

CONTROLLED LOW-TEMPERATURE PYROLYSIS OF BENZENE-EXTRACTED GREEN RIVER OIL SHALE

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INTRODUCTION

The present study was undertaken to determine the rate at which oil-shale kerogen decomposes and to determine the composition of the pyrolytic products formed at 300° and 350° C in a helium atmosphere at atmospheric pressure. A study of the thermal reaction at these low temperatures (150° to 200° C below normal retorting temperatures) is important because of the current interest in the in situ retorting processes of converting oil shale to shale oil. During in situ retorting it may take long periods of heating to raise the temperature of the oil shale from ambient temperature to the final retorting temperature, thus thermal reactions at intermediate temperatures may become important. The present study was made to investigate some of the possible variables in the thermal behavior of the oil-shale organic material as a function of time and temperature.

A number of investigators have studied the conversion of oil shale to pyrolytic products. Hubbard and Robinson⁶ investigated the oil-shale decomposition rates from 350° to 500° C. Dinneen³ studied the effect of various retorting temperatures on the composition of shale oil. Allred¹ presented some considerations on the kinetics of oil-shale pyrolysis. Hill and co-workers⁵ studied the thermal decomposition of kerogen in the presence of methane.

The present study extends the published data to a lower temperature range by discussing the kinds of products obtained at pyrolysis temperatures of 300° and 350° C and at pyrolysis times ranging from 12 to 96 hours.

EXPERIMENTAL

One-hundred-gram samples of benzene-extracted oil shale were heated at 300° or 350° C for selected periods of 12, 24, 48, 72, or 96 hours in a helium atmosphere at atmospheric pressure. The amounts of pyrolytic products that formed during the heating process (except gas and carbon residue) were determined. No attempt was made to determine the amount of gas and carbon produced because only small amounts are formed at these temperatures. The pyrolytic product that volatilized during the heating is called oil. The pyrolytic product that did not volatilize was recovered by extracting the heated residue and is called bitumen.

Oil-Shale Sample. The sample of Green River oil shale used in this study was obtained from the Bureau of Mines demonstration mine near Rifle, Colorado. The sample assayed about 66 gallons of oil per ton of shale, contained 30.2 percent organic carbon, and contained 7 percent benzene-soluble bitumen. Prior to heating, the shale was crushed to pass a 100-mesh sieve and then benzene extracted five times, each time with fresh solvent, until it was essentially free of soluble organic material. This was demonstrated by the decreasing recovery with each successive extraction. The extracted sample was then dried at 60° C under reduced pressure until free of benzene.

The percent organic carbon in the extracted oil shale and in the pyrolytic residues was determined by combustion analysis. The results were used as a measure of the kerogen decomposition.

Apparatus. The pyrolysis apparatus used in this investigation is capable of heating a 100-gram sample of oil shale. Weighed samples were pyrolyzed in a stainless-steel boat housed in a Pyrex combustion tube 800-mm long x 50-mm o.d. One end of the combustion tube was equipped with a metal cap having a sliding metal bar through the middle of the cap and a gas inlet tube in the side of the cap. The metal bar was used to move the boat in or out of the hot zone of the furnace. The other end of the combustion tube was connected to two traps in series, a water-cooled trap followed by a Dry Ice trap.

Recovery of the Products. The volatile product (oil) that condensed in the water-cooled trap was recovered with benzene. After the benzene was removed, the product was dried and weighed. The heated residue was cooled in the outer end of the combustion tube in the presence of helium. After cooling, the heated residue was placed in a Soxhlet extractor and extracted with benzene for 16 hours. The nonvolatile product (bitumen) recovered from the benzene solution by evaporation of the benzene, was dried and weighed. The residue was dried under vacuum at 60° C and weighed. The percent organic carbon remaining in the heated residue was determined, and the percent unconverted organic carbon was calculated from this determination and from the results of a similar determination on the starting material. Most of the pyrolytic gases were trapped in the Dry Ice trap. The trap was allowed to warm to room temperature. The weight of the product was used to estimate the amount of gas formed.

Fractionation of the Oil and Bitumen. Each oil and each bitumen were fractionated using standard procedures.² The product was allowed to stand in pentane at 0° C for 16 hours thereby separating the material into pentane-soluble and pentane-insoluble fractions. After the pentane was removed, the pentane-soluble material was placed on an alumina column using a 1 to 25 ratio of sample to alumina and was fractionated by elution chromatography into hydrocarbon concentrate and resin fraction. The hydrocarbon concentrate was placed on a silica-gel column, using a 1 to 25 ratio of sample to silica gel, and separated into an alkanes-plus-olefins fraction and an aromatic-oil fraction. The alkanes plus olefins were placed on a silica-gel column using a 1 to 60 ratio of sample to silica gel and fractionated into alkane and olefin fractions using a method developed by Dinneen and co-workers.⁴ The alkanes were placed on 5 Å molecular sieves and separated into an n-alkane fraction and a branched-plus-cyclic alkane fraction. The n-alkanes were fractionated using a programmed GLC at a heating rate of 7.5° C min⁻¹ and using a 5-foot, 1/4-inch SE 30 column.

RESULTS AND DISCUSSION

The results of this study will be discussed in terms of the amount of pyrolytic products formed, the conversion of kerogen to oil and bitumen, and the order of thermal reactions. In addition, the distribution of individual components of the thermal products and their rates of formation will be discussed. As an aid to planning future studies, the conversion of kerogen to pyrolytic products at temperatures lower than 300° C was estimated.

At low temperatures kerogen is converted mainly to oil and bitumen. The amount of gas formed at 300° and 350° C was less than 1 percent of the total pyrolytic products. The amount of carbon residue formed at 300° and 350° C, although not determined, was assumed to be less than 1 percent of the pyrolytic product. Thus, the pyrolytic gas and carbon residue formed were

not considered separately in this report. Any carbon residue formed was included in the unconverted kerogen value and any gas formed was included in the kerogen converted value.

The amounts of pyrolytic products formed at 300° and 350° C at different time intervals appear in table 1. The percent of the kerogen converted to pyrolytic products is based on the

TABLE 1. - The amount of pyrolytic products formed

Time, hours	$(100X)^{1/2}$	1-X	Log (1-X)	Weight percent of pyrolytic products	
				Oil	Bitumen
300° C					
12	5.4	0.946	-0.0241	73	27
24	7.4	.926	- .0334	69	31
48	8.6	.914	- .0391	77	23
72	9.7	.903	- .0443	78	22
96	11.0	.890	- .0506	76	24
350° C					
12	34.9	.651	- .1864	62	38
24	40.2	.598	- .2233	63	37
48	51.4	.486	- .3134	72	28
72	61.8	.382	- .4179	77	23
96	64.3	.357	- .4473	94	6

$1/2$ Kerogen converted, weight percent of total kerogen.

difference between the organic carbon content of the sample before heating and the organic carbon content of the heated residue after the removal of the volatile and soluble products. At each temperature, the amount of kerogen converted to pyrolytic products doubled when the heating time was increased from 12 to 96 hours. Approximately a sixfold increase in the amount of kerogen converted was obtained when the temperature was increased from 300° to 350° C.

The kerogen is converted to a volatile oil product and to a nonvolatile bitumen during pyrolysis. At both temperatures the amount of volatile oil formed is greater than the amount of bitumen formed. A large decrease in the amount of bitumen was obtained at 96 hours over that obtained at 72 hours at 350° C. This indicates that the bitumen degraded and volatilized as oil.

The conversion of kerogen to oil and bitumen at 300° C is shown in Figure 1 where concentration is plotted against time. The oil-plus-bitumen curve rises sharply for the first 24 hours, then tends to level off from 24 to 96 hours. Similar trends are apparent in the oil and bitumen curves. These trends suggest that the conversion of bitumen to oil is negligible at 300° C. In contrast, a similar plot of the 350° C data (Figure 2) shows that the bitumen curve decreases after 72 hours and tends toward zero at 96 hours. The oil curve continues to rise between 72 and 96 hours. The latter results support the findings of Allred¹ and Hubbard and Robinson⁶ who suggest that kerogen is converted to bitumen and the bitumen is in turn converted to oil.

To determine the order of the thermal reaction of kerogen at 300° and 350° C, the log of the kerogen concentration [$\log(1-X)$ shown in table 1] was plotted against time for each temperature. Reasonably straight line relationships were obtained for the 300° C data (Figure 3) and the 350° C data (Figure 4) showing that the overall thermal conversion of kerogen at these temperatures is probably first order.

The specific reaction rates at each temperature were calculated from the slope of the curves in the log concentration-time plots and equal 2.303 times the slope of the curve. The determined specific reaction rate (k) of the total thermal product at 300° C equals 0.7×10^{-3} hour⁻¹ and at 350° C equals 7.6×10^{-3} hour⁻¹. From this, it appears that the reaction rate at 350° C is about 11 times the rate at 300° C. The calculated activation energy between 300° and 350° C is about 33 kilocalories mole⁻¹.

Each oil and each bitumen were fractionated to ascertain any existing differences in their compositions. The oils and bitumens were fractionated into the following type components: n-Alkanes, branched-plus-cyclic alkanes, olefins, aromatic oil, resins and pentane-insoluble material. The distribution of these fractions appears in table 2 where the results obtained for

TABLE 2. - Distribution of components present in the thermal product

Time, hours	Weight percent of kerogen					Pentane- insoluble material
	n-Alkanes	Branched-plus- cyclic alkanes	Olefins	Aromatic oil	Resins	
300° C						
12	0.17	0.30	0.05	0.17	4.00	0.71
24	.11	.71	.17	.17	2.93	3.31
48	.13	.79	---	.43	7.05	.20
72	.15	1.00	.15	.61	7.14	.65
96	.26	1.02	.19	1.02	8.01	.50
350° C						
12	.80	2.48	.56	1.95	25.93	3.18
24	2.17	3.70	.64	3.38	25.97	4.34
48	1.39	3.86	.36	1.75	35.87	8.17
72	2.72	3.52	.80	1.17	35.98	17.61
96	3.02	4.82	1.22	4.24	48.24	2.76

the volatile oil and the nonvolatile bitumen were calculated as one pyrolytic product. In general, the thermal products from both temperatures contained more polar materials (resins plus pentane-insoluble materials) than hydrocarbons.

The data from the fractionation of the oils and bitumens prior to combining showed the oil fractions to contain more hydrocarbons than did the bitumen fractions. The hydrocarbon content of the oil fractions ranged from 20 to 26 percent of the total fraction, and the hydrocarbon content of the bitumen fractions ranged from 1 to 7 percent. These results show that during oil-shale

pyrolysis the high-molecular-weight nonvolatile polar bitumen degrades to a less polar and lower-molecular-weight oil. These results are different than those from a previous study⁶ where kerogen was pyrolyzed at 350° C in tetralin to soluble products. In that study more than half of the products remained as high-molecular-weight pentane-insoluble material. This indicated that further degradation to volatile products is not a major factor when kerogen is converted to pyrolytic products in the presence of tetralin.

The specific reaction rates were calculated for the individual components of the pyrolytic products using the method previously described. The results are shown in table 3. At

TABLE 3. - Reaction rates for the production of the individual components present in the thermal products

Fraction	k, hours ⁻¹		$\frac{350^\circ \text{ C rate}}{300^\circ \text{ C rate}}$
	300° C	350° C	
n-Alkanes	3×10^{-5}	6×10^{-4}	20
Branched-plus-cyclic alkanes	1×10^{-4}	3×10^{-4}	3
Olefins	1×10^{-4}	7×10^{-4}	5
Aromatic oil	9×10^{-5}	4×10^{-4}	4
Resins	5×10^{-4}	4×10^{-3}	8
Pentane-insoluble material	2×10^{-4}	2×10^{-3}	9
Total product	1×10^{-3}	8×10^{-3}	7

300° C the n-alkanes are formed at the slowest rate while the resins are formed at the fastest rate. At 350° C the branched-plus-cyclic alkanes are formed at the slowest rate while the resins are formed at the fastest rate. The total product rate agrees favorably with the overall rate given previously. The 350° C rate divided by the 300° C rate shows the proportional rate of increase of the individual components between 300° and 350° C and their relationship to the overall rate. Normal alkanes formed 20 times as fast at 350° C as at 300° C. Branched-plus-cyclic alkanes formed three times as fast at 350° C as at 300° C. The change in production of the other fractions is not much different from the change in the total product rate.

The n-alkanes from the oil fractions were separated by GLC and chromatograms were obtained for each fraction. Plots of carbon numbers of the n-alkanes versus concentration were made to determine the effect of pyrolytic time and temperature on the composition of the n-alkanes. The data from the 300° C n-alkanes produced envelopes at C₁₃ to C₂₆ and envelopes at C₂₇ to C₃₅. The data from the 350° C alkanes produced envelopes at C₁₂ to C₂₆ and C₂₇ to C₄₀. In general, the percent of n-alkanes in the C₁₂ to C₂₆ range increased with increase in heating time at both temperatures. Also, the percent of n-alkanes in the C₂₇ to C₄₀ range decreased with increase in heating time at both temperatures. These results indicate that more low-molecular-weight n-alkanes than high-molecular-weight n-alkanes are thermally degraded from the kerogen or degraded from the bitumen with increased time and temperature.

A plot of percentage of kerogen converted, in terms of the yearly rates ($R \times 10^2$), versus the reciprocal of absolute temperature was made to determine if it is practical to study the thermal reaction rate of kerogen at temperatures lower than 300° C. The plot (Figure 5), based on the thermal reaction rate per year at 300° and 350° C, is extrapolated to 50° C. The figure shows that 100 percent of the kerogen would be converted to soluble products in 1 year at 265° C.

About 30 percent of the kerogen would be converted to soluble products in 1 year at 250° C while about 1 percent would be converted in 1 year at 200° C. It is evident from this plot that extended periods of time would be required to study the rate of conversion at temperatures lower than 300° C. One interesting aspect of this plot is the indication that about 6 percent of the kerogen should be converted to soluble products at 50° C in 100 million years. This suggests that the soluble bitumen present in the oil shale could have been derived from the kerogen at temperatures as low as 50° C during the life span of the Green River Formation (Eocene, 60 million years).

SUMMARY

A twofold increase was obtained in the amount of pyrolytic product at constant temperature (300° or 350° C) when the length of heating time was increased from 12 to 96 hours. A sixfold increase was obtained in the amount of pyrolytic product at constant heating time when the temperature was increased from 300° to 350° C.

The overall thermal decomposition of kerogen at 300° and 350° C appears to be a first-order reaction. The specific reaction rate constant at 300° C was determined as 0.7×10^{-3} hour⁻¹ and at 350° C as 7.6×10^{-3} hour⁻¹.

Differences in the rate of formation of individual type components of the pyrolytic product are apparent. Between 300° and 350° C, n-alkanes formed faster than the overall average rate of product formation while the branched-plus-cyclic alkanes formed slower than the overall average rate. Rate of formation of the other fractions was nearly equal to the average rate.

The average molecular weight of the n-alkane fraction decreased with increase in heating time and heating temperature.

Extrapolation of the rate data to temperatures below 300° C indicated that the amount of natural bitumen present in oil shale could have been thermally degraded from kerogen at 50° C in a period of time equivalent to the estimated age of the Green River Formation.

ACKNOWLEDGMENT

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REFERENCES

1. Allred, V. D. Some Considerations on the Kinetics of Oil Shale Pyrolysis. Presented at the Symposium on Oil Shale and Shale Oil Processing, Fifty-Eighth National A.I.C.E. Meeting, Dallas, Texas, February 1966.
2. Cummins, J. J., and W. E. Robinson. Normal and Isoprenoid Hydrocarbons Isolated from Oil-Shale Bitumen. *J. Chem. Eng. Data*, v. 9, No. 2, 1964, pp. 304-307.
3. Dinneen, G. U. Effects of Retorting Temperature on the Composition of Shale Oil. *Chem. Eng. Progr.*, v. 61, No. 54, 1965, pp. 42-47.

4. Dinneen, G. U., J. R. Smith, R. A. Van Meter, C. S. Allbright, and W. R. Anthony. Application of Separation Techniques to a High Boiling Shale-Oil Distillate. *Anal. Chem.*, v. 27, 1955, p. 185.
5. Hill, G. R., D. J. Johnson, L. Miller, and J. L. Dougan. Direct Production of a Low Pour Point High Gravity Shale Oil. *Ind. and Eng. Chem., Product Research and Development*, v. 6, No. 1, 1967, pp. 52-59.
6. Hubbard, A. B., and W. E. Robinson. A Thermal Decomposition Study of Colorado Oil Shale. *BuMines Rept. of Inv. 4744*, 1950, 24 pp.
7. Robinson, W. E., and J. J. Cummins. Composition of Low-Temperature Thermal Extracts from Colorado Oil Shale. *J. Chem. Eng. Data*, v. 5, 1960, pp. 74-80.

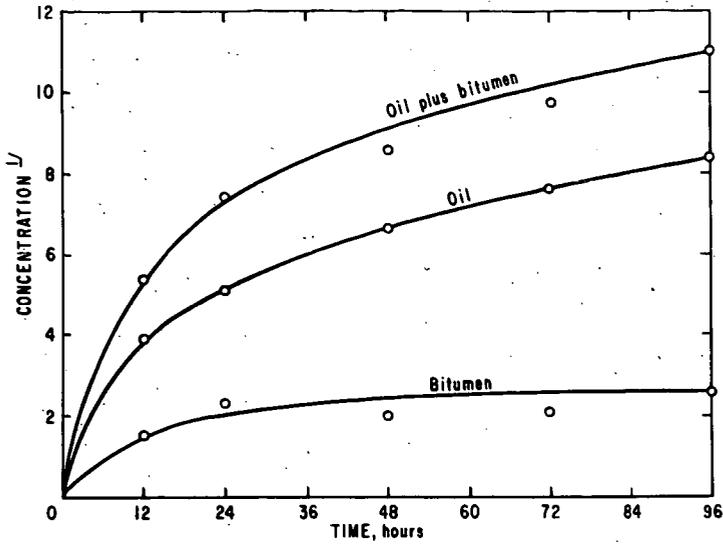


FIGURE 1.-Conversion of Kerogen to Oil and Bitumen at 300 °C.
(% Kerogen converted, wt pct of total kerogen)

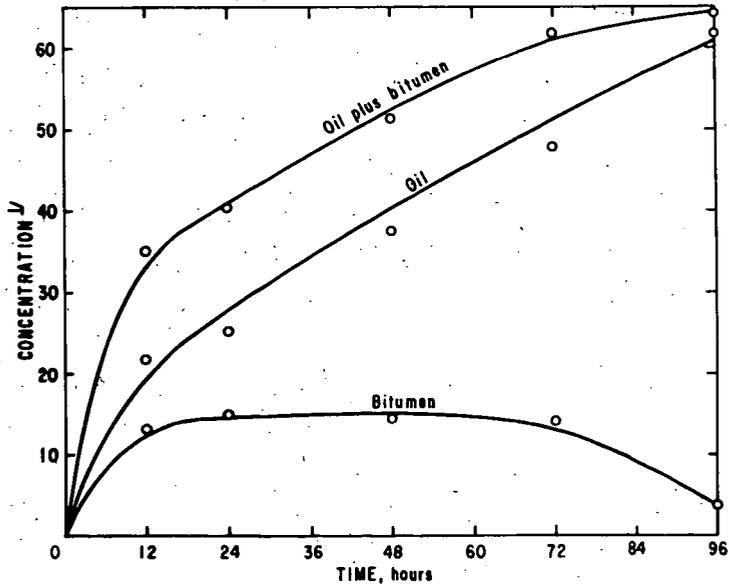


FIGURE 2.-Conversion of Kerogen to Oil and Bitumen at 350 °C.
(% Kerogen converted, wt pct of total kerogen)

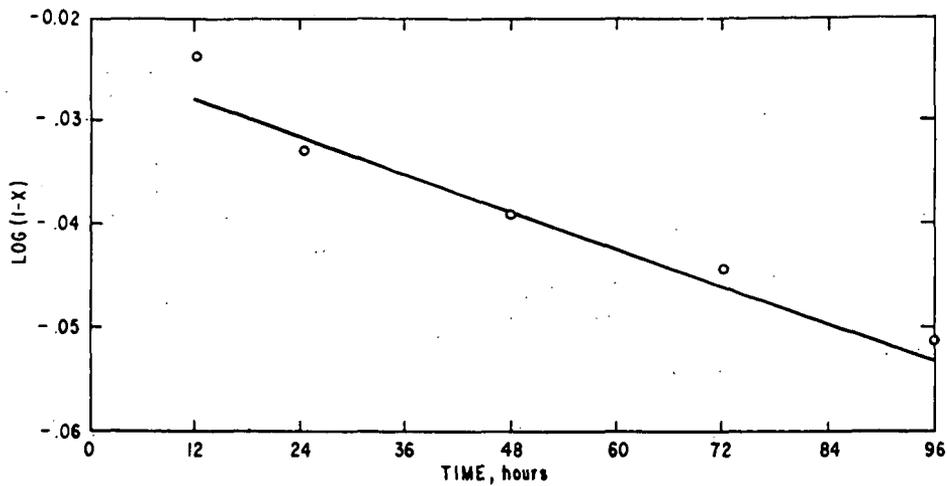


FIGURE 3.-First-Order Plot of Kerogen Conversion at 300 °C.

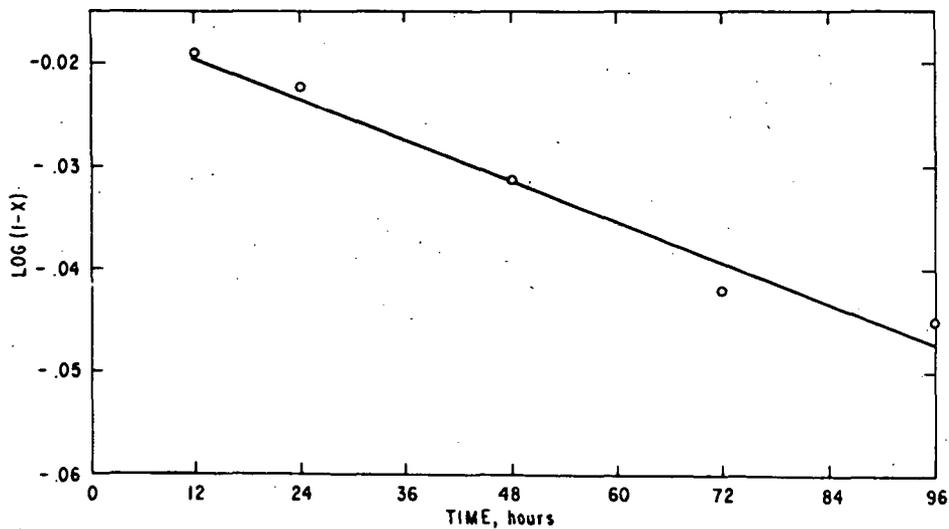


FIGURE 4.-First-Order Plot of Kerogen Conversion at 350 °C.

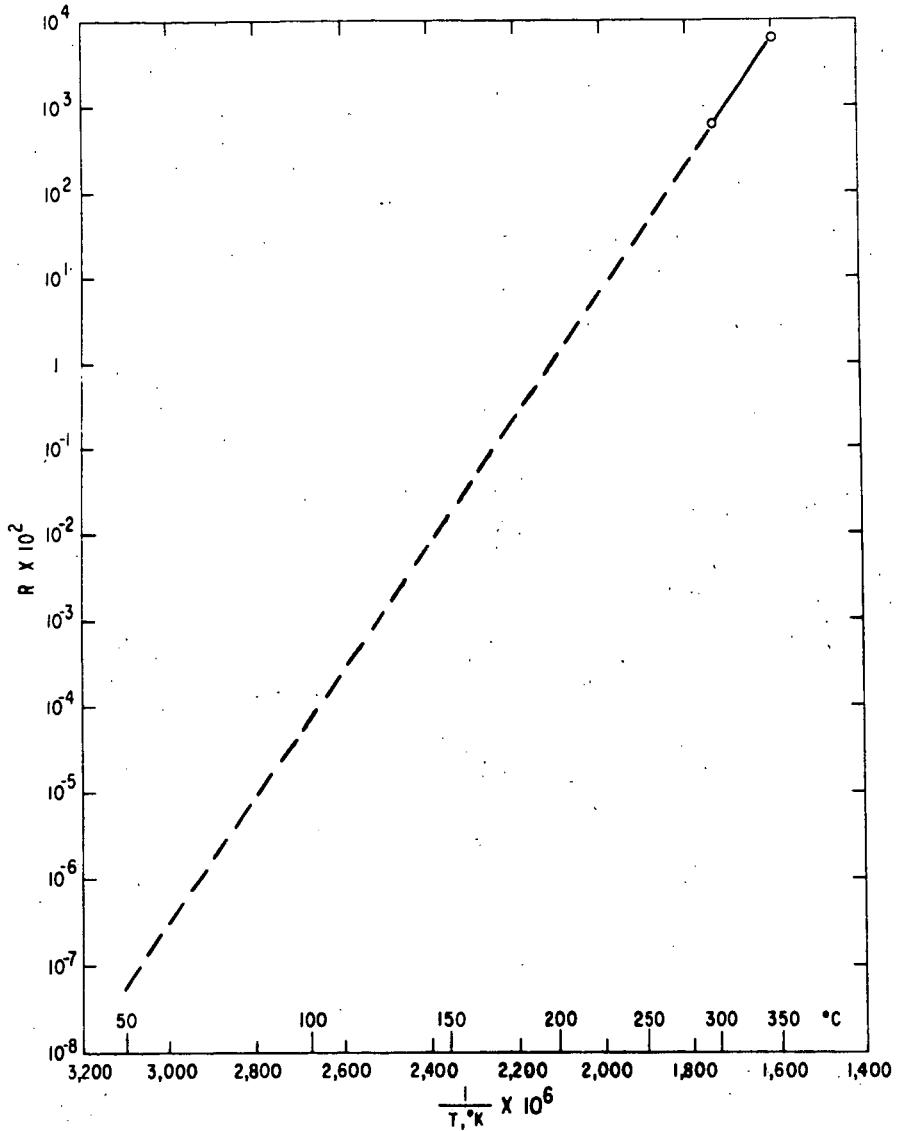


FIGURE 5.- Percent Conversion of Kerogen to Pyrolytic Products in One Year at Various Temperatures.