

## PRELIMINARY STUDIES ON THE RECOVERY OF OIL FROM CHATTANOOGA SHALE

ASTOR Y. HERRELL

*Knoxville College, Knoxville, Tenn. (U.S.A.)*

CHARLES ARNOLD, JR.

*Sandia Laboratories, Albuquerque, N.M. (U.S.A.)*

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### ABSTRACT

Three exploratory investigations have been performed to examine the recovery of oil from the Chattanooga black shale formation. Thermogravimetric data were analyzed to yield an average activation energy of  $57.1 \text{ kcal mol}^{-1}$  for the conversion process; positive deviations from a reaction order of 3.7 were observed suggesting the presence of autocatalytic effects at low conversion levels. Thermal chromatographic analysis indicated that the maximum organic product release occurred at approximately  $435^\circ\text{C}$  and resulted in an oil of relatively low distillation range. A packed bed of shale was retorted in the self-sustained combustion mode thus suggesting the feasibility of this mode for in situ oil recovery. Comparisons with oil shale from Colorado's Green River formation have been made throughout.

### INTRODUCTION

During the Late Devonian Age, a blanket of black shale was deposited over a large area of North America from the ancient Chattanooga Sea. Typical exposures of the shale in Tennessee appear within the city limits of Chattanooga—the area from which it gets its name<sup>1</sup>. It is the most consistent stratigraphic unit in Tennessee<sup>2</sup> and is usually subdivided into the Gassaway, Dowelltown and Hardin members. The shale generally has a thickness of about 20 ft. and outcrops at many locations in Tennessee. An exception is the Flynn Creek Disturbance in Jackson County which covers an area two miles in diameter and where the shale has an average thickness<sup>3</sup> of 250 ft.

Chattanooga shale typically contains 20 to 25% quartz, 25 to 30% clay and mica, 10% feldspar, 10 to 15% pyrite, 15 to 20% organic matter and 5% other constituents. Unlike oil shale from Colorado's Green River Formation it undoubtedly contains no true bitumen<sup>1,4</sup>. It is the organic content of the shale that makes it particularly attractive for study at this time since it has long been known that oil can be obtained by pyrolysis of the shale.

Historically, Chattanooga shale has been of little economical value even though it has been known for more than one hundred years that oil can be distilled from this shale<sup>1,5</sup>. Unlike its western counterpart, the Green River oil shale, it has not been

considered in the past in calculating this nation's oil shale reserves due to its low oil yield ( $\sim 10 \text{ gal ton}^{-1}$ ). With the depletion of natural oil reserves and coupled with its potentially valuable by-products (paint pigment, phosphate and uranium)<sup>1</sup>, the cost of recovering oil from the Chattanooga shale may become competitive with other energy sources in the near future.

In an effort to obtain a better understanding concerning the potential recovery of oil from Chattanooga shale, three investigations, exploratory in nature, were carried out:

(1) Thermogravimetric analysis (TG) of the shale was studied in order to obtain kinetic parameters associated with pyrolysis.

(2) Thermal chromatographic analysis of the shale was studied in order to identify some of its hydrocarbon constituents in the pyrolysis products.

(3) Packed bed retorting of the shale in the combustion mode was made in order to assess the feasibility of this mode of in situ processing.

This report presents the results of these preliminary investigations.

#### SAMPLE DESCRIPTION

The shale used in these investigations was obtained from an outcrop near Oak Ridge, Tenn., and was supplied through the courtesy of Oak Ridge National Laboratory. Petrographic examination of thin sections, through the courtesy of the Department of Geology, University of New Mexico, show the shale sample to be composed mainly of fine grained quartz with feldspar, pyrite, and various clay minerals also visible. The examination gave no indication of the presence of carbonates which are characteristic of Green River Oil shale. X-ray diffraction patterns obtained on a powdered (200 mesh) sample of the shale also show the main constituent to be quartz with a positive indication for the clay mineral, illite. A Fischer assay of the shale was made by the U.S. Bureau of Mines at Laramie, Wyoming, and the oil and water yield were found to be  $8.1 \pm 0.6$  and  $6.6 \pm 0.7 \text{ gal ton}^{-1}$ , respectively. These assays show the samples to be slightly below average in terms of oil yield of the Chattanooga shale<sup>1</sup>. Carbon, hydrogen, nitrogen analyses were obtained and the overall shale composition is C = 12.02%, N = 0.40% and H = 1.36%. No attempt was made to obtain or analyze an organic fraction or concentrate in this study as was performed for Kentucky's New Albany Shale<sup>5</sup>.

#### KINETIC ANALYSIS

Kinetic parameters for the thermal degradation of solids have been determined from thermogravimetric data obtained at single heating rates in a number of studies<sup>4,7-9</sup>. More recently, Friedman<sup>10</sup> made kinetic calculations for the thermal degradation of a polymer based on measurements made at four different heating rates. The Friedman method makes use of the fact that the TG curves are shifted to higher temperatures with increasing heating rates. The method is generally considered more reliable than those based on a single TG trace at one heating rate<sup>11</sup>.

In the Friedman method, degradation rates are determined from the slopes of the family of TG curves at a given conversion level. Assuming that the Arrhenius relationship holds and that the weight functionality  $f(w)$  is independent of the temperature functionality,  $Ae^{-E_a/RT}$ , the following equation can be used to determine the kinetic parameters for the decomposition

$$-\frac{1}{w_0} \frac{dw}{dt} = Ae^{-E_a/RT} f\left(\frac{w}{w_0}\right) \quad (1)$$

where

- $w$  = weight of sample (mg)
- $w_0$  = original weight of sample
- $E_a$  = activation energy (kcal/mole)
- $T$  = temperature ( $^{\circ}$ K)
- $A$  = frequency factor
- $t$  = time (min)

No assumptions are made with regard to reaction order; sufficient data are available using the Friedman method, so that an independent determination of the reaction order is not required.

Samples of the Chattanooga shale were prepared by grinding a representative rock so as to pass through a 200 mesh screen. Without further preconditioning the powdered shale samples, which weighed 4 to 9 mg, were placed in the sample pan of a Perkin-Elmer TG apparatus (Model TGS-1) and subjected to linear heating rates of 0.62, 5, 10, 20, 40, 80, and 160 $^{\circ}$ C min $^{-1}$  in a dry stream of helium. The maximum temperature attained in these runs was 594 $^{\circ}$ C. The total weight of organic matter present in the shale,  $w_0$ , was determined by oxidation in air at 459 $^{\circ}$ C. Decomposition rates were obtained by determination of the slopes of the TG curves. This was done graphically by construction of tangents to the curves at selected conversion levels.

The TG curves of the residual weight fraction vs. temperature that were obtained are given in Fig. 1. The rather large range of weight loss that was observed at the lower heating rates (0.625 and 5 $^{\circ}$ C min $^{-1}$ ) is expanded in Fig. 2. As would be expected from kinetic theory, the curves are shifted to higher temperature with increased heating rates.

Eleven values of  $w/w_0$  were selected at equal intervals in the range of 0.65 to 0.99 and corresponding values of  $1/w_0 dw/dt$ , and  $T$  were determined. Regression analysis was utilized to determine the intercepts and slopes of  $\ln(-1/w_0 dw/dt)$  vs.  $1/T$  for each value of  $w/w_0$ . The slope values are equivalent to  $-E_a/R$  and the intercepts correspond to  $\ln[A \cdot f(w/w_0)]$ . Plots of both  $E_a$  and  $\ln[A \cdot f(w/w_0)]$  vs.  $w/w_0$  are shown in Fig. 3. It is immediately apparent from these plots that both the activation energy and  $\ln[A \cdot f(w/w_0)]$  increase with increasing conversion. Similar results were obtained from the Piceance Basin in Colorado. Two hypotheses have been proposed to explain these results. Arnold<sup>1,2</sup> has proposed that the initial degradation products have a catalytic effect on the degradation of the remaining organic residue, whereas

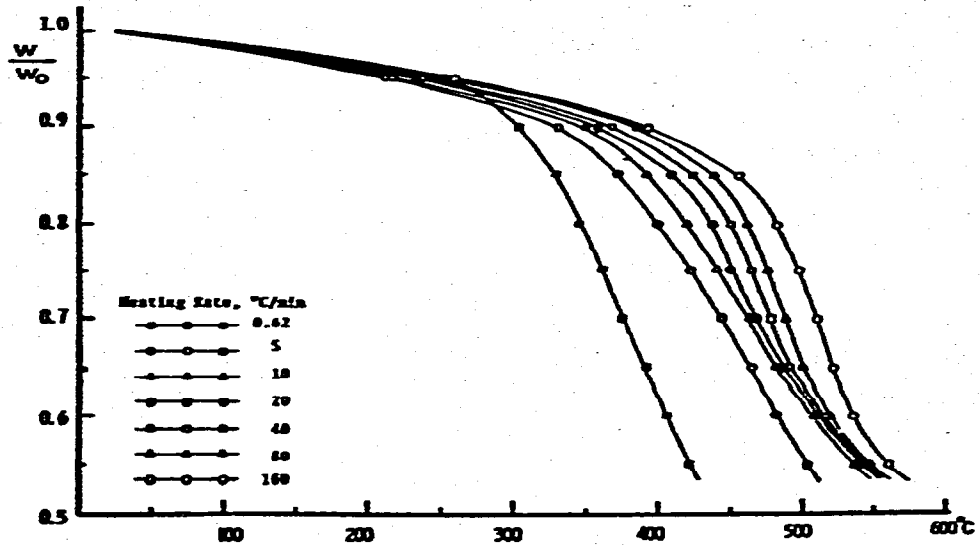


Fig. 1. TG curves for Chattanooga Shale as a function of heating rate.

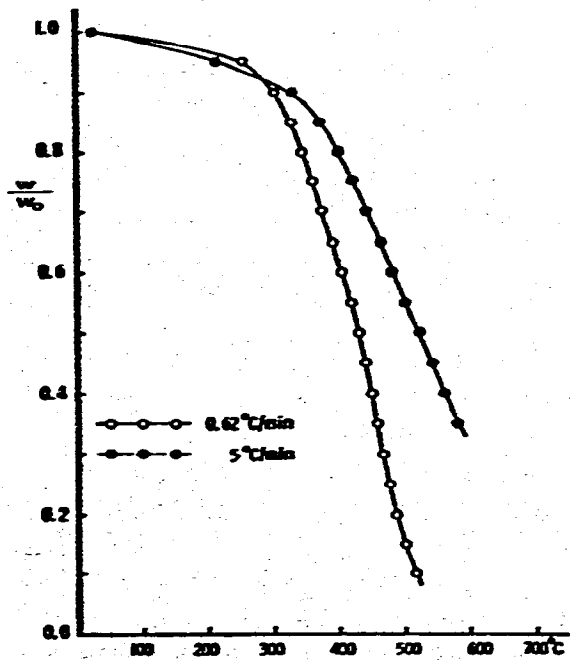


Fig. 2. Extended TG curves for the lower heating rates.

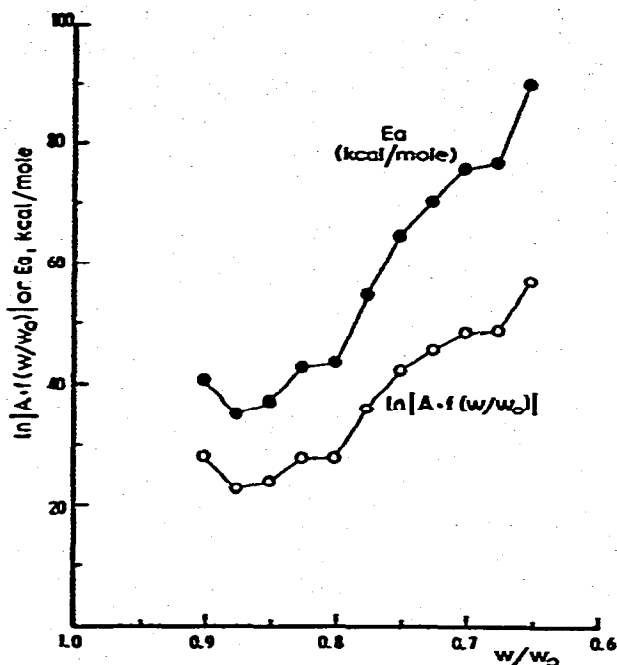


Fig. 3. The kinetic parameters as a function of degree of conversion.

Weitkampff and Gutberlet<sup>12</sup> proposed that such trends could be explained on the basis of diffusional effects.

The average activation energy over the entire conversion range was 57.1 kcal mol<sup>-1</sup> for the Chattanooga shale. In contrast, the average activation energies reported in previous studies on Colorado shales were in the range of 40–48 kcal mol<sup>-1</sup>. The difference in this kinetic parameter is probably attributable to differences in the chemical constitution of the two types of shale.

The assumption is made in the kinetic method of Friedman that the following form of the weight functionality holds.

$$f\left(\frac{w}{w_0}\right) = \left(\frac{w - w_f}{w_0}\right)^n \quad (2)$$

$n$  = reaction order

$w_f$  = residual char weight

In this study, the residual organic weight was taken as the organic residue remaining after heating the samples to 594°C. Equation (3) can then readily be derived from eqn (2):

$$\ln\left(A \cdot f\left(\frac{w}{w_0}\right)\right) = \ln A + n \ln\left(\frac{w - w_f}{w_0}\right) \quad (3)$$

Values for  $\ln(A \cdot f(w))$  are available from previous steps in the kinetic analysis. The

reaction order,  $n$ , and pre-exponential factor,  $A$ , can be obtained from a plot of  $\ln(A \cdot f(w))$  vs.  $\ln(w - w_f/w_0)$ . Such a plot is shown in Fig. 4. The values of  $n$  and  $A$ , determined from this plot were 3.7 and  $1.7 \times 10^{13} \text{ min}^{-1}$ , respectively. The positive deviation from linearity that was noted for  $n$  at the lower conversion levels is believed to be attributable to catalytic effects of the initial pyrolysis products on the decom-

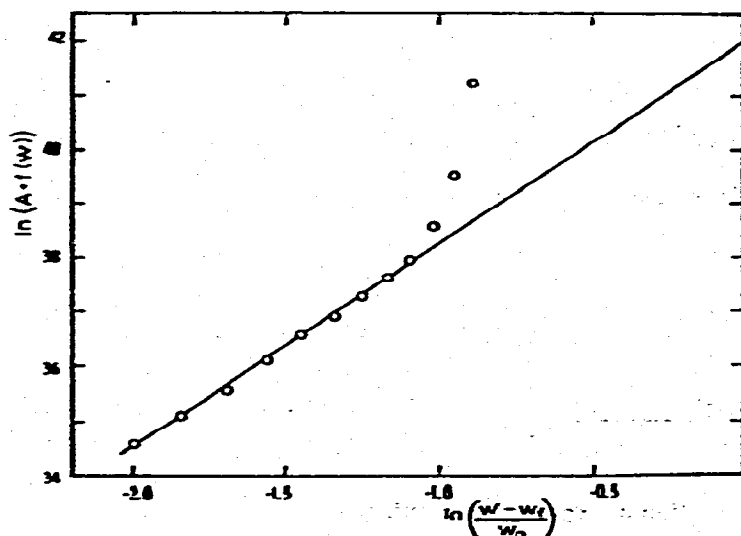


Fig. 4. Determination of the reaction order,  $n$ ; and pre-exponential factor,  $A$ .

position of the remaining undegraded organic matter. Those autocatalytic effects are also believed to be the reason that the activation energies were low at the lower conversion levels. At the upper conversion levels, however, the pyrolysis of Chattanooga shale can be defined by the following rate expression:

$$\frac{1}{w_0} \frac{dw}{dt} = 1.7 \times 10^{13} e^{-57,100/RT} \left( \frac{w - w_f}{w_0} \right)^{3.7} \quad (4)$$

The trends noted in the kinetic parameters  $n$  and  $E_a$  for the decomposition of Chattanooga shale suggest the possibility that autocatalysis is occurring especially during the early stages of the pyrolysis. Similar trends have been reported by Arnold<sup>12</sup> for the pyrolysis of Colorado shale. Furthermore, autocatalytic effects of bitumen on the decomposition of kerogen were proposed previously by Allred. Although weight dependence orders greater than one are somewhat unusual for the decomposition of organic polymers, a fifth order of dependence was recently reported for a glass supported phenolic<sup>10</sup>. Composite materials of this type resemble oil shale in that both consist of an organic matrix bound to an inorganic substrate.

#### THERMAL CHROMATOGRAPHY

This investigation was initiated to determine what possible differences or similarities there might be between the pyrolysis of Chattanooga and Colorado

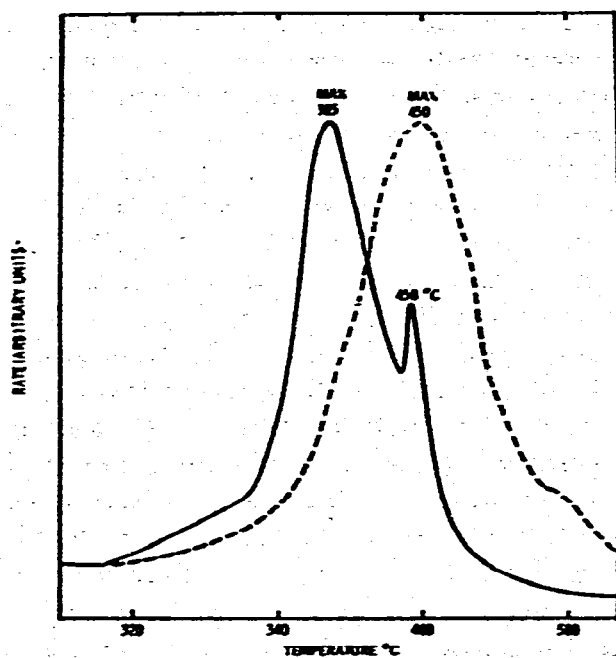


Fig. 5. Comparative total product thermograms for the Chattanooga Black Shale (solid line) and a 25 gal ton<sup>-1</sup> Colorado Green River Oil Shale (dashed line). Thermal conductivity detector and an 8°C min<sup>-1</sup> heating rate.

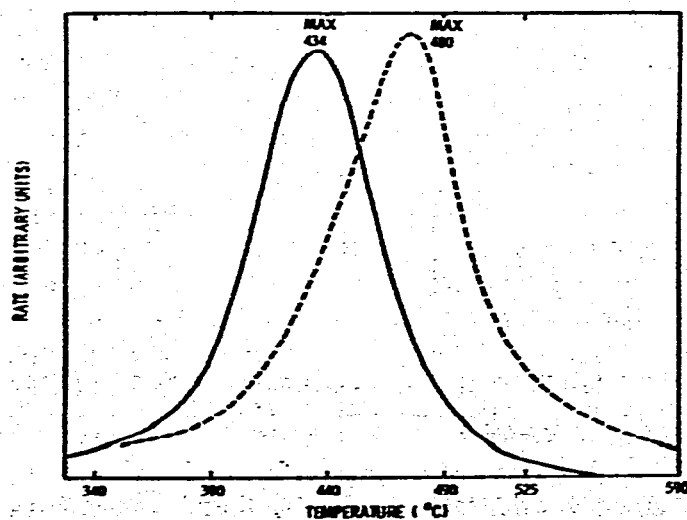


Fig. 6. Comparative organic fraction thermograms for the Chattanooga Black Shale (solid line) and a 25 gal ton<sup>-1</sup> Colorado Green River Oil Shale (dashed line). Flame-ionization detector and a 20°C min<sup>-1</sup> heating rate.

shales. These studies were carried out with a thermal chromatograph (Model MP-3) made by Chromolytics Corporation and equipped with both thermal conductivity and flame ionization detectors. The origin of the Colorado shale was the Piceance Basin in Rio Blanco County; this shale had a Fischer Assay of  $25.4 \text{ gal ton}^{-1}$  and was obtained through the courtesy of the Bureau of Mines at Laramie, Wyoming.

Powdered samples ( $2\text{--}150 \mu\text{m}$ ) of the shale were pyrolyzed at heating rates of 4, 8, and  $20^\circ\text{C min}^{-1}$  and the evolved products analyzed with both detectors. Typical thermograms that were obtained are shown in Figs. 5 and 6. It is apparent from these curves that although the initial temperature of volatilization for both shales is about the same ( $\sim 325^\circ\text{C}$ ), the Colorado shale decomposed over a much wider temperature range. Other noteworthy differences were: (1) the maximum in the rate of volatilization was shifted toward higher temperatures for the Colorado shale ( $434$  vs.  $480^\circ$  for organic products and  $385$  vs.  $450^\circ\text{C}$  for all products); and (2) an inorganic product evolved at  $\sim 450^\circ\text{C}$  from the Chattanooga shale that was not evolved from the Colorado shale. This temperature is characteristic for the loss of water of hydration from illite<sup>14</sup>, which is known to be a major mineral in the Chattanooga shale and was detected by X-ray diffraction in these samples. The evolved gases were collected in a trap located downstream from the thermal conductivity detector and backflushed into a gas chromatograph equipped with an SE-30 on Chromosorb P column<sup>15</sup>. The chromatograms obtained for both the Chattanooga and Colorado shales are shown in Fig. 7.

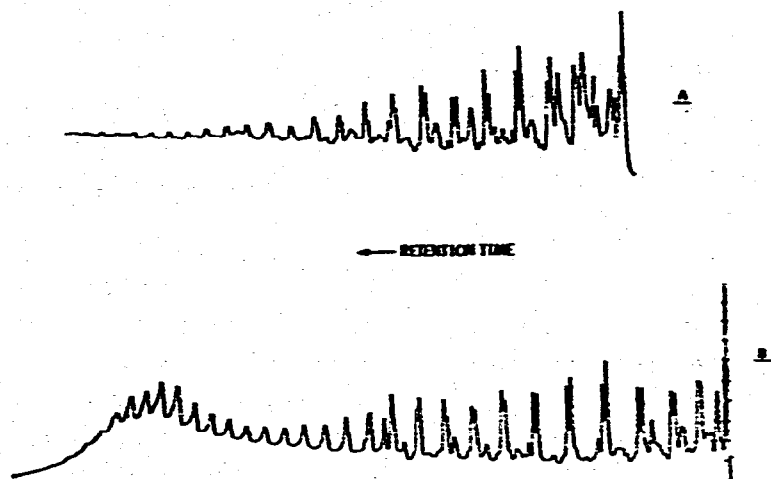


Fig. 7. Gas chromatograms of shale oil from Chattanooga Shale (A, upper plot) and Colorado shale from Piceance Creek Basin (B, lower plot). Conditions: helium flow-rate,  $28 \text{ ml min}^{-1}$ ; column, SE-30 on Chromosorb P; heating rate,  $20^\circ\text{C min}^{-1}$ .

Oils from both types of shale contained considerable amounts of the homologous alkanes and alkenes and suggests a common biogenesis for these organic materials. The Colorado shale oil, however, contained more higher boiling products as evidenced by the area under the peaks that eluted at longer retention times.



Pyrolysis of Chattanooga shales occurs at lower temperatures than those required for Colorado shales and the product oil has a lower distillation range. These findings, which are based on preliminary volatilization studies, have important economic implications on the potential recovery of oil from low-grade eastern shales.

#### PACKED BED RETORTING

The in situ recovery of oil from oil shale has been receiving increased attention<sup>16</sup>. One proposed method calls first for the fracturing or rubblelization of the shale formation to introduce sufficient permeability to allow the flow of gases and products. A combustion wave is then initiated and moves through the formation thus providing the heat necessary for retorting. The process is self-sustaining in that heat is supplied by the reaction of oxygen in the injected air with the carbonaceous or coke residue remaining on the shale after retorting. Packed bed reactors are being used to simulate the retorting of oil shale under such a self-sustained, combustion mode<sup>17-19</sup>.

A 3-in. diameter by 24-in. long bed of crushed Chattanooga shale was retorted in such a manner in a vertical quartz retort. Flow was from top to bottom through the bed and bed temperatures were recorded by thermocouples located axially at 2-in. intervals. The top of the bed was resistively heated to a temperature of 600°C and a flow mixture of 4 std l min<sup>-1</sup> air and 1 std l min<sup>-1</sup> nitrogen was initiated. The shale was readily ignited and maximum temperatures of 900°C were noted for this flow before various other flow conditions were examined. Initial experimental conditions were similar to those successfully used to retort typical Colorado shales<sup>19</sup>. However, the combustive characteristics of Chattanooga shale were found to be quite different for these conditions. Higher temperatures, a lower combustion front velocity and a wider combustion front were observed. Total gas flow rates were varied between 2.5-5.0 std l min<sup>-1</sup> with oxygen contents between 8 and 16.8% in an effort to reduce the temperature and to increase oil production. Flame temperatures of 700°C were achieved while sustaining combustion, but burn velocity was drastically reduced. Control of the reaction could not be maintained under these changing conditions and only part of the bed was retorted; thus, oil yield could not be determined.

The product oil was collected in an electrostatic precipitator which efficiently collects the oil mist or aerosol. The aerosol was nearly white, much lighter in color than that associated with Colorado oil shale which has a deep yellowish color. Little oil (~24 g) was produced during the experiment and most of that was obtained during the retorting of the first few inches of the bed. Subsequently, little aerosol was visible in the precipitator despite attempts to alter the combustive conditions as reported above. The oil was very fluid at 25°C and resembles, visually, that obtained from Colorado shale of low assay (12 gal ton<sup>-1</sup>). The high combustion temperature and low oil yield suggest that a significant amount of oil was consumed in combustion; copious amounts of water were also obtained throughout the collection system.

The bed was examined after the experiment and two distinctly different zones were noted for the unreacted particles. Immediately in front of the combustion zone

the particles of shale were lightly coated with oil. Several inches beyond, in the direction of flow, a yellowish white condensate containing needle-shaped crystals was observed. The condensate was present in sufficient quantity to completely mask the normally black surface of the shale particles. The shale particles behind the combusted zone contained a large unretorted or unreacted core which indicates that the permeability of the shale remained low and that the total organic constituent was not efficiently utilized. Unlike the western shales which are very impermeable but which delaminate upon retorting, the Chattanooga shale retains much of its strength and integrity after retorting.

This single preliminary experiment served to dramatize the large differences between the Chattanooga and Colorado oil shales. Differences in organic composition and concentration, accessory minerals, porosity, permeability and strength affect the conditions encountered during a combustion retorting process. Evidence from this experiment demonstrated that such a retorting process is probably feasible for Chattanooga shale based upon the ready ignition of the shale and early advance of the combustion front. A different set of retorting parameters will be required, however, and this suggests the direction of a future investigation.

#### CONCLUSIONS

Three exploratory investigations were performed to examine the recovery of oil from the Chattanooga black shale formation:

(1) Thermogravimetric data from finely powdered samples were analyzed according to the method of Friedman<sup>10</sup> to obtain the kinetic parameters for the conversion reaction. The average activation energy over the entire conversion range was found to be  $57.1 \text{ kcal mol}^{-1}$ . The reaction order,  $n$ , and pre-exponential factor,  $A$ , as obtained from these data were found to be 3.7 and  $1.7 \times 10^{18} \text{ min}^{-1}$ , respectively. Higher reaction orders and lower activation energies were observed at low conversion levels which is believed due to autocatalytic effects by the initial pyrolysis products on the remaining organic matter.

(2) Thermal chromatography showed that the initial temperature of volatilization of organic matter occurs at  $\sim 300^\circ\text{C}$  and that the maximum rate of volatilization (at heating rates of  $20^\circ\text{C min}^{-1}$ ) occurs approximately at  $435^\circ\text{C}$ . An inorganic product was evolved at  $\sim 450^\circ\text{C}$  and has been attributed to water from the decomposition of illite, an accessory mineral in this shale. Relative to Colorado oil shale, the organic product is released over a lower and narrower temperature range and the product has a lower distillation range.

(3) A packed bed of crushed shale was retorted in a self-sustained combustion mode. Ignition of the bed was readily attained and maximum bed temperatures of  $900^\circ\text{C}$  were observed for a gas containing 16% oxygen at a total flow of  $5 \text{ std l min}^{-1}$ . The bed was not uniformly retorted due to intentional changes in flow and oxygen content and yield data were not obtained. The experiment demonstrated that very different retorting parameters will be required for the recovery of oil from Chat-

tanooga shale as compared with Colorado oil shale, but that retorting by this technique is probably feasible.

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\*An extensive listing of references for Chattanooga shale is to be found in ref. 1.