

EFFECTS OF HIGH TEMPERATURE AND HEATING RATE ON KEROGEN DECOMPOSITION

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ABSTRACT

This study investigated oil shale pyrolysis under a high-temperature short contact time to gain a better understanding of the effect of temperature on kerogen decomposition and product composition and the relationship of the products to those from conventional retorting.

A pyrolysis-gas chromatography-mass spectrometry system was used in which the oil shale sample was rapidly heated to decompose kerogen and simultaneously produce volatile matter. The effluent product formed at the lower temperatures contained largely paraffinic components; at higher temperatures the product contained mostly olefinic and aromatic materials. Above 600°C, the relative production of the olefins and aromatics increases rapidly, while at the same time the relative yield of saturates declines. At temperatures about 1000°C, the simpler aromatic products are dominant. The major components, analyzed by GC/MS, consisted of benzene, toluene, styrene, xylenes, ethynylbenzene, naphthalenes, acenaphthylene, indene, and phenanthrene.

It was found that the important variables affecting the conversion of oil shale under the high temperature rapid heating are temperature, heating rate, particle size, and shale grade. The initial decomposition of shale organic matter under slow heating occurs by rupturing thermally unstable cross-linkages of kerogen to a soluble organic material (pyrobitumen) which then decomposes to form the final products of oil, gas, and coke (or carbonaceous residue) on the spent shale. However, upon rapid heating at high temperatures, cracking of the primary products from kerogen decomposition takes place within the shale matrix. Instead of the heavy, viscous paraffinic products generated by conventional retorting, the liquid products from ultrafast pyrolysis of oil shale are mainly aromatic hydrocarbons.

INTRODUCTION

It is known that upon heating, kerogen decomposes initially to a soluble organic material, pyrobitumen, which then subsequently decomposes to form the final products of oil, gas, and carbonaceous residue on the spent shale.^(1,2) Apparently, during retorting, shale oil escapes from the shale matrix as a vapor or mist which is released after sequential cracking and condensation. If the decomposition of kerogen could be controlled, such as cracking macromolecular kerogen to small aromatic fragments by ultrafast heating, the quality of oil produced could be improved, and the retorted coking or the repolymerization of shale oil could be eliminated. Premium shale liquid and gas produced by high temperature ultrafast heating would require only simple refining.

Early work carried out in the 1950s by Laramie's Bureau of Mines⁽³⁻⁵⁾ processed shale at temperatures of 700-950°C at short residence time (2-3 sec). The process produced light hydrocarbon gases; in particular, ethylene, propylene, methane, and hydrogen. The best organic recovery was 70% at 649°C and 90% at 982°C in their tests. Recent experiments at Rockwell conducted by D. Kahn et al.⁽⁶⁾ for flash hydrolysis of Eastern oil shale over a range of temperatures (590-770°C), residence times (68- 210 msec), and a pressure of 1000 psia resulted in carbon conversions of up to 70%, with as much as 50% conversion to liquid.

Ultrafast pyrolysis is an extension of pyrolysis in which the sample is rapidly heated to enhance its decomposition and simultaneously produce volatile matter. This study investigated oil shale pyrolysis under a high-temperature short contact time to gain a better understanding of the effect of temperature on kerogen decomposition and product composition and the relationship of the product to those from conventional retorting.

EXPERIMENTAL

Beneficiated Mahogany Zone oil shales from C-a tract, Green River Formation, having Fischer Assay ranging from 14 to 75 gal/t, were crushed and screened to 200 to 325 mesh for use in the experiments. The oil shale was beneficiated by sink/float separation in a heavy media cyclone system as recently described.^(7,8)

The microscale pyrolysis system used in this investigation consists of a solids pyrolyzer (CDS Model 120) attached to a gas chromatograph (HP Model 5730A) or a gas chromatograph-mass spectrometer (Finnigan MAT Model 4510). The heater device, or pyrolyzer, is equipped with a platinum ribbon probe which serves as both a temperature sensor and a reactor. During heating, a high electrical wattage is applied to the probe which raises the temperature and produces a fast and reproducible heating of the sample. The platinum probe has a rise time of less than 17 msec to 1000°C.

For a typical run, about 4-5 mg of the sample (equivalent to about one layer of shale particle on the heating element) was placed on the pyroprobe which was inserted in the GC or GC/MS heated interface. A constant flow rate of helium carrier gas (35 mL/min) was passed over the sample to sweep the product effluents through the probe housing (at 250°C) into the GC or capillary GC/MS column. This enables pyrolysis products to escape rapidly from the hot reaction zone. In general, the temperature programming of each pyrolysis experiment used preset final temperatures of 500° to 1400°C, constant heating rates from 60°C/min to 20°C/msec, and total heating times (sum of temperature ramp heating time and holding time at the final temperature) from 100 msec to 5 sec. Gas chromatographic separation of the pyrolysis product mixture was performed on a 3% Dexsil 300 column.

The C_3^+ product was characterized by gas chromatograph-mass spectrometer analysis using a Finnigan MAT 4510 GC/MS/DS mass spectrometer equipped with a Finnigan 9610 gas chromatograph and Incos 2000 data system. The chromatographic separation was accomplished on a 60 meter x 0.26 mm I.D. DB-5 (J&W Scientific) fused silica capillary column. The mass spectral data were acquired at a nominal 70 eV in the electron impact ionization

mode. The mass range 33-500 amu was scanned at 0.95 sec with a hold of 0.05 sec at the bottom of the scan ramp. Identification of the resulting peaks was done by manual interpretation or computerized matching of mass spectra with those of a reference spectral library. Absolute yields were not determined by these procedures.

The kerogen conversion was calculated (by difference) from the total organic content of the original shale and the residue organics in the spent shale determined by thermogravimetric (TGA) analysis. The TGA was used for measuring sequentially the organic content (weight loss 500°C), carbonate mineral (weight loss 500-900°C in nitrogen), fixed carbon (weight loss 900°C in air), and ash in the original and spent shales.

RESULTS AND DISCUSSION

Product Yields and Characterization

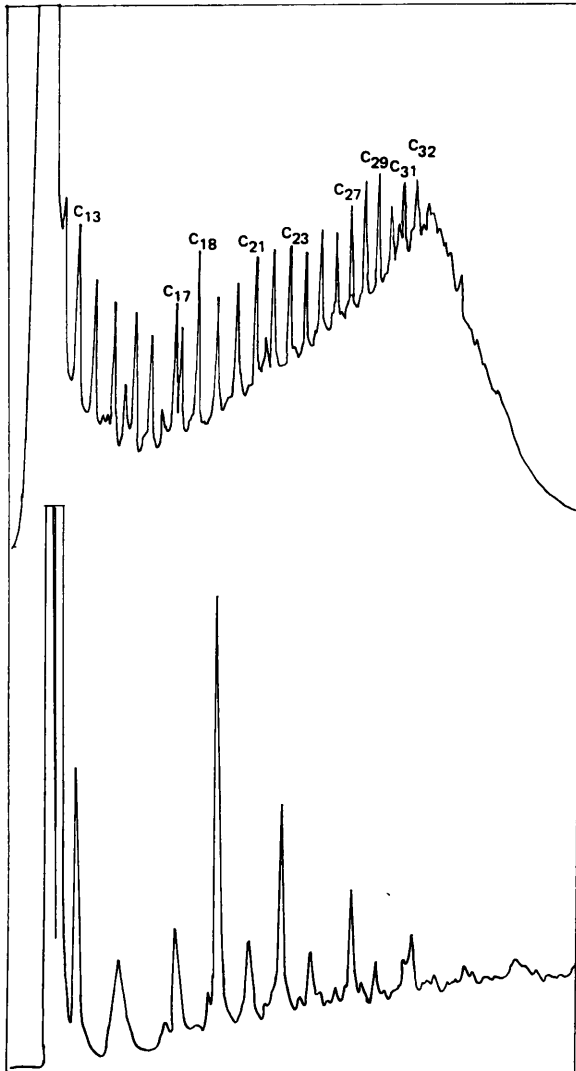
The pyrolysis of oil shale kerogen is a very complex reaction or group of reactions that results in the production of a myriad of hydrocarbons and hydrocarbon derivatives. Figure 1a shows the GC analysis of volatile products from a typical run of oil shale pyrolysis at 600°C with 6°C/min heating rate. The products shown in the analysis contain greater than 30 carbon atoms per molecule. The gas chromatogram also shows a broad envelope region above C_{17} which represents many unresolved hydrocarbons and/or heterocyclic compounds.

Conversely, an experimental run which was made under rapid heating (20°C/msec) at a high temperature (1400°C) and short contact time (500 msec) resulted in an entirely different product pattern (as shown in Figure 1b). A simpler pattern containing fewer types of compounds (mainly light aromatics as described below) was obtained under the high temperature rapid heating conditions. The unresolved region of GC peaks observed under slow heating (Figure 1a) has disappeared completely.

Further characterization of the C_3^+ products was obtained by using capillary gas chromatography/mass spectrometry. A GC/MS product pattern for rapid heating of oil shale at 1400°C is shown in Figure 2 where the GC peak number indicates the scan number at which mass spectra were recorded.

MAHOGANY ZONE C-α TRACT SHALE

(49.4 GPT, 200-325 MESH)



(a) 600 C
at
6 C/min.

(b) 1400 C
at
 1.2×10^6 C/min.

FIGURE 1. PYROLYSIS OF OIL SHALE AT 600 C AND 1400 C

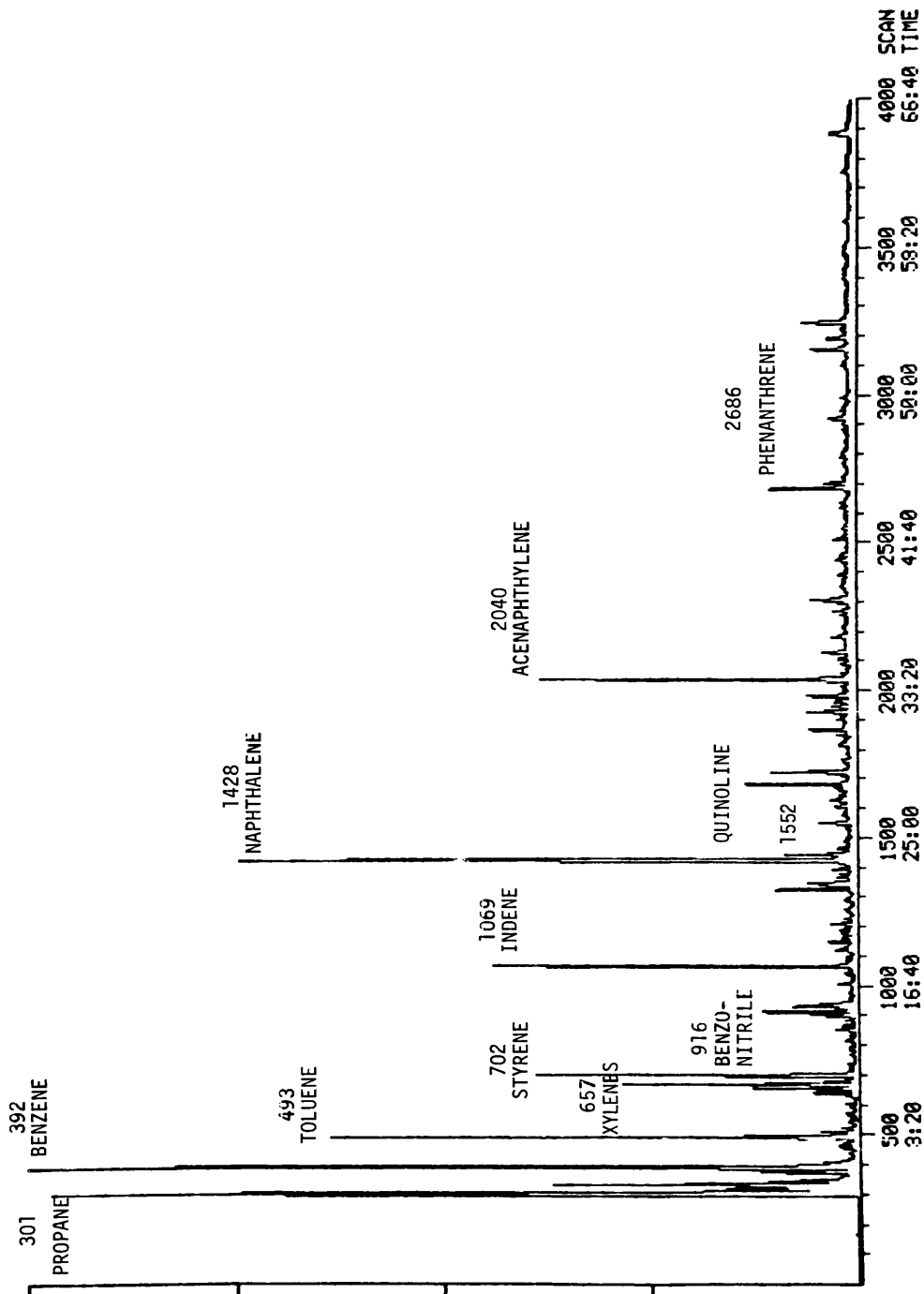


FIGURE 2. CAPILLARY GC/MS PRODUCT PATTERN OF OIL SHALE HIGH TEMPERATURE RAPID HEATING AT 20 C/MSEC AND 1400 C

The compounds identified from the GC/MS data along with relative amounts are given in Table I.

The products observed in Table I are primarily aromatics, either unsubstituted or with short side chains. The major components, analyzed by GC/MS, consist of benzene, toluene, styrene, xylenes, ethynyl benzene, naphthalenes, acenaphthylene, indene, and phenanthrene. The nitrogen compounds identified are pyridine, benzonitrile, methyl benzonitriles, quinoline, methyl quinoline, and indole. Compounds present in ordinary retorted shale oils, such as the normal hydrocarbons (olefin/paraffin pairs) as well as bitumen biomarker compounds (i.e., pristane, phytane, steranes, and triterpanes), are all absent. Under high temperature rapid heating, a light, highly aromatic liquid product (i.e., BTX), which is thermodynamically favored at high temperatures, is produced.

Effects of Reaction Variables on Oil Shale Conversion

In order to understand the differences in conversion chemistry at high temperatures, as compared to conventional retorting temperatures, four important variables affecting the conversion of oil shale under rapid heating were studied: temperature, heating rate, kerogen concentration (shale grade), and shale particle size.

Temperature

Figure 3 shows the gas chromatograms with the conversion results for oil shale pyrolyzed at various temperatures ranging between 600 and 1400°C. Each run was carried out at a heating rate of 20°C/msec (1.2×10^6 °C/min) and a total heating time of 500 msec. As would be expected, lower conversion was observed at lower temperatures. At temperatures below 900°C, the principal pyrolysis products are similar to those produced in conventional retorting. At temperatures above 900°C, a simple product mixture consisting primarily of unsubstituted aromatic compounds was observed.

In Figure 4, the product distribution analyzed by capillary column GC/MS is shown as a function of the final heating temperature. The predominant product types change as the temperature is increased from 500°C to 1400°C and show three dis-

tinct temperature intervals.

A homologous series of hydrocarbons (olefin/paraffin pairs) is the major component from rapid heating of oil shale at temperatures below 700°C in which the 1-alkene is the dominant positional isomer. Alkene/alkane ratios, represented by 1-dodecene/n-dodecane in Table II, increase with an increase in reaction temperature, indicating that thermal cracking of generated oil occurs at higher temperatures.

Figure 4 also shows that the most pronounced alkene represented in the GC/MS spectra from rapid heating of oil shale at temperatures below 700°C is prist-1-ene, $C_{19}H_{38}$ isoprenoid with molecular weight 266. The relative concentration of prist-1-ene, as expressed by the ratio of prist-1-ene to $\Sigma C_{17}+C_{18}$ (n-alkanes plus 1-alkenes of C_{17} and C_{18}) in Table II, decreases with increasing temperature up to 900°C. Above 900°C, a relatively small quantity of prist-1-ene is observed by rapid heating and most of the normal hydrocarbons disappear. Table II also shows that the concentration of prist-1-ene is about 13.5 times that of pristane and about 10.1 times that of phytane at 500°C. The occurrence of isoprenoid alkenes has been reported to be strongly dependent on the heating rate and pyrolysis temperature.⁽⁹⁻¹¹⁾ Prist-1-ene could come from the dehydrogenation of pristane and/or demethanation of phytane under rapid heating. In general, phytane and pristane are abundantly present in oil shale bitumen.^(11,12)

Light aromatic compounds (i.e., BTX) become important at temperatures above 800°C (as shown in Figure 4). The peaks of multiple-ring compounds such as naphthalenes, acenaphthylene, and phenanthrene also increase rapidly at higher temperatures. Figure 5 plots the relative concentrations of aromatic compounds generated at different heating temperatures. For comparison, the relative yield data of prist-1-ene and ΣC_{12} (n-dodecane plus 1-dodecene) are also included. The results clearly indicate that higher temperatures favor the formation of aromatic compounds. At temperatures above 1000°C, there is little or no detectable alkanes or alkenes. Naphthalene which is not observed at temperatures below 700°C shows a relative increase at higher temperatures. The ratio of naphthalene to

Table I

<u>PRODUCT IDENTIFIED BY GC/MS^a</u>		
<u>Scan No.^b</u>	<u>Peak Compound</u>	<u>% of Total</u>
301	Propane C ₃ H ₈	14.27
308	Butadienes C ₄ H ₆	7.91
321	Methylcyclobutane C ₅ H ₁₀	2.05
335	1,3-Cyclopentadiene C ₅ H ₆	4.10
392	Benzene C ₆ H ₆	16.80
406	1-Heptene C ₇ H ₁₄	0.50
412	Heptane C ₇ H ₁₆	0.09
468	Pyridine C ₅ H ₅ N	0.32
493	Toluene C ₇ H ₈	7.01
512	1,2-Dimethylcyclohexane C ₈ H ₁₆	0.49
657	Dimethylbenzenes (Xylenes) C ₈ H ₁₀	1.19
671	Ethynylbenzene C ₈ H ₆	2.91
702	Ethenylbenzene (Styrene) C ₈ H ₈	2.97
916	Benzonitrile C ₇ H ₅ N	0.52
926	Decane C ₁₀ H ₂₂	0.40
934/943	Ethenylmethylbenzenes/Indan C ₉ H ₁₀	1.38
1069	Indene C ₉ H ₈	5.05
1123/1176	Methylbenzotrioles C ₈ H ₇ N	0.41
1428	Naphthalene C ₁₀ H ₈	12.10
1552	Quinoline C ₉ H ₇ N	0.48
1672	Indole C ₈ H ₇ N	0.20
1684	Methylnaphthalenes C ₁₁ H ₁₀	1.58
1713	Methylquinoline C ₁₀ H ₉ N	0.09
2040	Acenaphthylene C ₁₂ H ₈	6.05
2308	Fluorene C ₁₃ H ₁₀	0.84
2636	Dibenzothiophene C ₁₂ H ₈ S	0.10
2686	Phenanthrene C ₁₄ H ₁₀	2.35
3247	Pyrene C ₁₆ H ₁₀	1.03

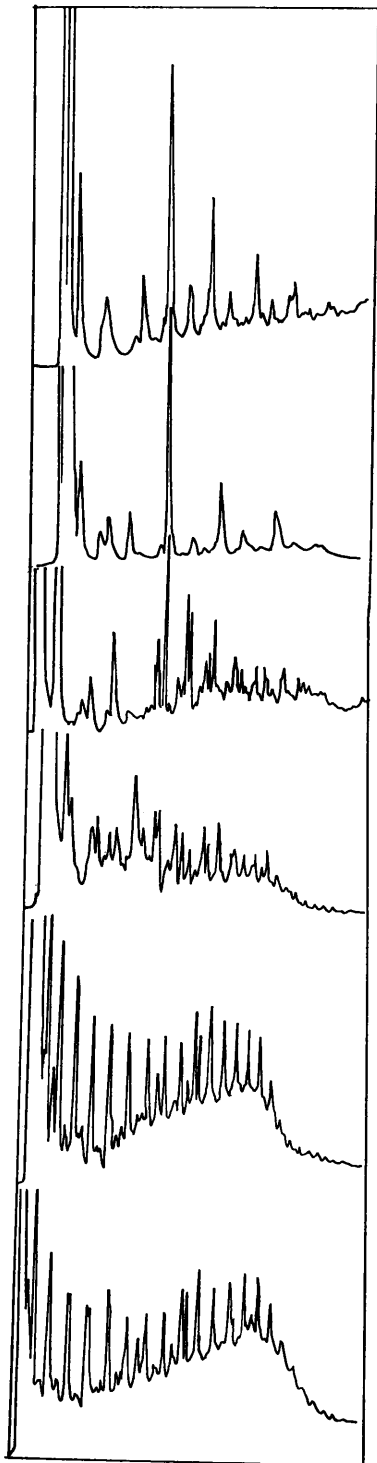
^a Oil shale heated at 1400°C, 20°C/msec, and 1 sec.

^b Scan numbers referred to Figure 2.

Table II

<u>PRODUCT RATIOS OF OIL SHALE RAPID HEATING^a</u>				
<u>Temperature (°C)</u>	<u>1-Dodecene</u> <u>n-Dodecane</u>	<u>Prist-1-ene</u> <u>ΣC₁₇+ C₁₈</u>	<u>Prist-1-ene</u> <u>Pristane</u>	<u>Prist-1-ene</u> <u>Phytane</u>
500	1.3	0.9	13.5	10.1
600	1.6	0.8	15.4	12.3
700	1.7	0.5	10.7	8.9
800	2.3	0.4	13.1	16.1
900	2.2	0.3	--	--

^a Oil shale rapid heating at 20°C/msec and 500 msec, except 1000 msec heating time for the run at 500°C.



49.4 GPT, 200-325 MESH AT 20 C/MSEC

<u>Temp.</u>	<u>Total Heating Time</u>	<u>Organic^(a) Conversion</u>	<u>Carbonates^(a) Decomposition</u>
1400 C	500 msec	94.8%	50.9%
1200 C	500	93.5%	45.5%
1000 C	500	89.1%	35.6%
900 C	500	83.8%	32.1%
800 C	500	82.6%	28.5%
600 C	500	35.6%	8.6%

(a) By TGA MEASUREMENT

(b) MAHOGANY ZONE C-a TRACT SHALE

FIGURE 3. TEMPERATURE EFFECT ON OIL SHALE RAPID HEATING (b)

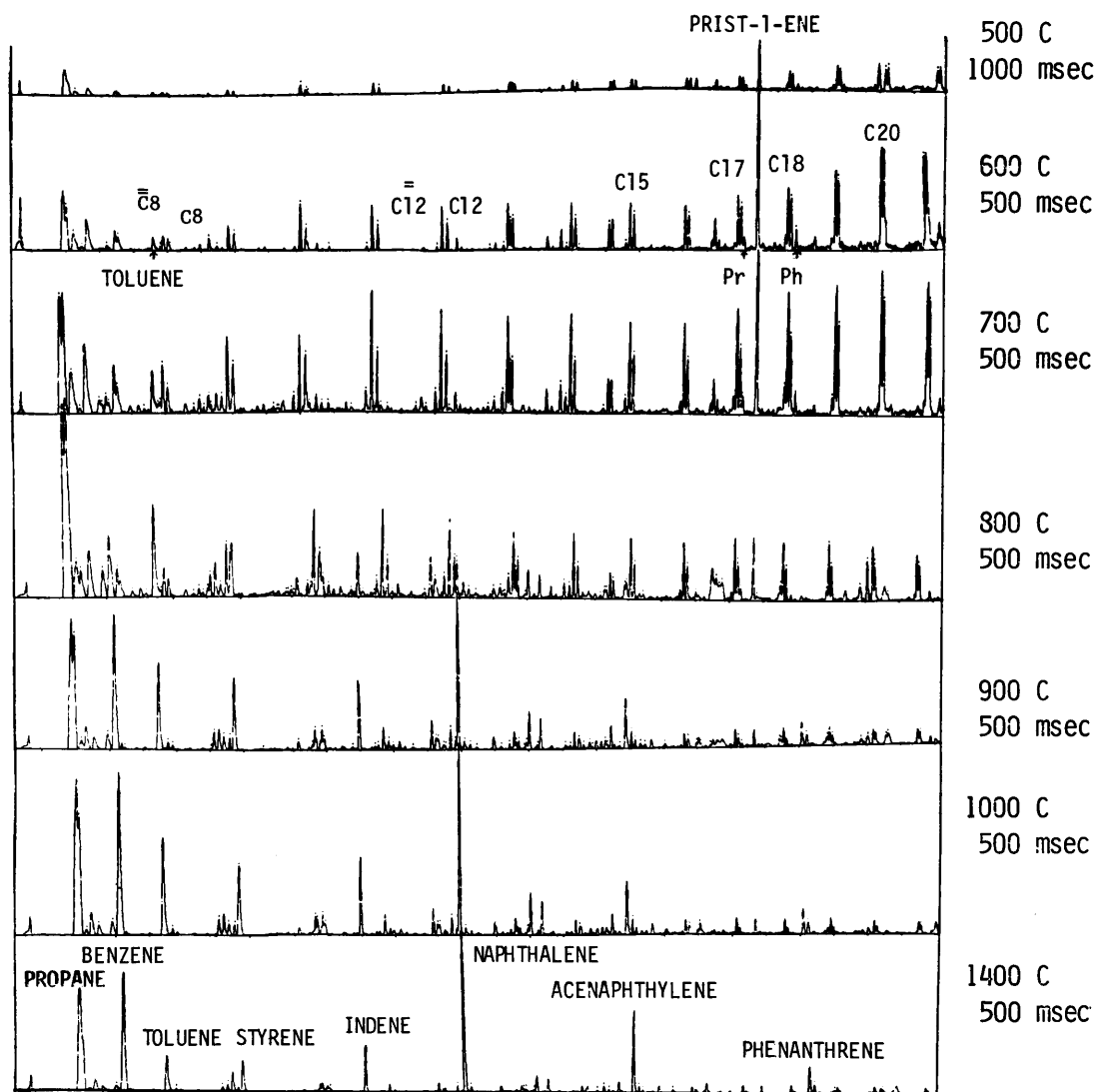


FIGURE 4. CAPILLARY GC/MS PRODUCT PATTERN OF OIL SHALE RAPID HEATING AT 20 C/MSEC AND VARIOUS TEMPERATURES

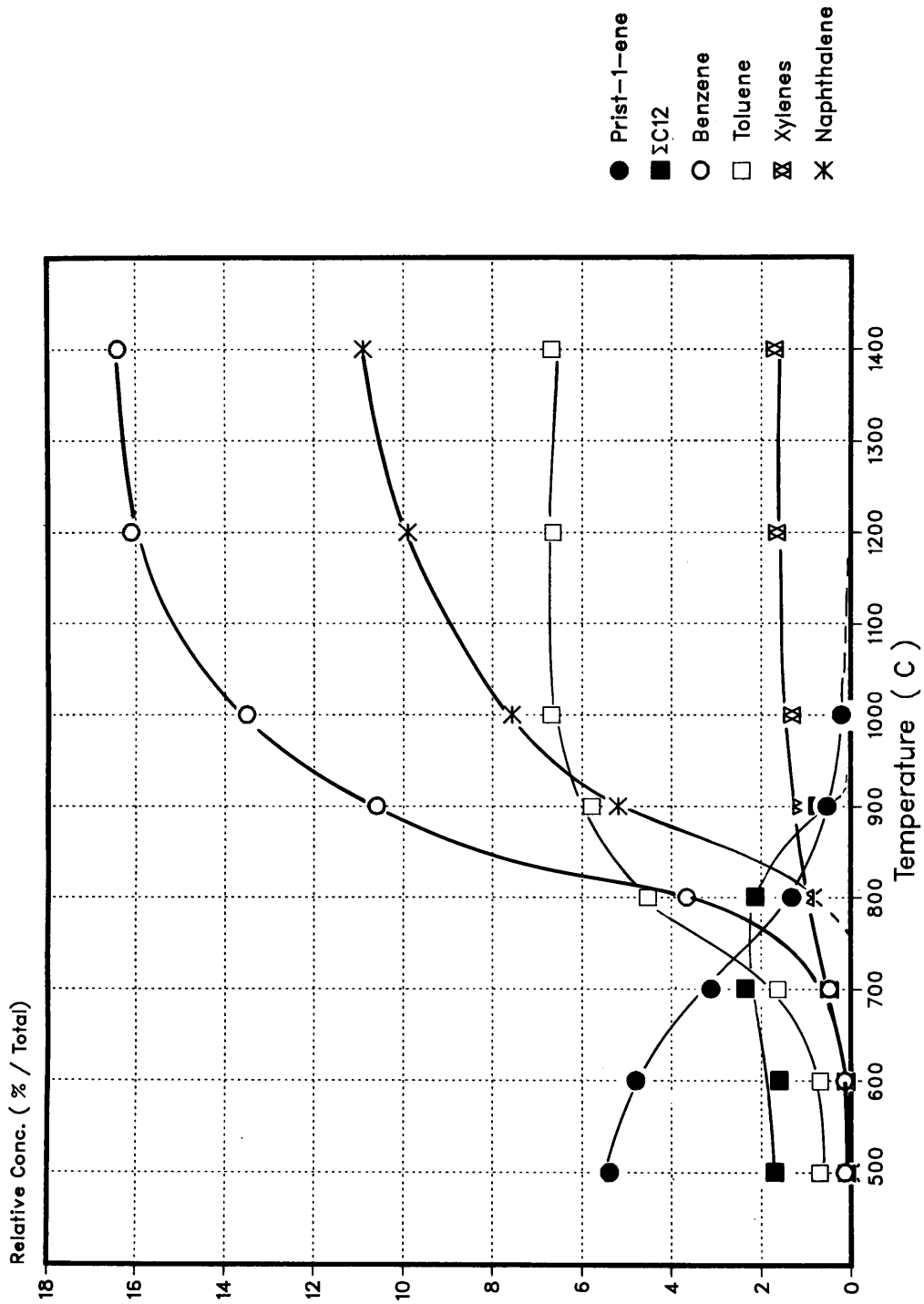


FIGURE 5. RELATIVE CONCENTRATION OF PRODUCTS GENERATED UNDER OIL SHALE RAPID HEATING AT 20 C/MSEC

benzene (Table III) is 0.23 at 800°C, increases to 0.56 at 1000°C, and levels off at about 0.65 above 1200°C, reflecting the degree of cracking/reforming occurring inside the shale mineral matrix as a function of temperature. A similar trend is found for phenanthrene. The relative concentration of phenanthrene is small, only about one-tenth that of benzene at temperatures above 1000°C.

The nitrogen compounds observed at low temperatures include substituted pyridines, indoles, and quinolines. However, under high temperature rapid heating of oil shale, two major types of nitrogen compounds present in the effluent products are benzonitriles and quinolines. Table III shows that the ratio of benzonitrile to quinoline increases with an increase in temperature. Quinolines have been commonly identified in conventional retorted shale oils.^(1,13-15) However, this is the first time benzonitrile was observed in products from shale oil pyrolysis.

Heating Rate

The effect of heating rate on coal flash pyrolysis has been widely studied.⁽¹⁶⁻¹⁸⁾ It is well known that at higher heating rates extensive fragmentation of the coal structure occurs resulting in an increase in BTX and light hydrocarbons. Figure 6 shows the gas chromatograms for oil shale conversion as a function of heating rate at 1400°C. Heating rates were varied between 300°C/min and 20°C/msec. At slower heating rates the sample remains at an elevated temperature range for a longer period of time; consequently, the degree of kerogen conversion and mineral decomposition is greater. The gas chromatograms show that at heating rates slower than 1°C/msec the products obtained are similar to conventional retorted shale oil. This is attributed to removal of the product oil from the shale mineral matrix at retorting temperatures (i.e., 500-600°C) before further decomposition can occur. Similar phenomena are observed at 1000°C with various heating rates (Figure 7). However, at 600°C (temperatures close to conventional retorting) the higher heating rate only shifts the products to lower carbon numbers (Figure 8) compared to those found in the lower heating rate runs. Nevertheless, the major components remain the same as

the conventional retorting products.

At 500°C, the effects of heating rate on the relative quantities of 1-alkene/alkane pairs and prist-1-ene, pristane, and phytane are shown in Table IV by capillary GC/MS determination. Results indicate that the ratios of prist-1-ene to $\Sigma C_{17}+C_{18}$, to pristane, and to phytane all increase with increasing heating rate. The relative concentration of prist-1-ene seems to depend strongly on the heating rate during oil shale pyrolysis. This is consistent with the findings reported in the literature.^(9,11) For C_7 through C_{24} , the total 1-alkene to n-alkane ratio is nearly constant over the heating-rate range of 0.1 to 20°C/msec (Table IV). However, for different carbon numbers the 1-alkene/ n-alkane ratios increase with increasing heating rate for lower carbon numbers (i.e., $<C_{12}$), whereas the ratios decrease with increasing heating rate for higher carbon numbers (i.e., $>C_{17}$). The overall ratio of 1-alkene to n-alkane is independent of heating rate because of the different degrees of thermal cracking occurring for individual components.

Particle Size

Figure 9 shows the gas chromatograms for the conversion results of different particle sizes ranging from 0.07 mm (325 mesh) to 2 mm. Samples were heated at 1400°C at a heating rate of 20°C/msec for a total heating time of 500 msec.

Although the results of GC analysis showed that there is no significant difference of major components among the various particle-size runs, increases of organic conversion and carbonate decomposition were obtained as the shale particle size was reduced from 1 x 2 mm to 32 x 60 mesh. For shale particle sizes between 60 and 325 mesh, the amount of organic conversion and carbonate decomposition remained about the same when the samples were heated at the same conditions. This indicates that the shale particle size has to be small enough to allow the entire particle to reach high temperatures rapidly. For larger particle sizes, the oil shale conversion is influenced by limitations of intraparticle heat transfer and mass diffusion.⁽¹⁹⁾

Table III

PRODUCT RATIOS OF AROMATIC AND NITROGEN COMPOUNDS
UNDER OIL SHALE RAPID HEATING^a

Temperature (°C)	<u>Naphthalene</u> <u>Benzene</u>	<u>Phenanthrene</u> <u>Benzene</u>	<u>Benzonitrile</u> <u>Quinoline</u>
800	0.23	--	--
900	0.49	0.10	1.06
1000	0.56	0.09	1.20
1200	0.65	0.11	1.40
1400	0.67	0.13	1.65

^a Oil shale rapid heating at 20°C/msec and 500 msec. Aromatics are not observable at 500-700°C.

MAHOGANY ZONE C-α TRACT SHALE

(49.4 GPT, 200-325 MESH)

1400 C

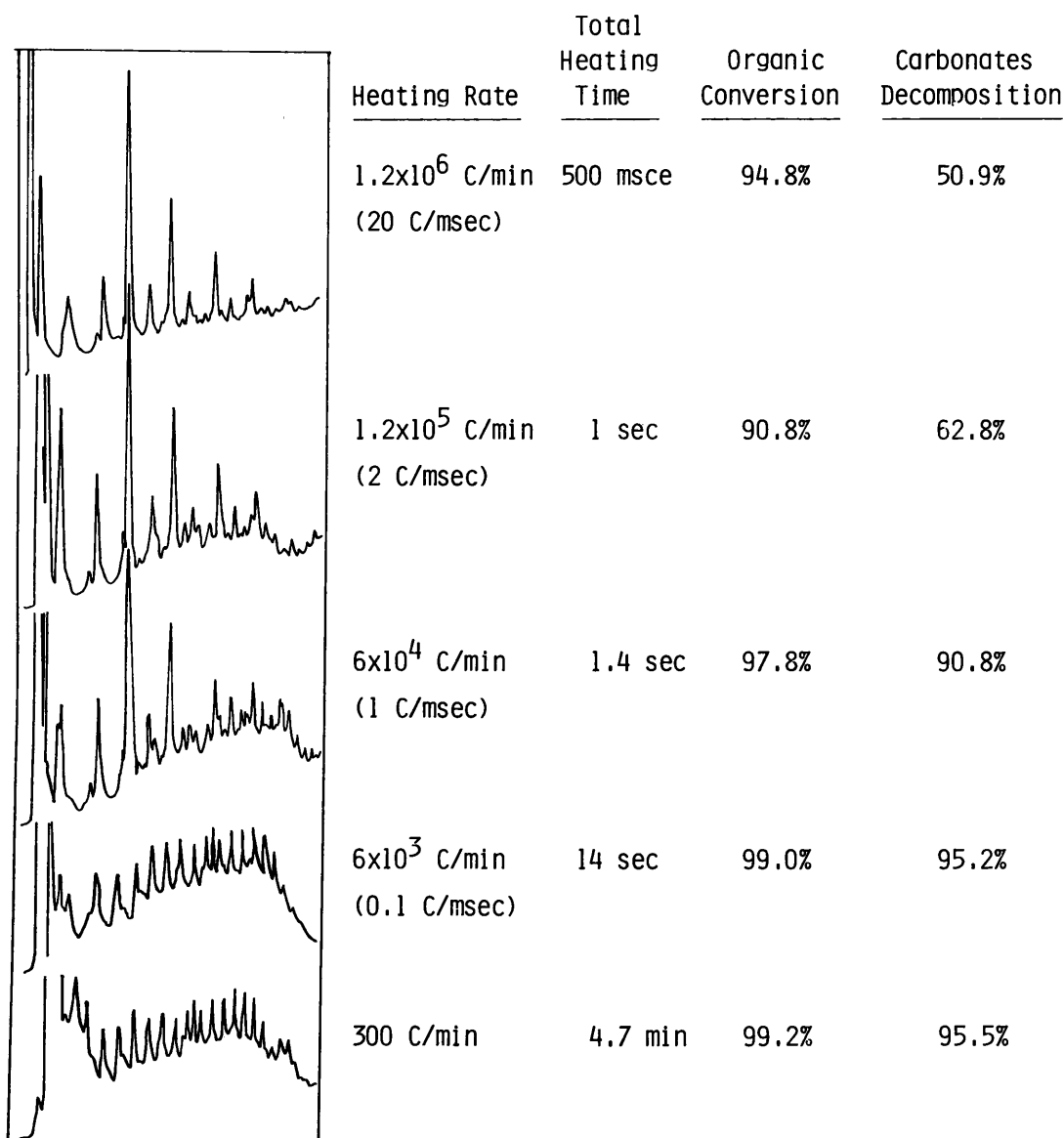


FIGURE 6. HEATING RATE EFFECT ON OIL SHALE CONVERSION

MAHOGANY ZONE C-a TRACT SHALE

(49.4 GPT, 200-325 MESH)

1000 C

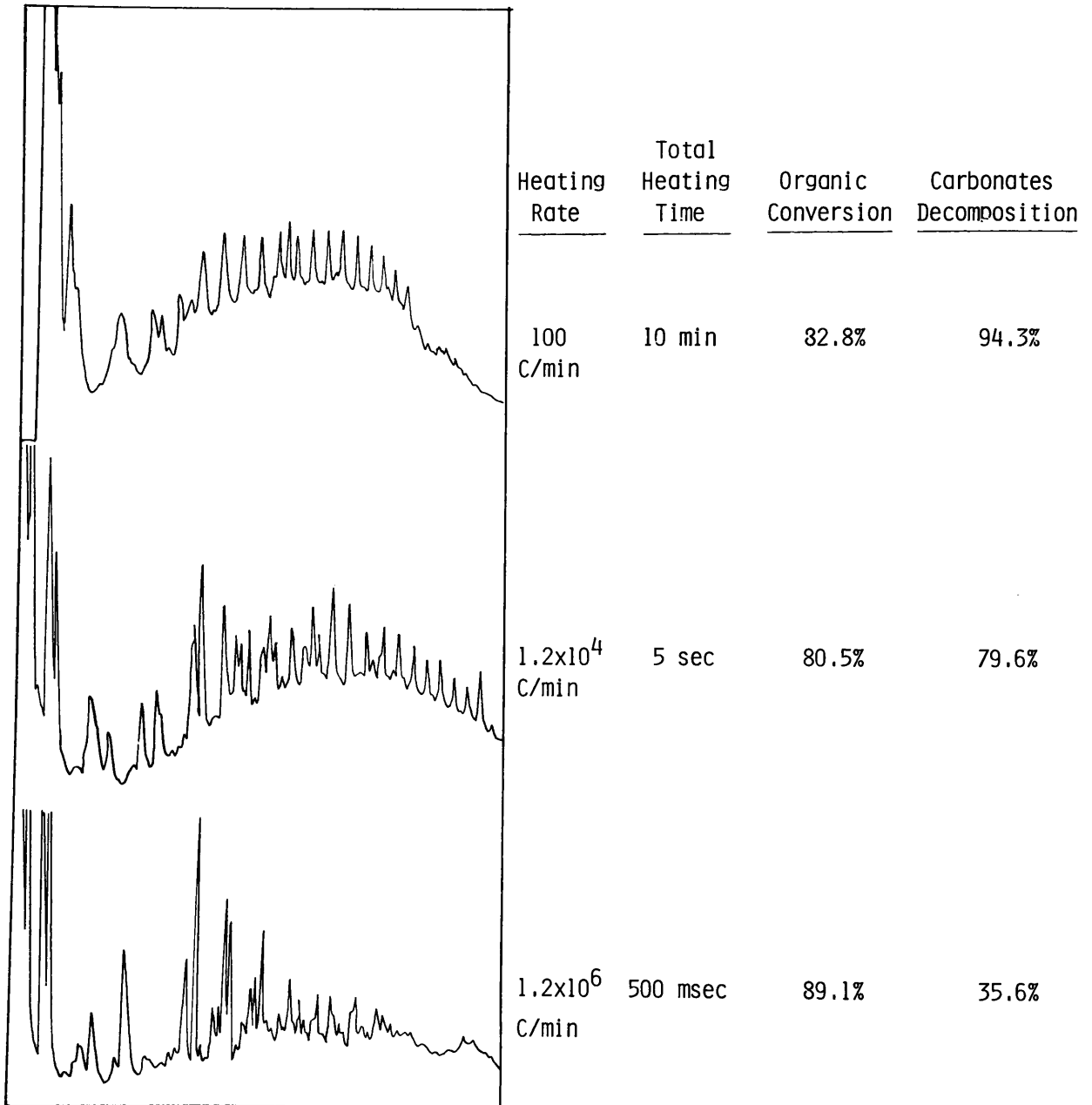
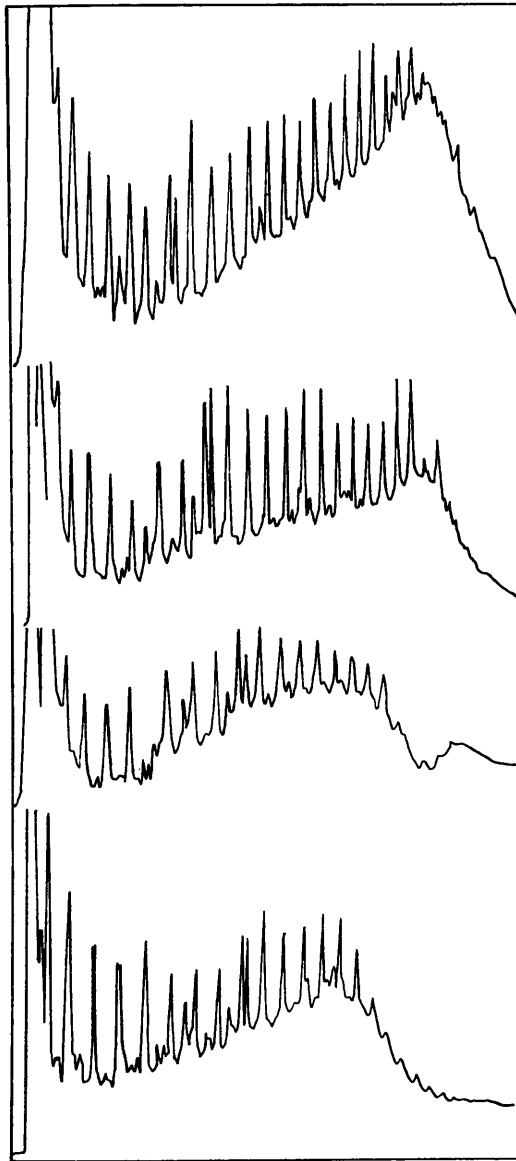


FIGURE 7. HEATING RATE EFFECT ON OIL SHALE CONVERSION

MAHOGANY ZONE C-a TRACT SHALE

(49.4 GPT, 200-325 MESH)

600 C



Heating Rate	Total Heating Time	Organic Conversion	Carbonates Decomposition
6 C/min	100 min	72.3%	21.8%
100 C/min	6 min	68.2%	17.9%
1.2×10^4 C/min	3.5 sec	53.5%	12.1%
1.2×10^6 C/min	500 msec	35.6%	8.6%

FIGURE 8. HEATING RATE EFFECT ON OIL SHALE CONVERSION

Table IV

PRODUCT RATIOS OF OIL SHALE HEATED AT 500°C
UNDER VARIOUS HEATING RATES

Heating Rate	Prist-1-ene $\Sigma C_{17+} C_{18}$	Prist-1-ene Pristane	Prist-1-ene Phytane	$\Sigma 1$ -Alkene (C ₇ -C ₂₄)	1-C ₈ n-C ₈	1-C ₁₂ n-C ₁₂	1-C ₁₇ n-C ₁₇	1-C ₂₁ n-C ₂₁
				Σn -Alkane (C ₇ -C ₂₄)				
60°C/min	0.5	3.5	2.7	0.95	0.85	0.92	1.12	1.01
0.1°C/msec	0.7	11.2	8.6	0.96	0.87	1.01	1.07	0.92
20°C/msec	0.9	13.5	10.1	0.98	1.31	1.28	0.98	0.85

MAHOGANY ZONE C-a TRACT SHALE, 49.4 GPT,
HEATED AT 1400 C, 20 C/MSEC FOR 500 MSEC

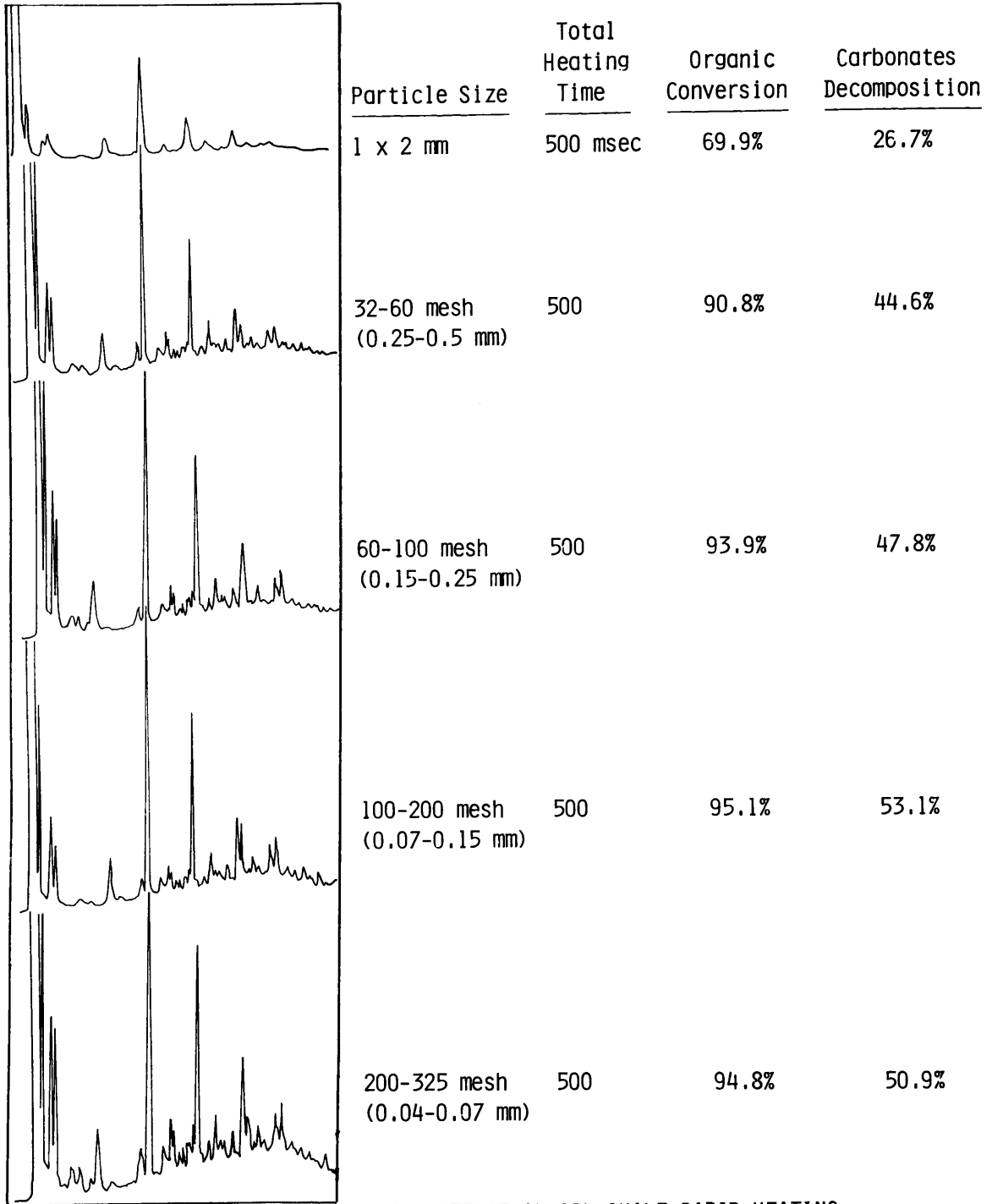


FIGURE 9. PARTICLE SIZE EFFECT ON OIL SHALE RAPID HEATING

Shale Grade

The effect of shale grade on shale conversion is shown in Figure 10 where three different grades of beneficiated Mahogany Zone C-a tract shale, 14 to 75 gpt, were heated identically at 1400°C with a heating rate of 20°C/msec for a total heating time of 500 msec. For all three grades, it was found that the GC product peaks were similar. The run of lower grade shale has an unresolved background of heavier components in the chromatogram unlike that of the higher grade oil shale. It appears that lean shale contains more refractory organic matter which makes it more difficult to crack to light products.

Reaction Mechanism of Oil Shale Pyrolysis

Considerable work⁽²⁰⁻²³⁾ has been reported in the literature on the reaction mechanism for kerogen decomposition. Generally, a stepwise reaction mechanism describes the thermal degradation of kerogen under ordinary retorting conditions (slow heating, 5-100°C/min, at relatively low temperatures of 500-600°C):



The initial decomposition of oil shale organic matter under slow heating occurs by rupturing kerogen to a soluble organic material (pyrobitumen) which then decomposes to form the final products of oil, gas, and coke (or carbonaceous residue) on the spent shale.

However, under ultrafast heating at high temperatures (i.e., 10⁶°C/min at 1400°C), the kerogen decomposition is sufficiently rapid that thermal cracking of the primary products occurs within the shale matrix before the products have the chance to diffuse from the matrix and vaporize. Thus, the products from ultrafast pyrolysis are mainly relatively light aromatic hydrocarbons which are thermodynamically favored at high temperatures rather than the waxy paraffinic shale oil products typically observed in conventional retorting.

To test the role of decomposition within the shale matrix in high heating rates, a set of experimental runs were carried out under high tempera-

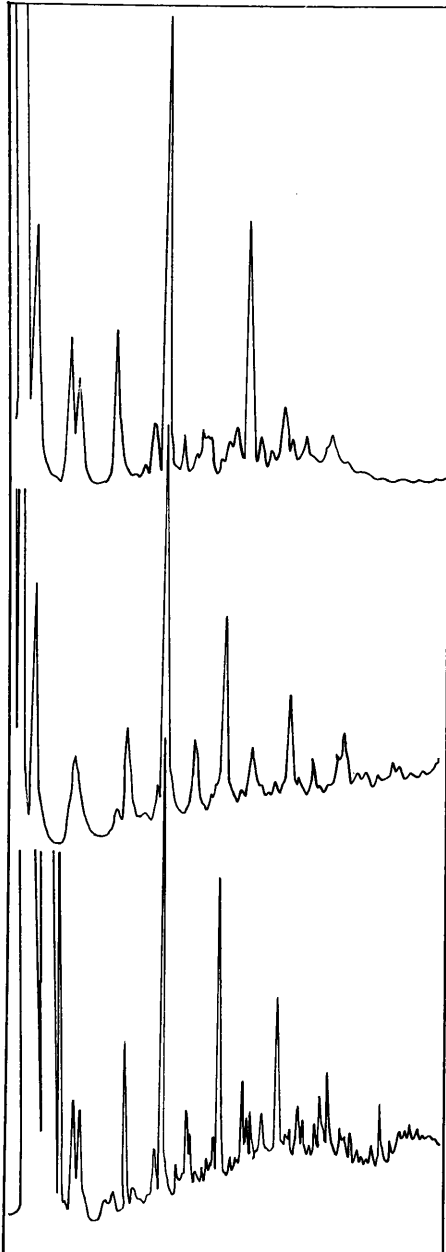
ture ultrafast pyrolysis conditions using shale oil as well as shale oil mixed with spent shale. Paraho shale oil was used in the experiments. The pyrolysis experiments were made at 1400°C with 20°C/msec heating rate. Figure 11 shows the gas chromatograms for the original shale oil, the products from shale oil, and the products from shale oil mixed with spent shale. Comparing these gas chromatograms, some cracking of the shale oil is observed in the ultrafast pyrolysis, but not to the degree observed on fast heating of the oil shale (as shown in Figure 3). Therefore, we conclude that these aromatic compounds are formed from decomposition of pyrolysis reactive intermediates before stable paraffinic products can be formed and diffuse out of the shale matrix.

In general, at high heating rates, the hydrocarbon products do not have time to escape the shale matrix during the period in which the temperature is increasing. Therefore, the products observed are more representative of the reactions occurring at the final temperature rather than the initial volatile intermediate products. The latter products exit the shale at lower heating rates while the temperature is still increasing and are similar to the products observed in conventional retorting. At lower temperatures (500- 600°C) the typical, predominantly paraffinic shale oil product distribution is observed; intermediate temperatures (600- 1000°C) an increase in alkenes is observed; above 1000°C unsubstituted aromatic (single-ring and multi-ring) compounds predominate. These trends of compound types with temperature reflect the thermodynamically favored hydrocarbon species one would expect. The presumed mechanism is that at the higher temperatures further reaction of the free radical intermediates occurs in the shale matrix before the radicals are stabilized as paraffinic compounds which are observed at lower temperatures. The high-temperature reactions favored include cyclization, cracking, and ring dehydrogenation to give single- and multi-ring aromatic compounds with a minimum of side chains.

CONCLUSION

Laboratory microscale study has led to a better understanding of kerogen decomposition at

MAHOGANY ZONE C-a TRACT SHALE, 200-325 MESH
 HEATED AT 1400 C WITH 20 C/MSEC FOR 500 MSEC



<u>Shale Grade</u>	<u>Organic Conversion</u>	<u>Carbonates Decomposition</u>
75 GPT	94.3%	43.8%
49.4 GPT	94.8%	50.9%
14 GPT	95.2%	58.7%

FIGURE 10. EFFECT OF SHALE GRADE ON OIL SHALE RAPID HEATING

higher temperatures and the relationship of the products obtained during rapid heating of oil shale to those from conventional retorting. In contrast to the lower temperature product which is mainly paraffinic, the higher temperatures enhance the olefinic and aromatic fractions. A homologous series of hydrocarbons (olefin/paraffin pairs) is the major component for rapid heating of oil shale at temperatures below 700°C in which the 1-alkene is the dominant positional isomer. However, light aromatic compounds (i.e., BTX) become important at heating temperatures above 800°C. Polynuclear compounds such as naphthalene, acenaphthylene, and phenanthrene and their short-chain substituted analogs increase rapidly at temperatures above 800°C. The nitrogen compounds observed at low temperatures are substituted pyridines, indoles, and quinolines. However, under high-temperature rapid heating, the two major nitrogen compound types present in the products are benzonitrile and quinoline compounds.

Rapid heating of oil shale involves complex mass and heat transfer effects and chemical reactions which are dependent on a wide range of parameters, particularly heating rate, final temperature, particle size, and shale grade. Under rapid heating at high temperatures, cracking of the primary products from kerogen decomposition within the shale matrix results in producing mainly aromatic hydrocarbons.

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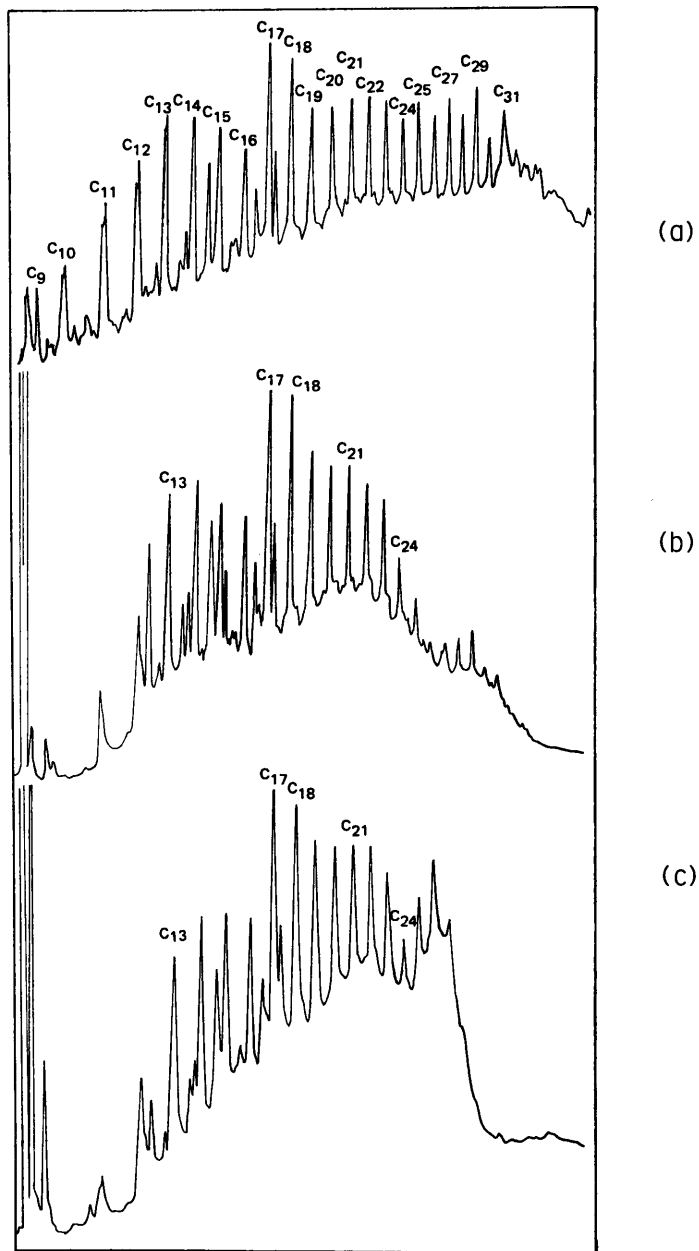


FIGURE 11. GAS CHROMATOGRAMS OF (a) SHALE OIL (PARAHO SHALE OIL LR 21816), (b) PRODUCTS OF SHALE OIL VIA RAPID PYROLYSIS, AND (c) PRODUCTS OF SHALE OIL MIXED WITH SPENT SHALE VIA RAPID PYROLYSIS (1400 C and 20 C/MSEC)