

DIFFERENTIAL THERMAL STUDY OF COLORADO OIL SHALE*

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ABSTRACT

Differential thermal curves of selected Colorado oil-shale samples showed endothermic dips in the temperature range of 450° to 475° C. These characteristic dips occurred within the temperature range of the conversion of organic material (kerogen) in oil shale to oil, gas, and organic residue. However, it is not known whether the dips resulted from heat absorbed in the vaporization of reaction products or possibly from endothermic reaction of kerogen. The thermal curves also showed the presence of calcite and/or dolomite but did not indicate the presence of clays.

INTRODUCTION

The method of differential thermal analysis, as suggested by Le Chatelier (7) in 1887, has undergone considerable development in recent years and emerged as an important means of studying the constitution of various substances. The theory of this analysis has been explained and applied by many investigators, such as Insley and Ewell (5), Norton (8), Hendricks *et al.* (4), Grim and Rowland (3) Speil (9), and Kerr and Kulp (6). Results obtained by most of these workers have shown that this method of analysis is especially valuable in the study of clay minerals.

In 1942 a similar technique of analysis was employed by Cane (2) of Australia to study torbanite, a rich oil shale. The investigation was concerned with the thermochemical properties of torbanite rather than its mineral constituents. In 1951, Sohns, Mitchell, Cox, Barnet, and Murphy (9) measured the heat requirements for retorting different grades of Colorado oil shale. They determined the over-all heat necessary to produce shale oil and accompanying byproducts under conditions that would exist in commercial practice. The data indicated that little heat was consumed in the conversion reaction; most of it appeared as sensible heat in the spent shale and retort products.

The investigation discussed herein is an application of differential thermal analysis to Colorado oil shale. Its purpose was to determine whether or not any mineral constituents, especially clays, could be identified in the oil shale and to determine the types of thermal reactions taking place during pyrolysis of the organic constituent of the shale.

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APPARATUS

The apparatus used in this study was patterned, in general, after Berkelhamer's design (1). A potentiometer was used in place of a reflecting galvanometer-photographic recorded arrangement, and a manually operated variable transformer was used in place of a motor-driven transformer. In brief, the equipment consisted of a tubular furnace, sample block and holder, thermocouples, two potentiometers, and a variable transformer.

One potentiometer recorded the differential temperature while another recorded the sample block temperature. Thermocouples were made of chromel-alumel wire (B&S gage No. 20). It was important that the size of the thermocouple hot-junction beads be uniform to prevent any effect on the slope of the base line of the thermal curves. To make smooth beads of approximately the same size, the thermocouples were dipped in flux and arc-welded with an apparatus consisting of two carbon rods and a small variable transformer. A uniform heating rate of about 11° to 12° C. was maintained during a run by manually changing the voltage setting of the variable transformer.

SAMPLES USED

Six Colorado oil-shale samples were selected to represent the types of oil shale being mined at the Bureau of Mines Oil-Shale Mine, near Rifle, Colorado. All of these samples were assayed according to the modified Fischer-retort method (10) to determine their oil yields. The oil yields, shown in Table 1, indicate the relative amount of organic material present in each sample, as it is this material that is converted to oil and gas upon heating.

TABLE 1. OIL YIELD OF OIL-SHALE SAMPLES

| Sample designation ^a | Oil yield (Gal./ton) |
|---------------------------------|----------------------|
| A | 2.2 |
| B | 10.5 |
| C | 26.7 |
| D | 36.3 |
| E | 61.8 |
| F | 75.0 |

^a Detailed analyses of five of these samples (B through F) are available in *Bureau of Mines Report of Investigations 4825*, (1951), Properties of Colorado Oil Shale, by K. E. Stanfield, I. C. Frost, W. S. McAuley, and H. N. Smith.

Other samples included in this study were quartz and various known mixtures of kaolinite, calcite, and dolomite with oil shale.

THERMAL EFFECT OF ORGANIC MATERIAL IN OIL SHALE

Differential thermal curves¹ (Fig. 1) of the oil-shale samples studied indicated the effect of shale pyrolysis. Each thermal curve showed an endothermic dip, the peak of which occurred in the temperature range 450° to 475° C. This dip, which was proportional to the amount of organic material in the sample, was attributed to absorption of heat by vaporization of the conversion products or possibly to absorption of heat by the organic material (kerogen) of the oil shale. The conversion of organic matter to volatile products during a run was noted by the evolution of smoke, starting at 375° to 400° C., and continuing to about 500° C.

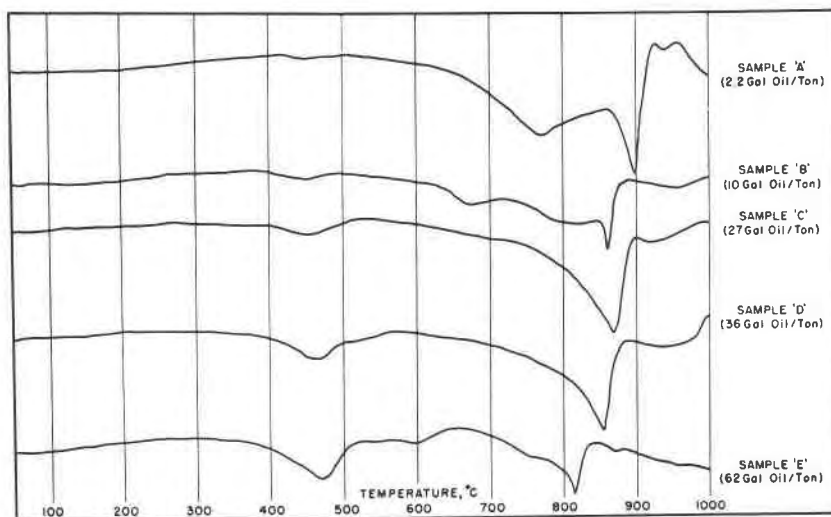


FIG. 1. Thermal curves of Colorado oil shales.

The thermal curve for sample *F* was not included in Fig. 1. To obtain a representative curve, it was necessary to mix an inert substance with this sample because the organic content of the sample was so high that, during a thermal run, the sample expanded, raising the cover of the sample block.

As was mentioned in the introduction, Cane applied this method of analysis in a study of Australian torbanite. In Cane's apparatus, two silica tubes were placed in a furnace, and thermocouples were placed in the tubes so as to constitute a differential thermocouple. One tube was packed with dehydrated fuller's earth and the other with dry powdered

¹ Similar curves were obtained by the Bureau of Mines Station, Tuscaloosa, Ala., for samples E and C shown in Fig. 1, using a galvanometer-recorder type apparatus with a resistance of 600 ohms.

torbanite. The thermal curve reported by this method indicated the reaction to be irregular; that is, it showed both endothermic and exothermic reactions. In the temperature range 360° to 400° C., the curve showed a marked exothermic reaction that was attributed to decomposition of sulfur- and oxygen-containing compounds. The curve also indicated an endothermic reaction for decomposition of the organic matter.

The thermal curves in Fig. 1 do not indicate an exothermic reaction as found by Cane. This difference in curves could possibly be due to differences in the samples or in the analysis technique.

IDENTIFICATION OF MINERALS IN OIL SHALE

According to a communication from T. A. Klinefelter, former mineral technologist, Bureau of Mines, Tuscaloosa, Ala., many oil shales contain

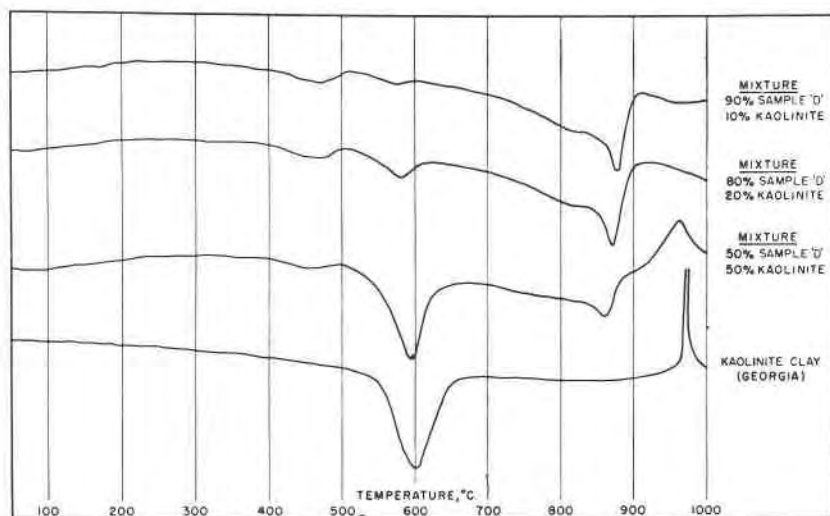


FIG. 2. Thermal curves of mixtures of oil shale and kaolinite clay.

illite and kaolinite. The thermal curves of Fig. 1 do not indicate the presence of either of these clay minerals. The presence of kaolinite in the shale samples would have been indicated because of its large thermal reactions. It can be seen from the thermal curves of kaolinite-oil-shale mixtures in Fig. 2 that, although the characteristic endothermic peak of kaolinite shifted to the left (lower temperature) as the percentage of kaolinite was decreased, it was still possible to detect the presence of small amounts of kaolinite. However, illite clay could have been present in appreciable quantity and yet not have been detected owing to lack of sensitivity of the apparatus. This sensitivity, as revealed by direct

potentiometer readings, was sufficient to detect small thermal changes in which the reaction was of short duration. For example, the alpha-beta inversion of quartz, which occurred suddenly at about 572°C . (Fig. 3), was readily indicated by a differential potential of between 0.05 to 0.08 millivolt (about 1° to 2°C .). However, for thermal changes of this same order of magnitude wherein the reactions occurred gradually, as in illite clay, the sensitivity proved to be insufficient.

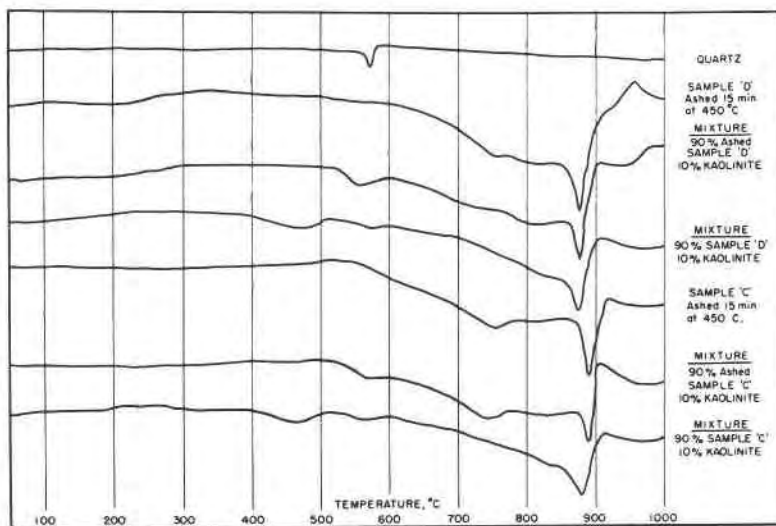


Fig. 3. Thermal curves of quartz and of mixtures of ashed oil shales and kaolinite clay.

The effect of decomposition of organic matter upon the identification of the clays in oil shale was studied. Two samples, *C* and *D*, were ashed 15 minutes in an open dish at 450°C . to burn off the organic matter, and runs were made on this ashed material, on mixtures of kaolinite and the ashed material, and on mixtures of kaolinite with the original shale. Thermal curves, Fig. 3, indicated a kaolinite dip in the temperature range of 550° to 580°C . for all the mixtures. Larger endothermic dips were obtained for the kaolinite-ashed shale mixtures than for the kaolinite-raw shale mixtures. This indicated that decomposition of the organic matter had an over-all effect of changing the thermal characteristics of any clays present in the oil shale.

On all the thermal curves in Fig. 1, an endothermic dip attributed to the presence of some form of carbonate was shown in the temperature range 800° to 900°C . The curves for samples *B*, *C*, and *D* showed an endothermic dip at about 850° to 875°C ., which is characteristic of calcite. The curve for sample *E* showed an endothermic dip at about

820° C. A thermal curve for a mixture of this sample with 5 per cent calcite, Fig. 4, showed a larger dip at about the same temperature which suggested that the thermal peak at 820° C. for sample *E* was due to calcite. Similarly, curves for mixtures of sample *A* with calcite and dolomite, Fig. 4, suggested that the endothermic dip at about 770° C. was due to dolomite and that the endothermic dip at about 900° C. was due to dolomite and/or calcite.

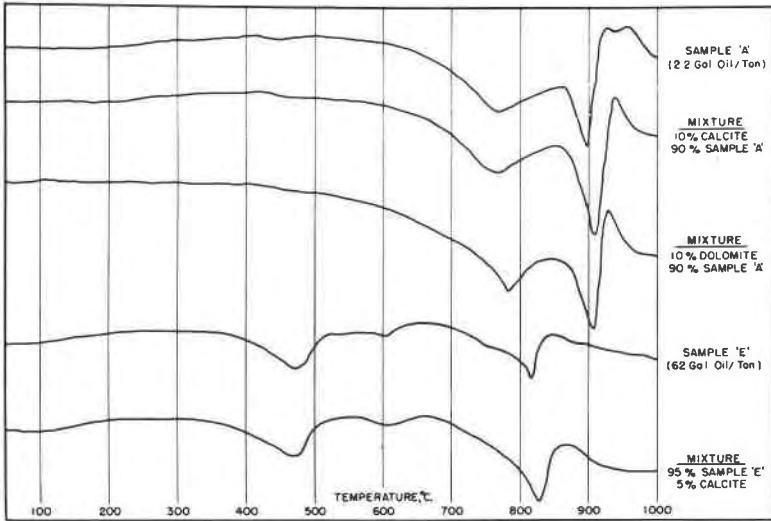


FIG. 4. Thermal curves of mixtures of oil shales and carbonates.

Petrographic analyses showed the presence of both dolomite and calcite in all the oil-shale samples. However, only the thermal curve for sample *A* clearly indicated the presence of dolomite. Sample *E* showed a slight dip characteristic of dolomite. A possible explanation of this is offered by use of the data in Table 2, which shows analyses of the oil-shale samples for magnesium and calcium content. The magnesium content of sample *A* was considerably higher than that of the others, which indicated the presence of more dolomite. In samples *B*, *C*, and *D* a large amount of CaO was shown, so it seems likely that the endothermic reaction due to calcite in these samples was sufficient to absorb completely the first dolomite dip occurring at about 770° C. In sample *E* less CaO was present, and the intensity of the calcite reaction was insufficient to absorb completely the first dolomite dip. It can be seen from the curves in Fig. 4 that the increased endothermic reaction due to the addition of 5 per cent calcite blocked out the small dolomite dip shown on the curve for sample *E*.

TABLE 2. PARTIAL CHEMICAL ANALYSIS OF SIX OIL-SHALE SAMPLES

| Sample designation | MgO per cent | CaO per cent |
|--------------------|--------------|--------------|
| <i>A</i> | 9.53 | 16.35 |
| <i>B</i> | 5.37 | 11.35 |
| <i>C</i> | 5.30 | 17.49 |
| <i>D</i> | 5.61 | 14.20 |
| <i>E</i> | 4.48 | 8.26 |
| <i>F</i> | 4.15 | 8.45 |

To supplement the differential thermal analyses, *x*-ray diffraction analyses were made of the six oil-shale samples. The following minerals were identified in all the samples: Quartz, calcite, dolomite, pyrite, illite clay, feldspar, and analcite. Only a small amount of illite clay, probably less than 10 per cent, was indicated.

CONCLUSION

Differential thermal analyses of six Colorado oil shales showed that: (1) An endothermic dip occurred within the thermal conversion range (450° to 475° C.) of kerogen to gas, oil, and organic residue, but it was not determined whether the conversion reaction was endothermic in character or whether heat was absorbed in the vaporization of the conversion products. (2) The decomposition of the organic matter affected any clays present in such a way that the magnitude of their characteristic thermal peaks was decreased. (3) Clays present in oil shale were not identified. (4) Carbonates, calcite, and/or dolomite, were present in all the samples studied.

X-ray analysis indicated the presence of a small amount of illite clay in all of the oil-shale samples. The combination of two factors—the effect of the decomposition of organic matter and insufficient sensitivity of the apparatus—prevented the identification of the illite clay by differential thermal analysis.

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