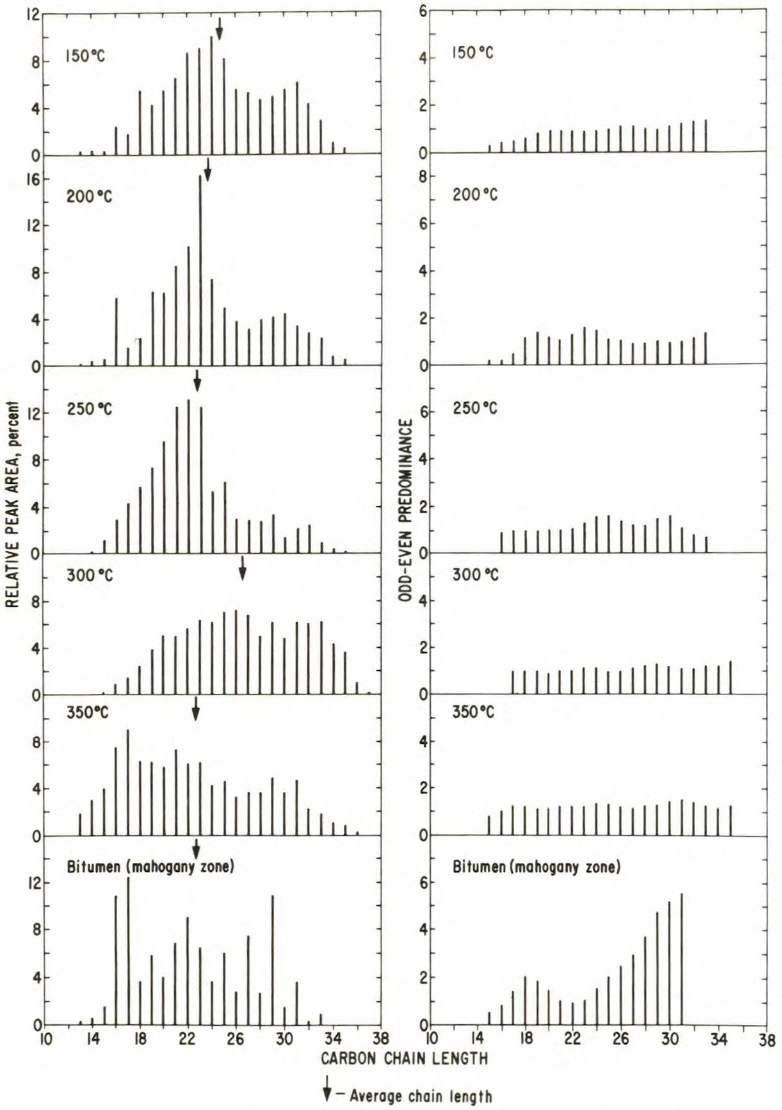

FIGURE 3. - Distribution and odd-even predominance of oil shale *n*-alkanes.

predominance (17) calculations for the average carbon chain distribution of the *n*-alkanes at each temperature range. The odd-even predominance calculation provides information about the dominance of the odd or even carbon numbered *n*-alkanes relative to a specific carbon chain length. A value of 1 for the odd-even predominance calculation at a specific carbon chain length for the *n*-alkanes shows an equal distribution of odd and even carbon chain lengths about this carbon number. Values higher than 1 show a predominance of odd-carbon-number *n*-alkanes, and a value below 1 shows a predominance of even-carbon-number *n*-alkanes. For comparative purposes, the distribution of the *n*-alkanes and the odd-even predominance of the *n*-alkanes obtained from the soluble bitumen from a Mahogany zone oil-shale sample (5) are shown in figure 3.

In general, the *n*-alkanes that were thermally degraded from the kerogen at 150° to 350° C have distributions of carbon numbers typical of thermally produced *n*-alkanes. Thermally produced *n*-alkanes usually have triangular distribution in which the amounts of low carbon numbers and high carbon numbers are small relative to the amounts of intermediate carbon numbers, thereby giving the so-called "envelope" distribution. As the temperature of the thermal reaction is increased, it would be expected that carbon-to-carbon bond cleavage would begin to occur and the average carbon chain length would begin to decrease. As illustrated by the arrows at the top of each inset in figure 3, the average chain length of the *n*-alkanes does decrease from 24.6 for the 150° C *n*-alkanes to 22.3 for the 350° C *n*-alkanes. However, the 300° C *n*-alkanes have an average chain length of 26.6. No explanation is evident for the increased average carbon chain length for the 300° C *n*-alkanes.

In all cases, the odd-even predominance of the thermally produced n-alkanes is near unity, showing very little dominance of either the odd or even carbon numbers. This again is typical of thermally produced n-alkanes. By contrast, there is a significant difference in the carbon-number distribution and odd-even predominance for the n-alkanes obtained from the soluble material (bitumen) present in a Mahogany zone oil shale sample. The distribution shown in figure 3 is typical of bitumens from the Mahogany zone of the Green River Formation and shows the characteristic large amount of C_{17}, the predominance of C_{22} over adjacent carbon numbers, and the high odd-carbon-number predominance in the C_{25} to C_{31} range. This significant difference between the distribution of carbon numbers for the n-alkanes derived from the natural bitumen and the thermally produced n-alkanes suggests that the natural bitumen was not degraded thermally from the insoluble kerogen during geologic time.

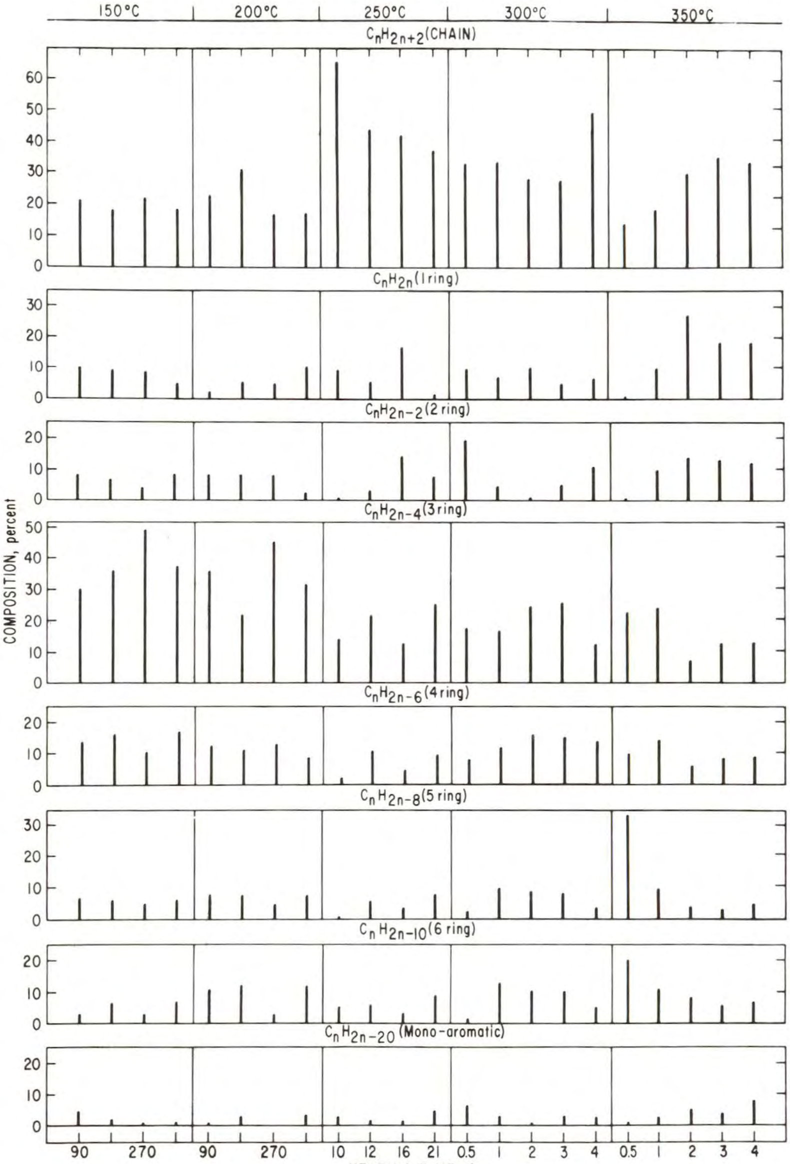

FIGURE 4. - Type analysis for branched plus cyclic alkanes.

Mass Spectral Analysis of the Branched Plus Cyclic Alkanes

The compositional distribution of the branched plus cyclic alkanes formed during the 150° to 350° C heating tests was determined using the standard ASTM method (1) with the results shown in figure 4. The alkane fractions contain 12 to 66 percent branched compounds, 32 to 87 percent cyclic compounds, and 1 to 8 percent of monoaromatic compounds. The cyclic alkanes contain from one to six rings.

Of the eight different types of compounds represented in the branched plus cyclic alkanes, the branched alkanes (C_nH_{2n+2} compounds) and the three-ring (C_nH_{2n-4} compounds) represent the largest amount of the alkanes. The amounts of branched alkanes ranged from about 12 percent to 66 percent, with the latter being from the 250° C thermal product. The amounts of three-ring alkanes ranged about 7 percent to 50 percent with the latter being from the 150° C thermal product and the former from the 350° C thermal product. This suggests a decrease in the amount of three-ring alkanes with increase in temperature which is verified by the plot shown in figure 4. A similar trend was not found for the branched alkanes. The one- and two-ring alkanes tended to increase with increase in temperature, suggesting that the three-ring alkanes may be degraded to one- and two-ring alkanes at the higher temperatures. Similar trends were not found for the four-, five-, and six-ring compounds. The product formed in 0.5 day at 350° C contained more than 30 percent five-ring compounds and 20 percent six-ring compounds.

Undoubtedly many of the compounds present in the branched plus cyclic alkane fraction of the thermal degradation products are the same or similar to compounds identified previously in the soluble bitumen from a Mahogany zone oil shale by Anders and Robinson (5). In particular, the mass spectra of the thermally produced alkanes show large amounts of fragment ions characteristic of the sterane and pentacyclic triterpane compounds identified in the bitumen. This suggests that the isoprenoid-type structure comprises a significant portion of the kerogen. Also, there is evidence for the presence of the chain isoprenoid compounds identified previously.

Aromatic Oil Composition

Hasting's fragment ion technique (13) was used for the semiquantitative determination of the major compound types present in the low-temperature aromatic oil fractions obtained during the low-temperature heating tests.

The aromatic oils are composed (table 3) of 59 to 84 percent monoaromatics, 9 to 30 percent diaromatics, <1 to 19 percent triaromatics, and <1 to 21 percent polyaromatic compounds. Average values for each temperature for the ring compounds present in the aromatic fractions ranged from 74 to 79 percent monoaromatics, 14 to 23 percent diaromatics, 3 to 6 percent triaromatics, and <1 to 6 percent polyaromatics. The polyaromatics were formed only at 200° C, and this is believed to be correct as several mass spectral analyses of this sample were made to determine the validity of the presence of the polyaromatics. The polyaromatics are not formed in the 250° to 350° C aromatic fractions.

Generally the aromatic composition results show that the aromatic oils are composed mostly of one-, two-, and three-ring compounds and that more one-ring compounds are formed as the temperature increases from 200° to 350° C. Some monoaromatic compounds isolated by Anders and others (4) from the oil-shale bitumen were identified as alkyltetralins. The fragment ions used to identify these structures appear in the mass spectral results obtained for the low-temperature diaromatic structures suggesting that both the oil-shale benzene-soluble bitumen and the insoluble kerogen were formed from some of the same biological source materials.

TABLE 3. - Aromatic oil composition

Heating time, days	Wt-pct of total			
	Monoaromatics	Diaromatics	Triaromatics	Polyaromatics
		150° C		
90	81.3	17.9	0.6	0.2
180	77.5	20.6	1.9	.0
270	77.5	14.4	8.1	.0
360	68.3	25.0	6.7	.0
Average	76.2	19.5	4.3	.0
		200° C		
90	78.1	19.5	0.6	1.8
180	80.7	18.3	1.0	.0
270	66.7	8.8	3.5	21.0
360	69.6	10.4	19.4	.6
Average	73.8	14.3	6.1	5.8
		250° C		
10	84.0	16.0	0.0	0.0
12	73.6	26.2	.2	.0
16	59.3	30.2	10.5	.0
21	78.6	20.0	1.4	.0
Average	73.9	23.1	3.0	.0
		300° C		
0.5	70.9	23.6	5.5	0.0
1.0	77.8	17.0	5.2	.0
2.0	84.2	14.6	1.2	.0
3.0	69.6	24.8	5.6	.0
4.0	77.4	19.6	3.0	.0
Average	76.0	20.0	4.0	.0
		350° C		
0.5	73.6	20.1	6.3	0.0
1.0	81.7	16.3	2.0	.0
2.0	80.6	16.4	3.0	.0
3.0	79.8	18.4	1.8	.0
4.0	81.0	18.7	.3	.0
Average	79.3	18.0	2.7	.0

Composition of the Polar Resins

Elemental analyses obtained on the polar resin fractions were used to calculate the oxygen-, hydrogen-, nitrogen-, and sulfur-to-carbon atomic ratios shown in figure 5. The ratios of oxygen, hydrogen, and sulfur contents of the polar resins change with increased temperature. The oxygen ratio (O/C) decreases from 150° to 200° C, increases from 200° to 300° C, and decreases almost seven times to a minimum at 350° C after heating for 4 days. The hydrogen (H/C) ratio decreases from about 1.5 to 1.4 and the nitrogen (N/C) ratio increases from 0.02 to 0.04, or two times more, with increased temperature from 150° to 350° C. The sulfur (S/C) ratio decreases slightly as the temperature increases from 150° to 350° C.

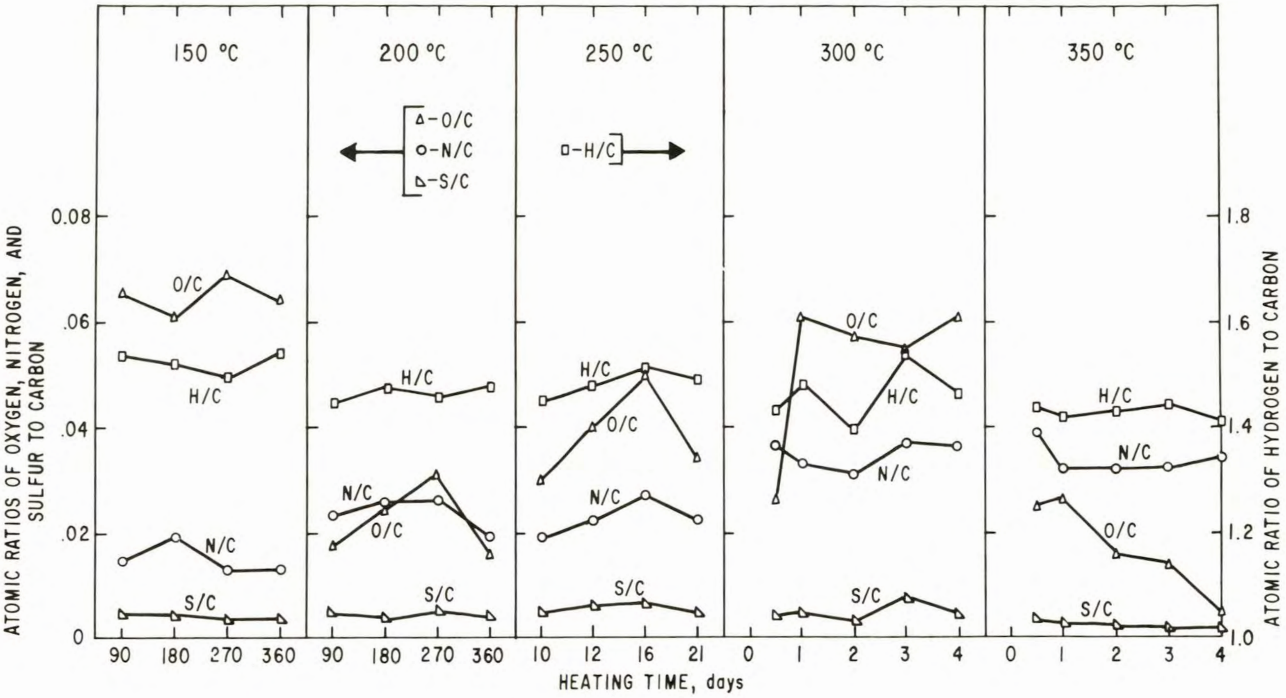

FIGURE 5. - Elemental ratios for polar resins on the atomic basis.

In general, these results show that the kerogen oxygen and nitrogen structures are thermally degraded and are an important part of the polar resins at each temperature from 150° to 350° C. Some of the kerogen's hydrogen and sulfur is degraded to form polar resins during the thermal treatment and some is evolved as gases. Because the compositions of these products vary in a predictable manner, the process engineer may find this useful in determining the conditions existing in outlying areas of the formation during in situ retorting operations.

Separation of the Polar Resins

The polar resins were separated on ion-exchange resins (14), and the results show (table 4) that the polar resin fractions contain about 84 to 93 percent neutral material, 6 to 13 percent acidic material, and 1 to 4 percent basic material. The ratio of acidic to basic material for the polar resins ranged from 2 to 10 and averaged about 4. The amount of acidic and basic materials varies with increased temperature and heating time. The acidic materials probably are derived from the kerogen oxygen structures and the basic materials from the kerogen nitrogen structures.

TABLE 4. - Composition of polar resins

Heating time, days	Wt-pct			Acid/base ratio
	Acid	Base	Neutral	
150° C				
90	8.2	3.1	88.7	2.7
180	9.5	2.1	88.4	4.5
270	9.1	3.0	87.9	3.0
360	7.0	3.0	90.0	2.3
200° C				
90	8.2	2.0	89.8	4.1
180	8.6	1.1	90.3	7.8
270	8.3	2.1	89.6	4.0
360	9.2	3.1	87.7	3.0
250° C				
10	6.2	1.0	92.8	6.2
12	7.1	1.0	91.9	7.1
16	7.1	3.1	89.8	2.3
21	13.1	3.0	83.9	4.4
300° C				
0.5	9.6	3.2	87.2	3.0
1.0	9.2	4.1	86.7	2.2
2.0	9.4	2.1	88.5	4.5
3.0	7.8	3.3	88.9	2.4
4.0	10.6	3.2	86.2	3.3
350° C				
0.5	12.8	2.1	85.1	6.1
1.0	10.8	2.2	87.0	4.9
2.0	12.0	1.2	86.8	10.0
3.0	10.8	1.1	88.1	9.8
4.0	6.3	3.2	90.5	2.0

Heated Residues

Five properties of the heated residues (table 5) related to structural differences are used to show the effect of low-temperature (150° to 350° C) heating for long heating times (0.5 to 360 days) on the thermal degradation of kerogen. These properties are atomic H/C ratio, volatile material ratio, carbon residue ratio, oxidation rate, and specific gravity of assay oil. The first four properties are used to show differences in the aromatic content of the kerogen, and the specific gravity of the assay oil is used to show differences in the oil-producing portion of the residual kerogen. The H/C ratio indicates the proportion of kerogen hydrogen atoms per kerogen carbon atom. (In a completely aromatic system the maximum ratio is 1.0.) The volatile material ratio, which represents the oil, gas, and water produced at 500° C per unit of organic carbon, is an indicator of the structure of the kerogen, because highly condensed cyclic aromatic structures produce little volatile material, but noncondensed or slightly condensed saturated structures and other aliphatic structures produce large yields of volatile material. The carbon residue ratio, which represents the amount of carbon residue formed at 500° C per unit of organic carbon, is an indicator of the amount of highly condensed cyclic structures that convert to carbon residue rather than produce volatile material. The rate of oxidation, using alkaline potassium permanganate, is an indicator of the type of structure present in the kerogen. Side chains on aromatic structures, partially unsaturated structures, and oxygen-containing groups or linkages are easily oxidized, whereas highly saturated hydrocarbon structures are oxidized quite slowly. The specific gravity of the assay oil from the oil shale samples is an indicator of the types of structures present in the oil-producing portion of the kerogen.

TABLE 5. - Properties relating differences in the kerogen of the heated residues

Heating time, days	Atomic H/C ratio	Volatile material ratio	Carbon residue ratio	Oxidation rate[1]	Specific gravity of assay oil
150° C					
90	1.37	96	30	1.34	0.914
180	1.32	102	33	1.49	.918
270	1.33	102	37	1.57	.913
360	1.30	95	41	1.39	.921
200° C					
90	1.31	99	29	1.35	0.920
180	1.27	98	33	1.12	.925
270	1.27	91	34	1.48	.924
360	1.21	100	43	2.30	.922
250° C					
10	1.34	98	25	1.19	0.920
12	1.34	103	27	1.33	.914
16	1.33	110	28	1.48	.913
21	1.28	109	29	1.27	.914
300° C					
0.5	1.38	106	24	1.25	0.916
1.0	1.37	98	28	1.27	.912
2.0	1.37	97	31	1.94	.909
3.0	1.36	96	45	2.23	.913
4.0	1.25	64	60	3.59	.911
350° C					
0.5	1.24	115	36	1.51	0.912
1.0	1.22	92	57	2.09	.906
2.0	1.00	76	61	2.55	.905
3.0	.81	53	71	3.85	.904
4.0	.64	45	86	5.49	.902

[1] Milliliters of 3 percent $KMnO_4$ solution consumed per gram of organic carbon per minute.

The atomic H/C ratio decreases with increased heating time at each temperature, and the lowest ratios are obtained at 350° C. The volatile material ratios vary with increased heating time to 300° C and decrease with increased heating time and temperature at 300° and 350° C. The carbon residue ratios increase with increased heating time at each temperature, and the largest ratios are obtained at 350° C after heating 2 to 4 days. The oxidation rates vary with increased heating time and temperature to 300° C and increase with increased heating time at 300° and 350° C. The fastest oxidation rates are obtained at 350° C after heating 3 and 4 days. The lowest specific gravities of the oil are obtained at 350° C.

In general these results show that long-time heating of the kerogen at 150° to 350° C, comparable to conditions associated with in situ retorting operations, will solubilize some of the kerogen, and as the kerogen oil-forming components are solubilized, the structure of the unconverted kerogen becomes more aromatic. At 250° to 350° C, thermal degradation results show that the kerogen was thermally degraded to low-molecular-weight oil products. The values obtained for the 350° C heated residues show that the residual organic material has become very aromatic and has up to one-half of the oil-producing constituents removed.

SUMMARY AND CONCLUSIONS

The elemental composition of the soluble pyrolytic products depended upon the heating temperature and heating time. The n-alkanes are thermally formed from the kerogen structure during the 150° to 350° C pyrolysis. The n-alkanes have a carbon-number distribution similar to thermally altered n-alkanes and differ from the carbon-number distribution of the n-alkanes of the natural bitumen of the oil shale. The 250° C heating temperature produced the largest amount of branched plus cyclic alkanes. All of the branched plus cyclic alkanes contained structures similar to the chain isoprenoid, sterane, and pentacyclic triterpane compounds found in the natural bitumen.

The aromatic oils may contain alkyltetralin structures similar to the alkyltetralin compounds isolated and identified in the benzene-soluble bitumen from the Green River shale, indicating that both the insoluble kerogen and the soluble bitumen may be formed from some of the same source materials.

The polar resins contain an average ratio of four times more acidic than basic materials. The large amount of more than 75 percent polar materials present in the soluble thermal products plus the amount of oxygen present in the polar resins show that the oxygen in the kerogen structure has a direct effect on the composition of the soluble thermal products. The heated kerogen residues lose some of their oil-forming components and become more aromatic with increased temperature (150° to 350° C) and increased heating time (0.5 to 360 days).

This study raised some questions that were unanswered in the present study. For example, it must be determined why most hydrocarbons are found in the 250° C thermal product, and what type of thermally resistant nitrogen compound is formed at 350° C. Additional research could result in the solution to these questions and provide information on the nature of the organic structures present in the kerogen. Also increased knowledge about the conversion of kerogen by thermal degradation to useful products would probably be gained by additional study in these temperature ranges.

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