KINETIC STUDIES ON KEROGEN DECOMPOSITION

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ABSTRACT

In the past, several schemes to extract oil from oil shale have been proposed and tested. The fluidized bed reactor for processing crushed oil shales offers several advantages, viz., uniform bed temperature, high processing rates, and high heat transfer rates. An investigation was conducted to analyze the factors affecting the conversion of kerogen into bitumen and light hydrocarbons in a fluidized bed.

Influence of a variety of parameters has been investigated and their relative influence has been compared. Bed volume as a function of particle size, temperature, capacity, and flow pattern can be determined. Relative values of conversion are presented in this paper. The amount of each fraction extracted has been calculated as a function of dispersion number and residence time. From the time required for a desired conversion, the bed dimensions can be estimated.

INTRODUCTION

One of the "Synthetic fuels" that appears attractive is oil derived from shale, a sedimentary rock which contains an organic solid called kerogen. The conversion of oil shale kerogen into liquid and gaseous products is the focus of considerable research in this country at present.

Several oil shale reactors for surface retorting have been proposed and tested in the past in order to achieve maximum yield of high quality oil. Some of the configurations used are moving bed, rotary retort and fluidized bed. The fluidized systems appear to be attractive for retorting shale because of very high heat transfer rates and extremely uniform temperatures that can be maintained in all parts of the bed.

The kerogen in Green River oil shale, when pyrolyzed at 500°C, yields approximately 66% oil, 9% gas, 5% water and 20% carbon residue.

The present investigation is a study of the factors influencing the conversion of kerogen into bitumens and light hydrocarbons.

Effect of Temperature and Particle Size

Tests were conducted in a thermogravimetic apparatus using 3 mesh (6 mm) and 10 mesh (1.6 mm) oil shale particles. Two runs were made at 900°F (482°C) and 1000°F (538°C), respectively. The effect of temperature on the conversion of retortable residue is shown in Figure 1. The effect of particle size on retorting is shown in Figure 2. These results were compared with data obtained from literature (1, 3, 4) as shown in Table 1. A rise in pyrolysis temperature of 56°C cuts the time required for 90% conversion by half. The effect of particle size on the rate of pyrolysis is very little under the test conditions studied.

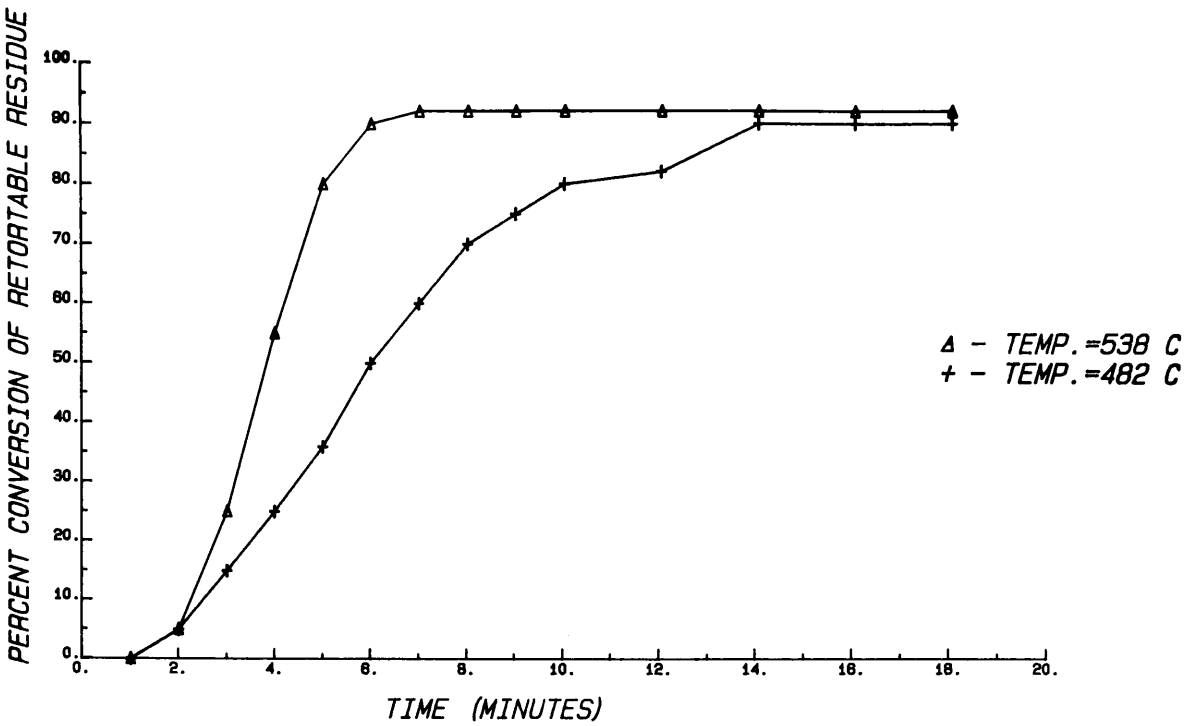

FIGURE 1. EFFECT OF TEMPERATURE ON RETORTING WITH 1.6 MM DIAMETER PARTICLES

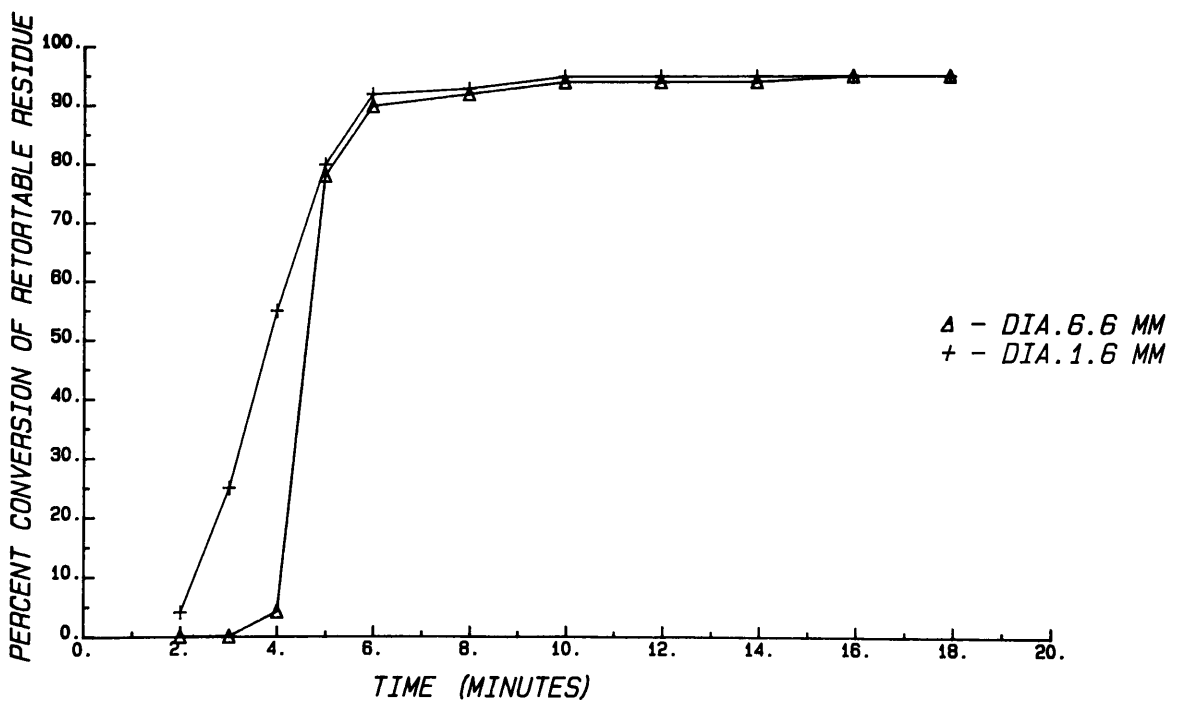

FIGURE 2. EFFECT OF PARTICLE SIZE ON RETORTING AT 538 DEGREES CELCIUS

Table 1 - Comparison of Conversion Times

Temperature of the Run, °C	Time Required for 90% Conversion (Minutes)			
	Ref. 3	Ref. 1	Ref. 4	Our Results
482	2.0	8	10	13
538	0.5	4	5	6

Estimation of Pyrolysis Time

Total time required for the pyrolysis can be estimated by using both the kinetic and heat transfer information. According to Wallman et al (4), pyrolysis of shale can be approximated by two first order processes. Fraction (f_1) or organic matter in kerogen decomposes into light hydrocarbons (gaseous products) and the remaining fraction (f_2) into heavy hydrocarbons (oil and coke). Combining the two first order reactions, rate expression for the formation of the products can be given as:

$$\text{Rate} = f_1 K_1 Co\, e^{-K_1 t} + f_2 K_2 Co\, e^{-(K_2 + Kc)t} \qquad (1)$$

where $f_1 = 0.616$

$f_2 = 0.24$

$$K_1 = 5.78 \times 10^{12} \exp\left(-\frac{43{,}600 \text{ KCal/Mole}}{RT}\right)$$

$$K_2 = 1.8 \times 10^{5} \exp\left(-\frac{22{,}600 \text{ KCal/Mole}}{RT}\right)$$

$$K_c = 3.0 \times 10^{5} \exp\left(-\frac{22{,}600 \text{ KCal/Mole}}{RT}\right)$$

Time required for the necessary conversion under isothermal conditions can be calculated using equation (1). However, heat transfer plays a key role in attaining the reaction temperature. Total time (t) required to achieve pyrolysis can be estimated using the following equation:

t = Heat-up time required for the particles to reach the reaction temperature (T) + time required for the decomposition of the kerogen at T (2)

Even though part of pyrolysis occurs during the heat-up time, rate of the pyrolysis is very low at low temperatures.

In order to determine the heat-up time for particles in the fluid bed reactor, the heat transfer coefficient must be known. Preliminary heat transfer tests in a bench scale fluid bed reactor were conducted using electrically heated finned tubes immersed in the bed. The average heat transfer coefficient from the finned tubes to particles was estimated to be 122 KCal/hr. sq. M°C. Heat-up times were calculated using this data for two particle sizes and two retort temperatures. The results are summarized in Table 2. Total pyrolysis time is longer for larger sized particles than for smaller sized particles. Also, the pyrolysis time decreases as the temperature is increased.

Table 2 - Total Time Required for Pyrolysis

Part. Size (mm)	Retort Temp. (°C)	Heat Up Time (Min)	Reaction Time (Min)	Total Time Required for Pyrolysis
6.6	538	1.2	0.5	1.7
6.6	482	1.5	2.0	3.5
1.6	538	0.25	0.5	0.75
1.6	482	0.20	2.0	2.2

Pyrolysis rates were also measured at a higher temperature of 704°C. The results were interesting. Total weight loss recorded (25%) seems to be a little higher than the average weight loss measured (15%) in the other runs at lower temperatures. This additional weight loss is due to the decomposition of mineral carbonates present in oil shale. Typically, a thirty gallon per ton oil shale will contain about 23% dolomite (calcium/magnesium carbonate) and about

16% calcite (calcium carbonate). Literature survey indicates that dolomite decomposition begins at 566°C and calcite decomposition at 621°C. Dolomite requires about 278 cal/gram and calcite about 389 cal/gram for decomposition, which would consume about 8% of the combustible matter of the shale, if these minerals were allowed to decompose. However, at temperatures below 649°C, dolomite might decompose rapidly, but the decomposition of the remaining carbonates is extremely low.

Effect of Residence Time Distribution on Kerogen Conversion

The oil yield in an oil shale fluidized bed reactor will depend on the residence time distribution of oil shale particles in the reactor. The residence time distribution of solids in a fluid bed reactor should be as narrow as possible (plug flow). Since the typical backmix reactor is always larger than the plug reactor for all positive reaction orders, it is preferable to remain as close to plug flow regime as possible or minimize solids mixing in the axial direction. A number of cold tests were conducted using tracer technique to study the residence time distribution of solids. It was found that the bed behavior was between plug flow and backmix flow. The cold test data were analyzed using a dispersed plug flow model. The dispersion number (D/UL) was calculated for each set of data. There was good agreement between calculated and experimental values for the dispersion number. Using the dispersion number, the oil yield can be calculated by the following equation:

$$\text{yield, } Y = \int_0^t \frac{\exp[-\frac{(1-t)^2}{2.32t}]}{2\sqrt{(D/UL)\pi t}} X(t)\, dt \qquad (3)$$

where

t = residence time

X (t) = conversion of oil shale particles as a function of time

D/UL = 0.58 (experimentally found dispersion number)

The expressions for kerogen conversion have been experimentally determined by Wallman et al [4] and are given as follows:

for 1 mm diameter particles at 538°C

$$X(t) = 0.619\ (1-e^{-10.27t}) + 0.20\ (1-e^{-0.587t}) \qquad (4)$$

for 1 mm diameter particles at 560°C

$$X(t) = 0.619\ (1-e^{-20.98t}) + 0.205(1-e^{-0.799t}) \qquad (5)$$

Calculated light hydrocarbon conversion, bitumen conversion and total conversion at these temperatures are given in Table 3.

Relative conversion values (C) are presented in this table, i.e., the ratio of the substance of the fraction extracted to its total amount in shale. The amount of substance of each fraction extracted can be calculated from this table as function of time. For example, after 8 minutes of pyrolysis at 1000°F or 538°C, we will have: $C_{\text{light hydr.}} = 97.4\%$ and $C_{\text{bitumen}} = 57.1\%$. The composition of kerogen in shale for this case is: light hydrocarbon - 0.619, bitumen - 0.20 and residual carbon - 0.181. So the amount of light hydrocarbon extracted will be $C_{L.H.} = 0.619 \times 0.974 = 0.603$, and bitumen $C_{bit} = 0.20 \times 0.571 = 0.114$. The total amount of kerogen decomposition at pyrolysis is $C_{pyr} = C_{L.H.} + C_{bit} = 0.717$. This value can be also calculated from the table data: $C_{tot} = 0.819 \times 0.874 = 0.716$.

Table 3 - Conversion of Kerogen at Different Residence Times

T°C	t (min)	4	6	8	10	12
538	Light Hydrocarbon conversion (%)	85.5	94.8	97.4	98.6	99.1
538	Bitumen conversion (%)	45.8	54.0	57.1	58.3	58.8
538	Total conversion (%)	75.6	84.2	87.4	88.6	89.1
560	Light hydrocarbon conversion (%)	86.1	94.8	98.0	99.2	99.6
560	Bitumen conversion (%)	53.2	62.2	65.4	66.6	67.0
560	Total conversion (%)	78.0	86.7	89.9	91.1	91.5

The conversion values of kerogen decomposition for particles with 0.4 mm and 2 mm diameter can be determined from experimental data of Wallman et al [4] by the following formulas:

for particles with 0.4 mm diameter and at 538°C

$$X(t) = 0.616\ (1-e^{-10.27t})+0.21\ (1-e^{-0.384t}) \quad (6)$$

and for particles with 2 mm diameter and at 538°C

$$X(t) = 0.616\ (1-e^{-10.27t})+0.20\ (1-e^{-0.864t}) \quad (7)$$

Relative values of conversion are presented in Tables 4, 5 and 6 and are graphically represented in Figures 3, 4 and 5. For a given value of dispersion number, the conversion increases up to about six minutes residence time and remains more or less constant. For a given residence time, the conversion decreases with increasing dispersion numbers indicating that the departure from plug flow conditions results in decreased conversion and require longer residence times to achieve a given conversion.

Sizing of Retort Zone

Knowing the residence time for a desired conversion of kerogen, the retort zone can be sized presuming a maximum particle diameter and a maximum temperature of 560°C. If it is assumed that a fluidized bed reactor has to be sized for 91% total conversion of kerogen, then from Table 3, for 91% conversion, the required residence time is 10 minutes according to the following calculations:

$$\text{Volume of Bed, } V = \frac{W}{(1-\varepsilon)\rho s} \quad (8)$$

where:

w = weight of bed, Kg

ε = void fraction

ρs = density of oil shale, Kg/m^3

$$\text{Weight of Bed, } W = tFo \quad (9)$$

where:

w = weight of bed, Kg

t = residence time for a required conversion, min

Fo = feed rate, Kg/min

As an example, let us assume

t = 10 minutes (from Table 3, for 91% conversion)

Fo = 3000 Kg/min

ε = 0.50

ρs = 2112 Kg/m^3

Volume of bed required for 91% total conversion of kerogen =

$$\frac{(10)\ (3000)}{(1-0.5)(2112)} = 28.4 m^3$$

The bed volume for any desired kerogen conversion can be estimated for design purposes using these data.

Bed volume can obviously be reduced by approaching plug flow and by reducing particle size. If CO_2 generation must be expected, temperature increase is not advisable. Using fluidized bed reactors for clean up of fines appears to have technical and economical merit.

Table 4 - Kerogen Decomposition for Particles With 0.4 mm Diameter at T = 538°C

D/UL	Time (Min) / Conversion %	2	4	6	8	10
0.2	Light Hydrocarbon	80.9	98.5	99.8	99.9	99.9
	Bitumen	25.8	31.4	31.8	31.9	31.9
	Total	67.1	83.1	84.3	84.4	84.5
0.4	Light Hydrocarbon	67.8	92.2	98.0	99.5	99.8
	Bitumen	21.6	29.4	31.2	31.7	31.8
	Total	56.0	78.2	83.8	85.2	85.6
0.6	Light Hydrocarbon	60.1	85.5	94.5	97.8	99.1
	Bitumen	19.1	27.3	30.1	31.2	31.6
	Total	49.5	72.6	81.3	84.6	85.8
0.8	Light Hydrocarbon	54.9	79.8	90.5	95.4	97.7
	Bitumen	17.5	25.5	28.9	30.4	31.2
	Total	45.1	67.9	78.1	82.9	85.2
1.0	Light Hydrocarbon	51.0	75.1	86.7	92.7	95.9
	Bitumen	16.3	24.0	27.6	29.5	30.6
	Total	41.8	63.8	74.9	80.8	84.0

Table 5 - Kerogen Decomposition for Particles

With 1 mm Diameter at T = 538°C

D/UL	Time (Min) / Conversion %	2	4	6	8	10
0.2	Light Hydrocarbon	80.7	98.3	99.7	99.8	99.8
	Bitumen	36.4	50.1	51.4	51.5	51.5
	Total	70.0	86.7	88.0	88.1	88.1
0.4	Light Hydrocarbon	67.3	91.7	97.5	99.0	99.4
	Bitumen	29.2	48.6	54.1	55.5	55.9
	Total	58.3	81.5	87.3	88.7	89.1
0.6	Light Hydrocarbon	59.4	84.8	93.8	97.2	98.5
	Bitumen	25.1	45.5	53.9	57.2	58.5
	Total	51.6	75.7	84.6	87.9	89.2
0.8	Light Hydrocarbon	54.0	79.0	89.7	94.6	96.9
	Bitumen	22.4	42.4	52.5	57.3	59.6
	Total	46.9	70.7	81.2	86.1	88.4
1.0	Light Hydrocarbon	50.0	74.1	85.7	91.7	94.9
	Bitumen	20.4	39.8	50.7	56.6	59.8
	Total	43.5	66.5	77.9	83.9	87.1

Table 6 - Kerogen Decomposition for Particles

With 2 mm Diameter at T = 538°C

D/UL	Time (Min) / Conversion %	2	4	6	8	10
0.2	Light Hydrocarbon	80.7	98.3	99.6	99.7	99.8
	Bitumen	46.6	62.3	63.6	63.7	63.7
	Total	72.4	89.5	90.8	90.9	91.0
0.4	Light Hydrocarbon	67.3	91.7	97.6	99.0	99.4
	Bitumen	37.5	59.4	65.2	66.6	67.0
	Total	60.0	83.8	89.6	91.1	91.4
0.6	Light Hydrocarbon	59.4	84.8	93.8	97.2	98.5
	Bitumen	32.2	55.2	64.0	67.4	68.7
	Total	52.8	77.6	86.5	89.8	91.1
0.8	Light Hydrocarbon	54.0	79.0	89.7	94.5	96.9
	Bitumen	28.8	51.4	61.9	66.8	69.1
	Total	47.8	72.2	82.8	87.7	90.0
1.0	Light Hydrocarbon	50.0	74.1	85.7	91.7	94.9
	Bitumen	26.3	48.1	59.5	65.5	68.7
	Total	44.2	67.7	79.3	85.3	88.5

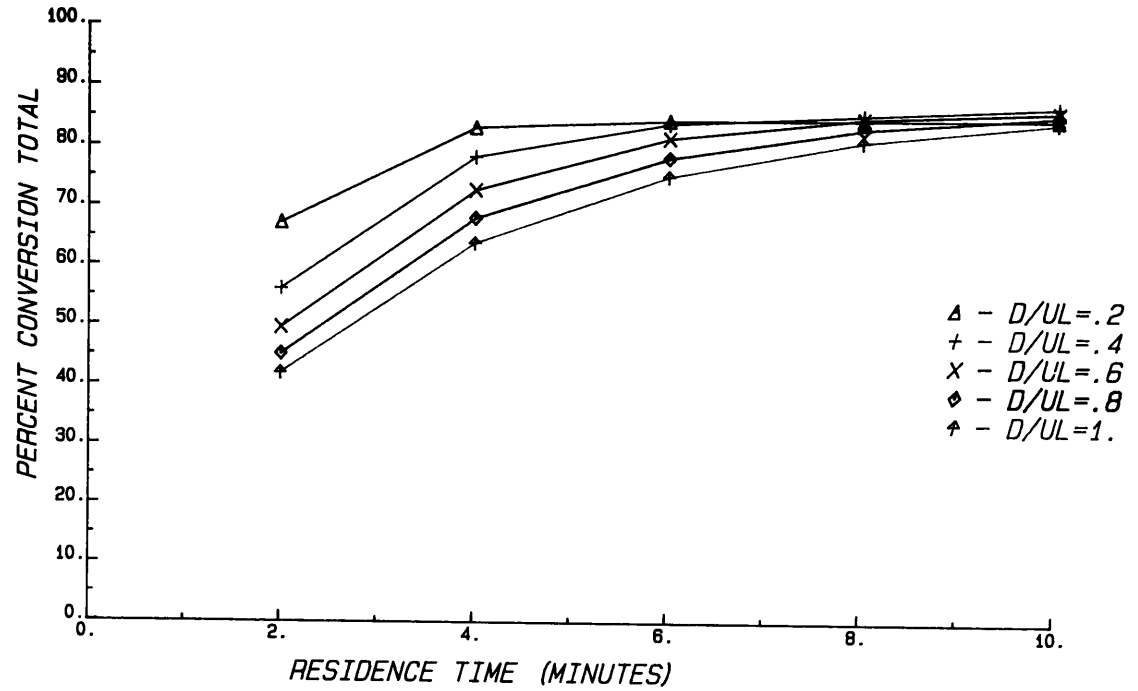

FIGURE 3. KEROGEN DECOMPOSITION FOR PARTICLES WITH 0.4 MM DIAMETER AT 538 DEGREES CELCIUS

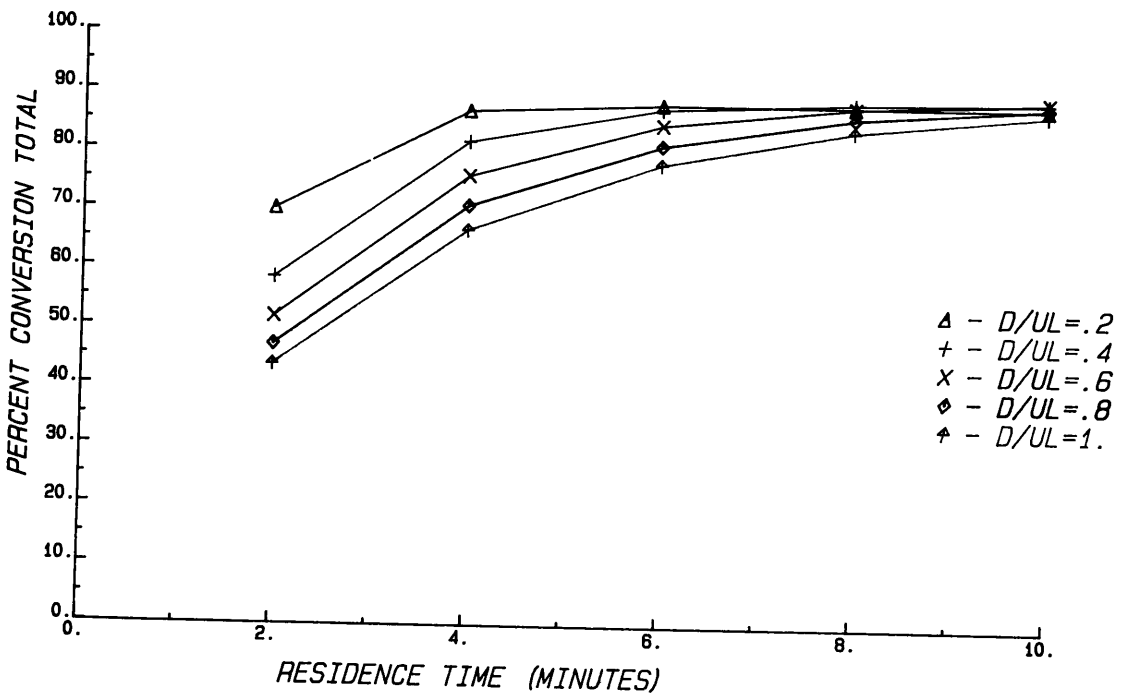

FIGURE 4. KEROGEN DECOMPOSITION FOR PARTICLES WITH 1.0 MM DIAMETER AT 538 DEGREES CELCIUS

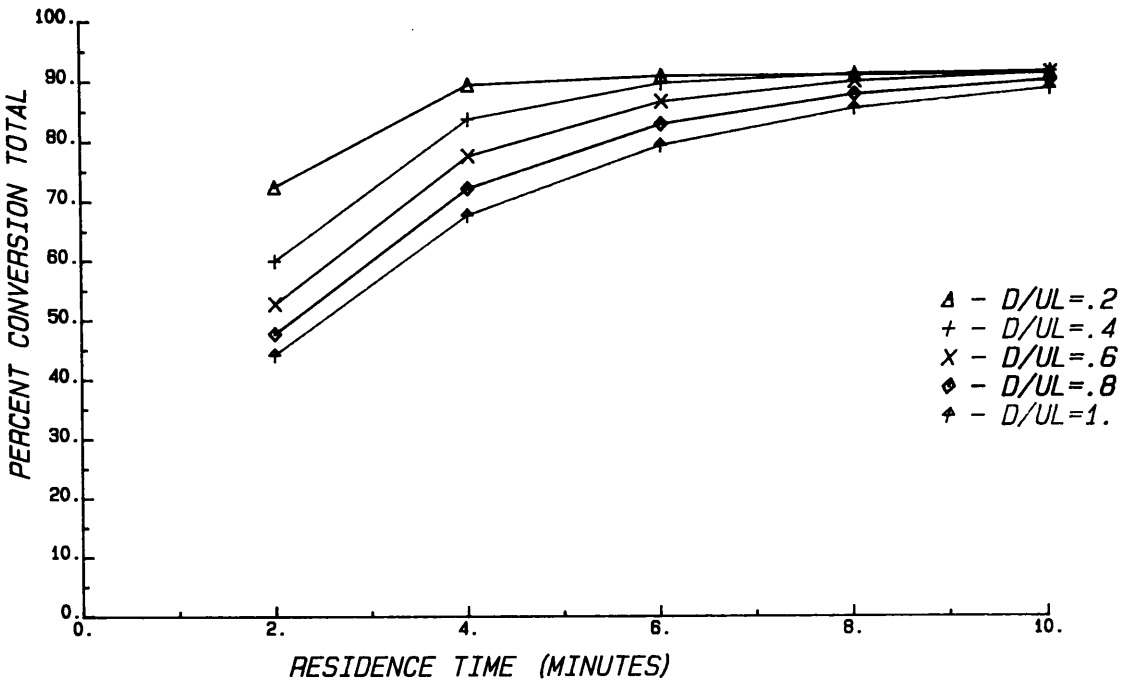

FIGURE 5. KEROGEN DECOMPOSITION FOR PARTICLES WITH 2.0 MM DIAMETER AT 538 DEGREES CELCIUS

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