FRACTIONATION OF SOLUBLE EXTRACTS OBTAINED FROM KEROGEN THERMAL DEGRADATION WITH CO AND H_2O

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INTRODUCTION

Various techniques (1, 2, 3)[1] have been developed for the conversion of oil-shale kerogen to usable products. Each technique of conversion produces a different product with different characteristics. The thermal degradation of oil-shale kerogen in the presence of carbon monoxide and water has been studied at the Laramie Energy Research Center (4, 5). It was shown from this study that more kerogen is converted to a benzene-methanol soluble extract at temperatures below 500° C than is converted to oil by dry retorting. Because this reaction appears to have some potential advantages (5) over other conversion methods, it is desirable to investigate the soluble extracts obtained from this reaction.

This study was conducted to determine the types of compounds present in the soluble extracts that represent as much as 90 percent of the kerogen in Green River oil shale. This was accomplished by separating the soluble extracts into acid, base, neutral nitrogen, *n*-alkane, branched plus cyclic, aromatic, and cyclohexane-insoluble fractions by the established method. The method was used to compare the amount of each fraction produced under various reaction conditions where the temperature was varied from 300° to 450° C and the time was varied from 0.25 to 6 hours at charged CO pressure of 1,000 psig.

Because most of the extracts showed very little solubility in *n*-pentane, the previous separation method used for the natural bitumen in this laboratory (6 - 8) was not applicable and another technique had to be used. The modified method incorporated the uses of ion exchange resins first suggested by Munday and Eaves (9) and some of the techniques developed by Jewell (10) to remove the acid, base, and neutral nitrogen fractions. The hydrocarbon fractions were separated into *n*-alkane, branched plus cyclic alkane, and aromatic fractions by using molecular sieves as described by O'Connor and others (11) and silica-gel chromatography.

The soluble extracts obtained from each of the time-temperature tests were fractionated by the separation techniques. Because of the similarity of the data, only a limited number of these separations will be discussed in this report. For evaluation and comparison of the soluble extracts obtained by thermal degradation of kerogen in the presence of CO and H_2O with other oil-shale degradation products, three shale oils (1, 2, 3) obtained by different conversion methods were fractionated by the same separation technique. The component distribution of the soluble extracts will be discussed relative to the shale oils.

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

It was found that below 375° C the fraction amounts of the soluble extracts were significantly different from those obtained from the three shale oils and that the temperature or the time of reaction had little effect upon the amount of each fraction. At 400° and 450° C, the fraction amounts of the soluble extracts changed with increase in temperature and at 450° C the soluble extracts resembled to some degree the shale oils.

EXPERIMENTAL

Materials

IRA-904 anion resin[2], A-15 cation resin (Rohm and Haas Company) and ferric chloride supported on clay were prepared and extracted similar to the procedures described by Jewell (10).

Silica gel (grade 12, 28-200 mesh, Davison Chemical Co.) was activated at 200° C for 24 hours and 5A molecular sieve (Matheson, Coleman, and Bell) was activated at 250° C for 24 hours.

N-pentane (99 percent, Phillips Petroleum) and 1,2 dichloroethane (reagent grade, Eastman Chemical Co.) were purified by flash distillation and by percolation through activated silica gel. Benzene, chloroform, methanol (reagent grade, J. T. Baker), and cyclohexane (99.5 percent, Phillips Petroleum) were flash distilled. The isopropylamine (reagent grade, J. T. Baker) and acetic acid (reagent grade, Eastman Chemical Co.) were used as received. Isooctane (99 percent, Phillips Petroleum) was purified by percolation through an activated 5A molecular sieve.

Samples of Soluble Extracts

The soluble extracts were obtained from the thermal conversion of Green River oil-shale kerogen in the presence of carbon monoxide and water as described by Cummins, et al. (4). The oil-shale samples were heated at temperatures from 300° to 450° C for 0.25 to 6 hours at charged CO pressure of 1,000 psig. The soluble extracts were obtained by treating the products of the $CO-H_2O$ reaction in benzene and methanol.

Fractionation Procedure

The fractionation scheme is shown in detail in figure 1 and is essentially the same as the one used by D. M. Jewell, et al. (10). Since the soluble extracts obtained from $CO-H_2O$ reaction with kerogen were generally polar, it was necessary to use cyclohexane rather than *n*-pentane as a solvent and to use a circulating system for all acid and base fractions to be removed from the extracts by IRA-904 anion resin and A-15 cation resin. The solution containing the acid and base components to be removed was circulated continuously over the resin bed for 24 hours by a pumping system. Excellent recoveries of acid and base fractions from the resins were obtained. Ferric chloride-Attapulgus clay was used to separate the acid and base-free fraction into hydrocarbon and neutral nitrogen fractions. The hydrocarbon fraction was then separated into *n*-alkane, branched plus cyclic alkane, and aromatic fractions by using silica-gel chromatography and molecular sieves.

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[2] Reference to specific trade names or manufacturers does not imply endorsement by the Energy Research and Development Administration.

All fractions obtained were freed of solvent and then dried under reduced pressure at 60° C and weighed. By using the various fractionation techniques the average recovery of the soluble extract amounted to more than 90 percent. All data shown was normalized to 100 percent.

Cyclohexane-insoluble fraction

Approximately 2 g of the benzene-methanol soluble extract was heated and stirred with 200 ml of cyclohexane at 80° C for 1 hour. After cooling to room temperature, the mixture was filtered. The cyclohexane-insoluble fraction was washed with fresh cyclohexane until the solvent became clear.

Acid fraction

The cyclohexane-soluble fraction was redissolved in cyclohexane and slowly pumped through the anion resin for 24 hours. A ratio of 7 parts of resin to 1 part of sample was used. The acid-free fraction was transferred to a flask and the resin was washed with fresh cyclohexane.

The total acid fraction was recovered from the resin by 2 percent of acetic acid in benzene with Soxhlet extraction for 24 hours.

Base fraction

The technique and the amount of resin used to remove the base fraction from the acid-free fraction were the same as for the removal of the acid fraction. The base fraction was recovered from A-15 cation resin by 8 percent isopropylamine in benzene and methanol with Soxhlet extraction for 24 hours.

Neutral nitrogen and hydrocarbon fractions

Five parts of IRA-904 anion resin to 1 part sample were packed into a column and 7 parts of ferric chloride-Attapulgus clay mixture to 1 part sample were packed on the top of the resin with a glass wool plug in between the two materials. The acid- and base-free fraction was dissolved in pentane and then percolated slowly downward through the column. The hydrocarbon fraction was obtained by pentane elution and the neutral nitrogen fraction was desorbed from the column by elution with 1,2 dichloroethane.

Alkane and aromatic fractions

Two hundred g of activated silica gel to 1 g of hydrocarbon fraction were packed into a column and the hydrocarbon fraction dissolved in pentane was charged to the column. The alkane fraction was obtained by elution with pentane. Chloroform was used to deactivate the column and the aromatic fraction was removed by elution with methanol.

Branched plus cyclic alkane and *n*-alkane fractions

The alkane fraction obtained from the silica-gel column was dissolved in isooctane (100 ml for 0.2 g of sample) and 20 parts of 5A molecular sieves to 1 part sample were added to the solution. The solution was refluxed for 24 hours then filtered. The branched plus cyclic alkane fraction was obtained by drying the filtrate of this solution.

The molecular sieves were extracted with benzene and methanol for 24 hours in order to remove any traces of polar materials. The *n*-alkane fraction was recovered from the molecular sieves by decomposing the sieves with HF in benzene. Gas chromatograms of the *n*-alkane fractions of the selected samples were obtained.

Gas Chromatography

All gas chromatographic results were obtained on a Hewlett-Packard Model 700 gas chromatograph equipped with a thermoconductivity detector using a 50 ft SE-30 SCOT column programmed from 100° to 275° C at 5°/min with a helium flow of 5 cc/min.

RESULTS AND DISCUSSION

The weight percents of kerogen converted and the elemental analyses of the soluble extracts for 1 hour reaction time at various temperatures are shown in table 1. From these data it appears that the soluble extracts prepared at

TABLE 1. - Weight percent of kerogen converted and elemental analyses of the soluble extracts

Temp., °C	Time, hrs	Kerogen converted, weight-percent	Weight-percent of total					H/C ratio
			C	H	N	S	O[1]	
300	1	26.2	83.4	10.8	1.3	0.7	3.8	1.6
325	1	29.9	82.6	11.0	1.3	0.9	4.2	1.6
350	1	31.3	81.1	10.9	1.2	0.5	6.3	1.6
375	1	46.8	83.6	11.3	1.5	0.5	3.1	1.6
400	1	76.9	82.1	11.1	1.7	0.3	4.8	1.6
425	1	93.9	83.3	11.5	1.4	0.4	3.4	1.7
450	1	97.9	83.4	10.5	2.7	0.5	2.9	1.5

[1] Oxygen was determined by difference.

different temperatures do not differ significantly in elemental contents. The weight percent of kerogen converted varied from 26.2 to 97.9 as temperatures increased from 300° to 450° C.

Effect of temperature

Seven soluble extracts obtained at 300°, 325°, 350°, 375°, 400°, 425°, and 450° C for 1 hour reaction time were fractionated to determine the effect of reaction temperature upon the composition of each extract. These results are shown in figure 2. Below 375° C the compositions of each extract remain fairly constant. Apparently the acid and the base fractions are fairly stable at this temperature range and do not undergo drastic changes. The polar materials which are the sum of acid, base, and neutral nitrogen fractions represent about 65 percent of the soluble extract. Above 375° C, the relative amounts of acid fractions decrease rapidly whereas the relative amounts of base and hydrocarbon fractions increase. This suggests that the acid fractions consist of bifunctional groups that presumably decarboxylate to give additional bases and hydrocarbons at higher temperatures. The concentrations of neutral nitrogen fractions remain about 1 to 2 percent and apparently are not affected by temperature.

Figure 3 shows the distribution of the *n*-alkane, the branched plus cyclic alkane, and the aromatic fractions. The increase in concentration in each fraction shows that more thermal degradation of the higher-molecular-weight kerogen to the lower-molecular-weight hydrocarbons occurs at high temperatures. The relative distribution of the various hydrocarbon components remains fairly constant showing that they are formed at approximately the same rate.

Effect of reaction time

The relationship of fraction amounts of the soluble extracts to reaction time at 300° C is shown in figure 4. It is obvious that the component distribution does not change appreciably with time of heating at 300° C and the amount of each fraction is independent of the time of heating.

The fraction amounts of the soluble extracts prepared at 450° C shown in figure 5 are almost time independent. This figure is broken into two sections for clarity. There is a slight decrease of cyclohexane-insoluble fractions and a slight increase of hydrocarbon fractions. This is probably due to the fact that as the reaction time increases at 450° C, the cyclohexane-insoluble fractions, presumably with high-molecular-weight, start to degrade to hydrocarbons. These changes are not drastic. It can be observed that the relative amounts of the fractions of the soluble extracts are not affected significantly by reaction time at 450° C.

Comparison with shale oils

Because there is some indication that the $CO-H_2O$ reaction with oil shale may have some advantages as a process reaction over other methods of thermal degradation, it is desirable to compare the soluble extracts obtained by the $CO-H_2O$ reaction with shale oils. This comparison is shown in table 2. The soluble

TABLE 2. - Comparison between the soluble extracts from $CO-H_2O$ reaction and shale oils

Sample	Weight-percent of total				
	Acid fractions	Base fractions	Neutral nitrogen fractions	Hydrocarbons	Cyclohexane-insoluble fractions
Soluble extract at 300° C[1]	54.4	12.6	1.4	18.8	12.8
Soluble extract at 375° C[1]	50.3	12.6	1.5	17.7	17.9
Soluble extract at 450° C[1]	24.5	23.2	1.3	38.4	12.6
In situ shale oil (Rock Springs)	16.9	14.4	0.7	58.4	9.6
Gas combustion shale oil	19.9	26.3	2.1	44.6	7.1
150-ton retort shale oil	13.5	20.5	2.1	55.7	8.2

[1] At 1 hr reaction time.

extracts from the 300° to 375° C tests were very polar and contained only about 20 percent hydrocarbons. As the temperature increased above 375° C, more hydrocarbons were produced, presumably because of more thermal cracking. At 450° C the hydrocarbon fractions represented 38.4 percent of the total extract which approximated the amount of hydrocarbons in the three shale oils chosen for this comparison. In general, the three shale oils (in situ shale oil from Site 4, Rock Springs; gas combustion shale oil, and 150-ton retort shale oil) are less polar and contain more hydrocarbons than the soluble extracts from the 300° to 375° C, CO-H_2O reaction of kerogen. This suggests that the latter products have been subjected to less thermal cracking and less destructive degradation. The soluble extract obtained at 450° C contains higher percentage of hydrocarbon fractions somewhat similar to the gas combustion shale oil and should be a suitable feedstock for further hydrocracking techniques.

Distribution of *n*-alkane fractions of the extracts and natural bitumen

The carbon-number distribution of the *n*-alkanes is a good indicator of the thermal history of the organic material in Green River oil shale. The natural bitumen and low-temperature thermal degradation products show odd-even predominance (OEP) (12) of the carbon numbers in the C_{25} to C_{31} range. Extensive thermal degradation causes a rearrangement of carbon numbers with a drastic decrease in the odd-even predominance for the *n*-alkanes.

Figure 6 shows the *n*-alkane distribution of the soluble extracts obtained at 300°, 350°, 400°, and 450° C for 1 hour reaction time and the *n*-alkane distribution of the benzene-soluble bitumen from a Mahogany zone oil-shale sample (13). The change in distribution from 300° to 450° C indicates that temperature has a strong effect on the carbon-number distribution of *n*-alkanes. At 300° C the *n*-alkane distribution appears to be more like that of natural bitumen where the OEP of the carbon number reaches four in the C_{29} to C_{31} area. The *n*-alkane distribution obtained at 300° C may be partly accounted for by the presence of the natural bitumen in the raw oil-shale samples used for the tests. At 450° C the distribution of *n*-alkanes becomes more envelope shaped which is the typical distribution for thermally degraded products. The OEP is about one indicating that there is little or no odd-even predominance. This shows that the soluble extracts prepared at 300° and 350° C for 1 hour have not been subjected to drastic thermal alteration and should be suitable products for constitutional study. Undoubtedly they contain many of the basic structures present in the original kerogen.

CONCLUSION

High recoveries of the various fractions show that this modified separation method works well with the high-molecular-weight and polar extracts from the CO-H_2O reaction of kerogen. The *n*-alkane distribution of the soluble extracts prepared below 350° C shows that the soluble extracts have not been subjected to drastic thermal degradation and will be suitable samples for compositional study. As temperature increases above 375° C, the relative amounts of acid fractions decrease but the base and hydrocarbon fractions increase. This indicates that the increases in the amounts of base and hydrocarbon fractions result from decomposition of the acid fraction above 375° C. The reaction time has no effect on the relative amount of each fraction at constant temperature from 300° to 450° C for 0.25 to 6 hrs, with the exception of hydrocarbons at the highest temperatures where a minor increase in amount is noted.

Increase in temperature of the $CO-H_2O$ reaction from 300° to 450° C results in a change of the relative amount of each fraction. As temperature of the $CO-H_2O$ reaction is increased to 450° C, the soluble extract obtained becomes more like a shale oil and should be a suitable feedstock for further hydrocracking techniques.

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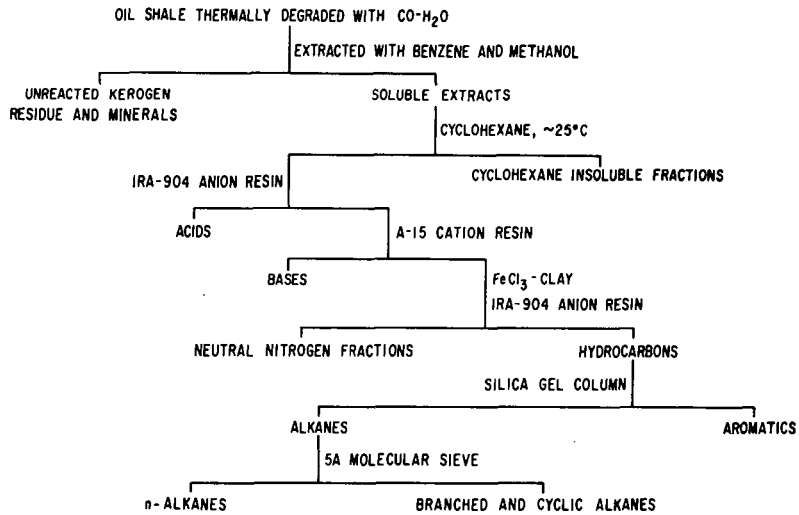

FIGURE 1.- FRACTIONATION SCHEME FOR THE SOLUBLE EXTRACTS FROM CO-H_2O REACTION.

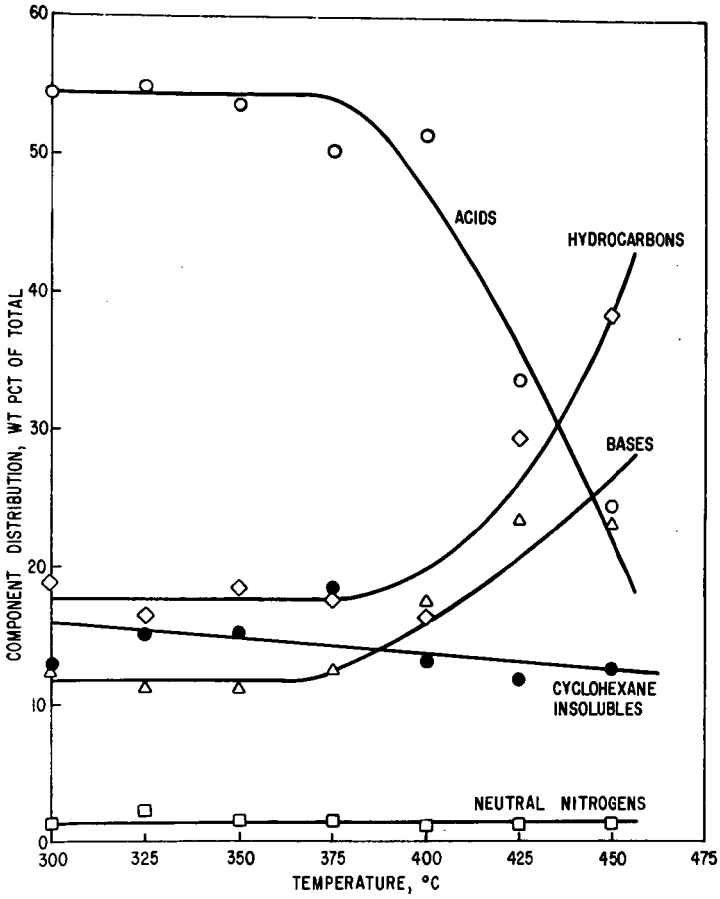

FIGURE 2.- RELATIONSHIP OF FRACTION AMOUNTS TO TEMPERATURE FOR ONE HOUR REACTION TIME.

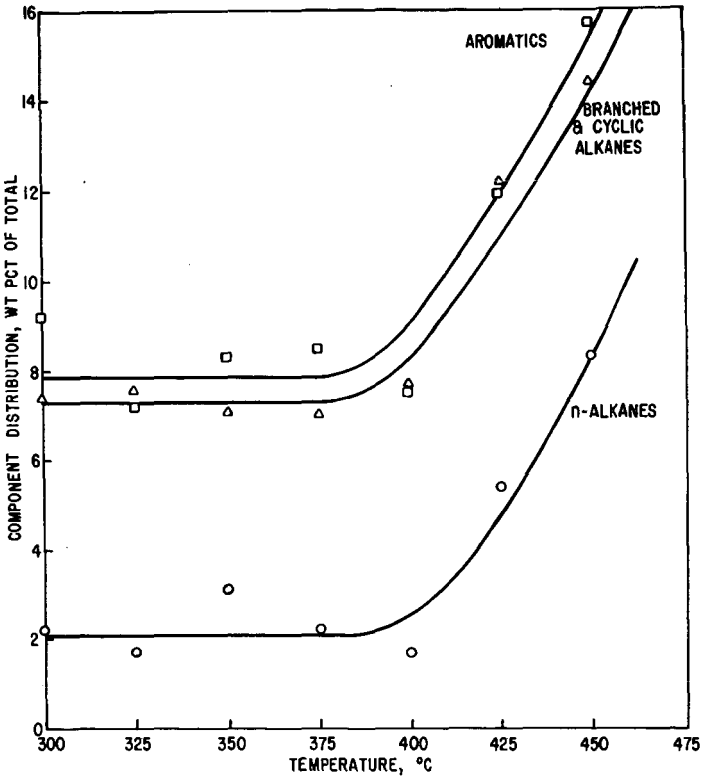

FIGURE 3.- RELATIONSHIP OF HYDROCARBONS TO TEMPERATURE FOR ONE HOUR REACTION TIME.

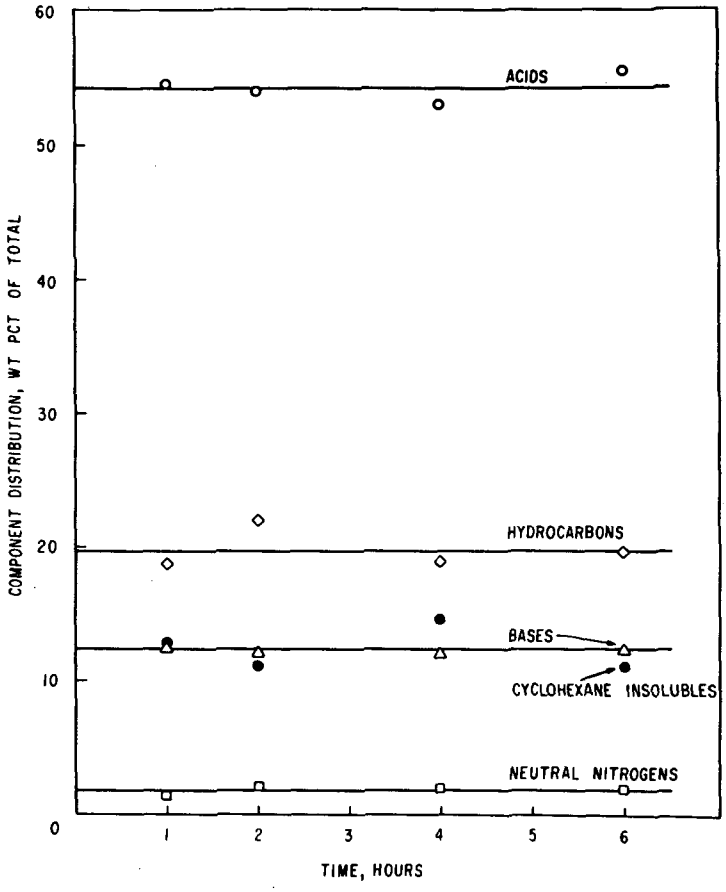

FIGURE 4.- RELATIONSHIP OF FRACTION AMOUNTS TO REACTION TIME AT 300°C.

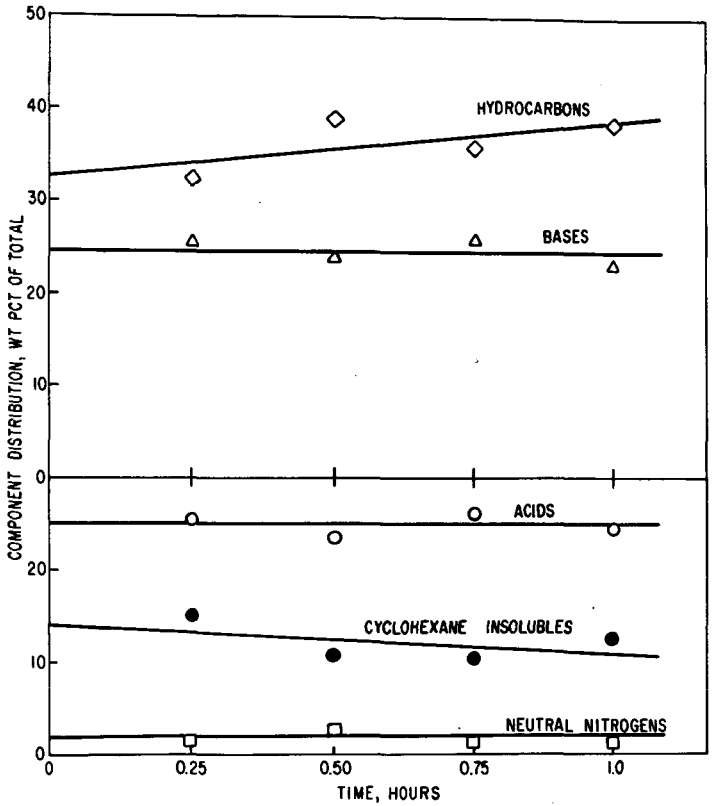

FIGURE 5.- RELATIONSHIP OF FRACTION AMOUNTS TO REACTION TIME AT 450 °C.

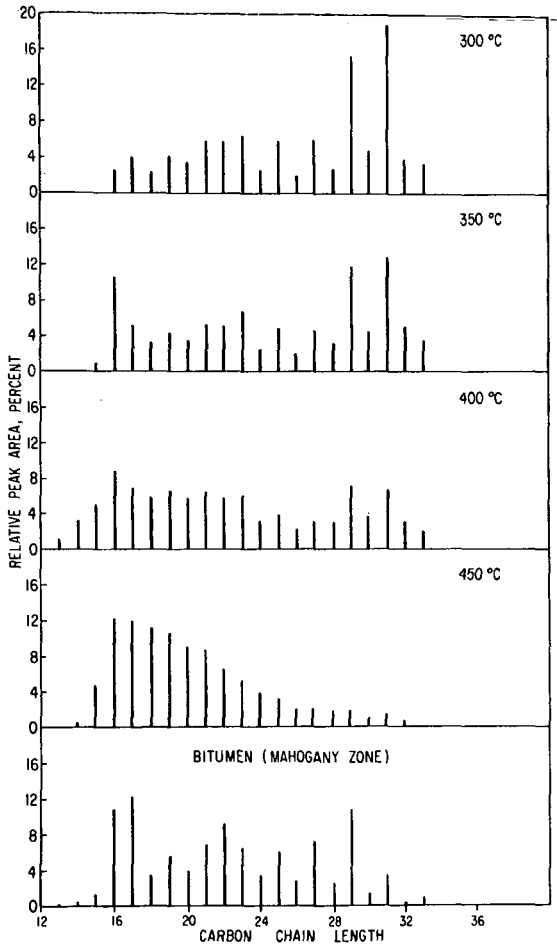

FIGURE 6.-DISTRIBUTION OF n-ALKANE FRACTIONS OF THE EXTRACTS AND NATURAL BITUMEN.