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COMPARATIVE TG–DTG OXIDATIVE PROFILES OF SELECTED AMERICAN AND AUSTRALIAN OIL SHALES

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ABSTRACT

The oxidative profiles for oil shale specimens of the U.S. Green River as well as the Australian Rundle, Glen Davis, and Alpha deposits obtained from microcomputer-controlled thermogravimetry in dynamic air atmospheres are reported. The oxidative behavior of these specimens is discussed relative to the organic maceral components and, in some cases, mineral matter content.

INTRODUCTION

Recent years have seen an increase in the scientific investigation and characterization of oil shales and other source rock of organic content of any level. This is evidenced by publication activity in this journal as well as the numerous published proceedings from many symposia related to the subject. This activity is due to the search for an economical alternative source of energy. At present, many favor the processing of oil shales to obtain the derived oil over that of the coal liquefaction routes. This is because the product oil is more directly achieved via thermal retorting of oil shales than in the more tedious routes employed by most present day coal liquefaction processes.

Since the process of thermal retorting is the most direct approach to the decomposition of the organic kerogen matrix to lower molecular weight species, the thermal methods of analysis offer direct approaches to the characterization of oil shales. In a recent study by the author [1], the pyrolysis profiles of six oil shale specimens, from both the U.S. and Australia, obtained by thermogravimetric studies in a dynamic nitrogen atmosphere were reported. The thermal stabilities and major kerogen decomposition peaks (DTG) were observed to correlate to the type of organic maceral components present in the oil shale specimens. The use of TG to study the U.S. Green River shale specimens both before and after thermal retorting was also demonstrated and discussed relative to energy balance

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requirements, from the economic standpoint, of thermal retorting of carbonate bearing shales. In the absence of certain interfering mineral components, the DTG pyrolysis peak area was observed to correlate to the Fisher Assay oil yield value for a core drilled Green River specimen.

In the following study, the microcomputer-controlled techniques of TG and DTG are employed to compare the oxidative profiles of the U.S. and Australian specimens. Although these studies were conducted primarily as a characterization experiment, the use of combustion retorting has been used experimentally as a means of modified in-situ retorting of the U.S. Western shales [2].

EXPERIMENTAL

The origin of the oil shale specimens used in this study has been previously described [1]. All thermogravimetric studies were performed using the Perkin-Elmer Model TGS-2 Thermogravimetric Analysis System used in conjunction with a Perkin-Elmer System 4 Microcomputer Controller. All derivative thermogravimetric (DTG) thermal curves were obtained simultaneously with the TG thermal curves through the use of a Perkin-Elmer Model FDC-1 First Derivative Computer which was connected to a special 10 V ordinate output located on the TGS-2 Balance Control Unit. A Perkin-Elmer XY_1Y_2 Thermal Analysis Recorder was employed to obtain the simultaneous TG and DTG thermal curves.

Both the electronic weight suppression dial of the TGS-2 Balance Control Unit and the ordinate scale of the XY_1Y_2 recorder were calibrated with a National Bureau of Standards Class M 100 mg standard weight. The linearized output of a stainless steel sheathed chromel–alumel thermocouple (Type K), positioned just beneath the TGS-2 sample pan, was used to drive the X-axis of the XY_1Y_2 recorder. As with the previously reported pyrolysis profiles [1], the temperature axis display was calibrated for actual sample pan temperature using a horseshoe magnet and Curie point standards supplied with the instrument. All TG–DTG thermal curves presented in this work were obtained using a heating rate of 10°C min^{-1} and a dynamic air purge of 45 cm^3 min^{-1}.

RESULTS AND DISCUSSION

The thermal behavior of oil shales in dynamic air atmospheres may exhibit characteristics of both the inorganic (mineral) and organic (kerogen plus bitumen) components. The early (low temperature) portion of the thermal curves may represent thermal decomposition identical to that observed in inert atmospheres while at higher temperatures (> 200°C) oxidative characteristics of the organic component generally predominate. Thermal events which may also appear in this region, although generally to a much lesser extent, include dehydroxylation of clay mineral components, decomposition and oxidation of siderite ($FeCO_3$), oxidation of pyrite (FeS_2) and/or marcasite (FeS_2), α–β inversion of quartz (not observed by TG), and decomposition of analcite ($NaAlSi_2O_6 \cdot H_2O$). In some Green River specimens, trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), nahcolite ($NaHCO_3$), and dawsonite ($NaAl(OH)_2CO_3$) are also possible contributors to the weight loss profile. At even higher temperatures (> 600°C) both the Rundle and Green River specimens exhibit thermal decomposition of the carbonates. Calcite ($CaCO_3$), dolomite [Ca, $Mg(CO_3)_2$], and iron-substituted dolomite specimens (ferroan dolomite and ankerite) are possible components.

In the results which are presented in the following discussion, major emphasis is placed on the comparative oxidative stabilities and characteristics of the DTG oxidative profiles.

Green River and Rundle shales

As was stated in the previous pyrolysis study [1], the organic matter in the U.S. Green River shales bear a striking resemblance and according to Cook et al. [3], are composed of entirely lamellar alginite with minor amounts of corpohuminite. The alginite in both the Green River and Rundle have been classified as Alginite B and originates from an historic blue-green algae (*Cyanophyceae*). The mineralogy of these shales is different, however, as is evidenced by the presence of the two low tempeature peaks in the Rundle (Figs. 2 and 4), which are absent in this particular U.S. Green River

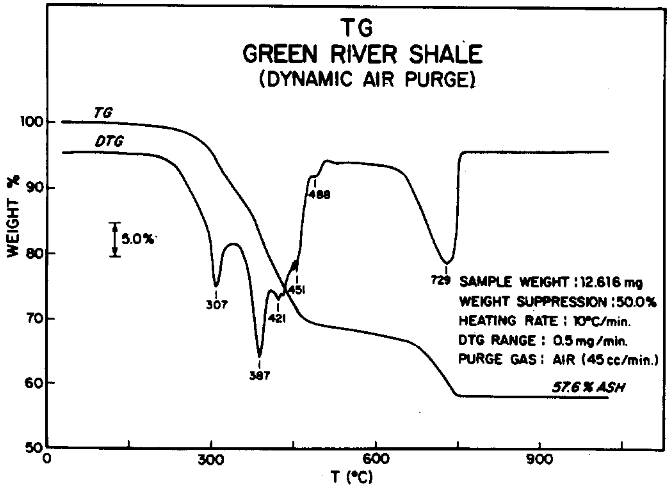

Fig. 1. TG and DTG thermal curves for SGR-1 Green River shale specimen in dynamic air atmosphere.

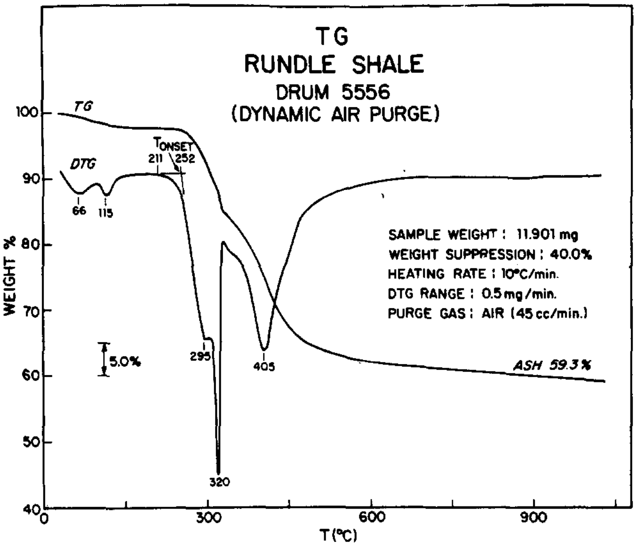

Fig. 2. TG and DTG thermal curves for Rundle Drum 5556 (as mined) shale specimen in dynamic air atmosphere.

specimen. These peaks are believed to be due to the loss of interlayer water from clay mineral components of the Rundle shales. This is in complete accord with that observed in the studies conducted in dynamic inert atmospheres [1]. The RAH-65 Rundle specimen was selected from a one ton lot which had been previously dried. As was observed in the earlier study [1], one of the dehydration peaks is absent.

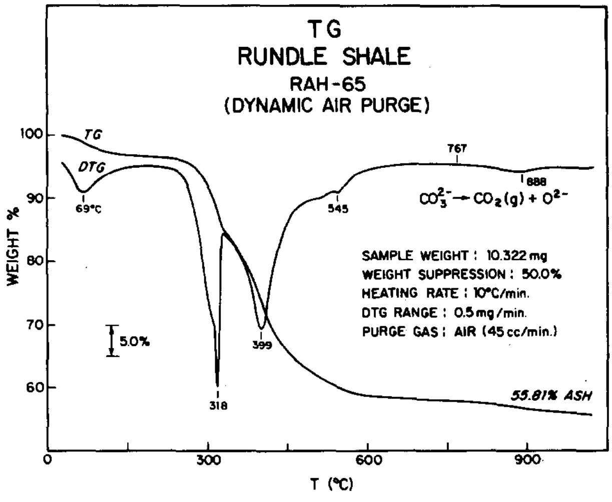

Fig. 3. TG and DTG thermal curves for Rundle (RAH-65) shale specimen in dynamic air atmosphere.

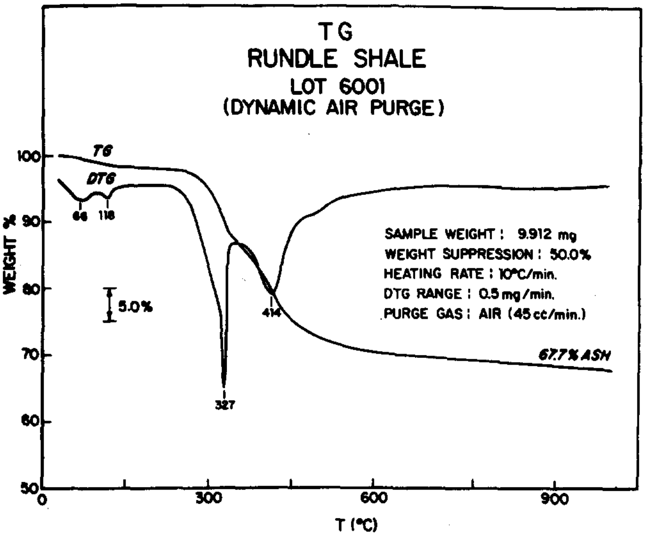

Fig. 4. TG and DTG thermal curves for Rundle (Lot 6001) shale specimen in dynamic air atmosphere.

The Green River specimen, on the other hand, exhibits a major carbonate decomposition peak (T_{max} = 729°C) while the Rundle specimens exhibit only minor carbonate decompositions in this temperature region. Quantitation at these carbonate levels was presented in the previous study and will not be repeated here. The carbonate decompositions are observed to shift to a higher temperature than that observed in dynamic nitrogen atmospheres due to the presence of carbon dioxide in the dynamic air purge.

The previous study [1] showed that the major DTG pyrolysis peak for the three Rundle specimens as well as the Green River specimen was singular in nature, with an average T_{onset} for the three Rundle specimens at 425°C and an average T_{max} at 478°C. The values for the DTG pyrolysis peak of the Green River specimen correlated closely with a T_{onset} of 429°C and a DTG pyrolysis peak maximum of 479°C.

By observing the simultaneous TG–DTG thermal curves given in Figs. 1–4, one will note that the oxidative characteristics of the organic components of these shales in the 200–550°C region are multistep in nature with two major oxidation events being clearly evident. Also, the onset of oxidation occurs at temperatures of at least 200°C lower than the corresponding pyrolysis onset temperatures which were previously reported. The DTG peak maxima are listed on the thermal curves in Figs. 1–4. The magnitude (rate of oxidative weight loss) of the first oxidative event is greater than the second event for the three Rundle specimens while in the Green River specimen the opposite is true. Also, it is clear that a shouldering effect is observed in the three Rundle specimens in the initial oxidation step.

This is more clearly observed in the Drum 5556 (as mined) specimen with the shoulder maximum labeled 295°C in Fig. 3. In an effort to determine if this phenomenon was related to particle size distribution or not, the Drum 5556 Rundle sample was reground and run ten consecutive times. In two of the runs the shoulder was separated into a separate distinguishable event while the other eight runs were as reported in Fig. 3. When the Drum 5556 specimen was washed with both *n*-pentane and toluene, the leading edge of the initial oxidative peak was identical to that of the RAH-65 and Lot 6001 specimens in appearance. Although the DTG peak maxima for the first two oxidative events will vary with sample weight and particle size, it is observed from the three specimens studied that the Rundle Shales exhibit peak maxima near 320 and 400°C and that the Green River specimen exhibits these two events at some 15°C lower in temperature.

On the returning edge of the second major DTG oxidation peak, the RAH-65 and Lot 6001 Rundle specimen exhibit additional weak shouldering activity at temperatures above 400°C. This is believed to be from mineral matter decomposition and/or oxidation of mineral matter. Based on the peak temperature and sharpness, as well as a knowledge of the mineralogy of the Rundle Shales, the peak in the RAH-65 specimen at 545°C is believed to be due to oxidation of pyrite while the less intense shouldering is probably dehydroxylation of clay mineral component. Although these statements may seem somewhat speculative, the mineralogy of the Rundle Shales is not a complex one.

In Fig. 1, the Green River specimen exhibits continued oxidation above 400°C with several shouldering maxima in the DTG trace. The spiking or

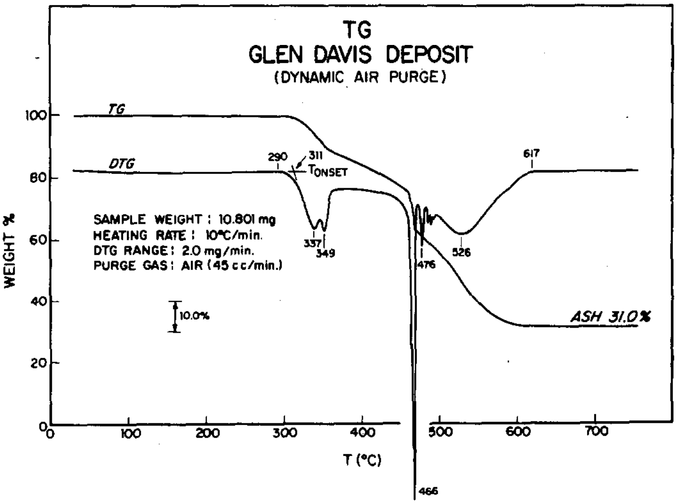

Fig. 5. TG and DTG thermal curves for Glen Davis torbanite specimen in dynamic air atmosphere.

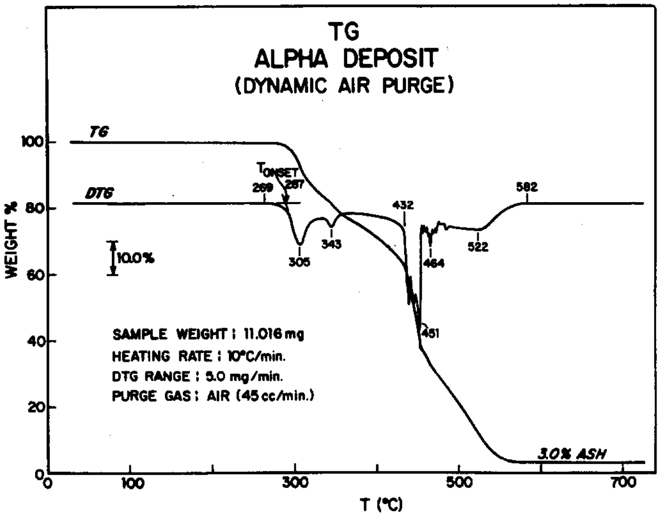

Fig. 6. TG and DTG thermal curves for Alpha torbanite specimen in dynamic air purge.

rapid oxidation at 451°C, although to a smaller extent here, will be seen to be in common with the torbanite deposits shown in Figs. 5 and 6. Although chalcogenides are noted for this type of behavior [4], this is not believed by the author to be due to decomposition and/or oxidation of mineral matter. At these temperatures, unoxidized kerogen can thermally decompose to lower molecular weight species which exhibit immediate oxidation.

Uden [5] reported a two stage profile using an evolved gas detection (flame ionization) technique for a Green River specimen heated in a dynamic air purge. Uden observed the second stage of his EGD profile to begin at ca. 450°C which is the region of the non-symmetrical portion (with minor spiking) of the DTG thermal curve in Fig. 1. He attributes the second stage of the EGD profile to the physical relationship between the organic component and mineral matter in the raw shale. This means that the unoxidized kerogen component surrounded by mineral matter at these temperatures would exhibit pyrolysis. Uden's postulation is supported by an increased FID response. Furthermore, the TG pyrolysis profiles of the previous study [1] show that the Green River specimen is well into the pyrolysis temperature region at 450°C.

Whereas, everyone enjoys both the assignment and use of peak maxima as a fingerprinting tool for characterization of materials, the comparison of oxidative stabilities is best assigned by either the temperature of initiation (T_i) of the oxidation or the corresponding extrapolated oxidative onset temperature (T_{onset}). Table 1 lists these values for all six shale specimens included in this study. On comparing these values for the Rundle and Green River specimens, it is observed that the Green River specimen is at lower oxidative stability ($T_i = 197°C$) than the Rundle specimens (average T_i for

TABLE 1

TG Characterization of oil shales in a dynamic air atmosphere

		Ash (wt. %)	Oxidation temperature (°C)	
			T_i	T_{onset}
Rundle	Drum 5556	58.87	211	253
	RAH-65	55.85	216	263
	Lot-6001	67.63	219	261
Alpha deposit		3.0	269	287, 432
Glen Davis deposit		31.55	290	311, 459
Green River (SGR-1)		57.64	197	231

the three specimens in 215°C). Also, although not in exact agreement as the pyrolysis temperatures were, both are of much lower oxidative stability and characteristically different from the two torbanite specimens.

Glen Davis and Alpha deposits

The Australian torbanite deposits represent some of the richest oil shales in the world. Oil yields of up to 1250 l tonne^{-1} with probable averages up to 330 l tonne^{-1} have been reported [6]. The Glen Davis shales are located in the Sydney Basin in New South Wales. This seam was reported [7] to have an average oil yield of 590 l tonne^{-1}. The specimen in this study contained 8.3% more carbon and 13.0% less ash than the average values reported [7] for the main seam.

The Queensland Alpha torbanite specimen in this study was the richest shale specimen ever to reach our laboratories for characterization. As may be seen in Table 1 and Fig. 6, it contained very little mineral matter and gave an ash residue of only 3.0% by thermogravimetry in a dynamic air purge. In the previous TG studies in dynamic nitrogen atmospheres, this specimen showed a weight loss of 87.2% on pyrolysis. Elemental analysis also showed this specimen to be 78.00% carbon, 10.50% hydrogen, and 0.96% nitrogen per unit weight of raw shale. Hence, this specimen could be considered a natural kerogen concentrate.

Previous microscopy studies [3] have shown that both the Alpha and Glen Davis torbanites contain a different type of alginite than that found in the U.S. Green River and Australian Rundle shales. This form of alginite has been classified by Cook et al. [3] as Alginite A and originates from a form of historic green algae (*Chlorophyceae*). Furthermore, this microscopy work showed that both the Glen Davis and Alpha deposits contain minor amounts of vitrinite, inertite, and sporinite as non-algal maceral components.

With this close similarity in organic composition, one would predict a similarity in the thermal behavior of these two torbanite specimens. In the pyrolysis study reported earlier [1], this speculation was confirmed with regard to thermal stability of the organic kerogen components. Both torbanite deposits showed a higher thermal stability than the U.S. Green River and Australian Rundle shales.

Figures 5 and 6 give the TG and DTG thermal curves obtained in a dynamic air atmosphere for the Glen Davis and Alpha torbanite specimens, respectively. The sample weights used for these two specimens differ by only 0.215 mg. It is noted that the oxidation of the organic matter occurs over a 327°C range (290°–617°C) for the Glen Davis deposit and 313°C range (269–582°C) for the Alpha torbanite specimen. The oxidative profiles are remarkably similar. As was the case with respect to thermal stability in inert atmospheres, the Glen Davis specimen also shows the greater oxidative stability with an oxidative initiation temperature (T_i) 21°C higher than that of the Alpha deposit specimen. This difference could be associated with the fact that the Glen Davis specimen contained approximately ten times as much mineral matter as the Alpha specimen of this study. Although mineral matter can often exhibit a catalytic effect on the oxidation of organics, in this case it may hinder oxygen availability to the organic component. A better comparison could be made with a demineralized specimen of the Glen Davis shale.

The spiking observed in the DTG thermal curves for both of these torbanite specimens in the 425 to 500°C temperature range, which was observed in the Green River specimen with much less intensity, corresponds to a drastic increase in the rate of oxidation of the organic kerogen component. The magnitude of the weight loss associated with this rapid rate increase excludes the association of this activity with chalcogenides such as pyrite or marcacite (FeS_2). With reference to the previous TG pyrolysis study [1], it seems that the mechanism of this observed phenomenon is one of "flashing" of lower molecular weight components which are formed by thermal decomposition of the kerogen at these temperatures. The breaking of intramolecular bonds, via either thermal degradation or selective oxidation of aliphatic bridge groups, at these temperatures produces specimens which are above their flash points, hence immediate oxidation occurs. The reader should not be misled by the difference in intensity of this phenomenon shown by the DTG thermal curves in Figs. 5 and 6 for Glen Davis and Alpha Torbanite specimens, respectively. The DTG thermal curve in the Glen Davis specimen was obtained using a DTG ordinate scale sensitivity of 2.5 times that the Alpha Torbanite specimen. The magnitude of the DTG spiking is similar for both specimens.

CONCLUSION

The TG–DTG oxidative profiles are characteristically different for the lamosite and torbanite raw shale specimens of this study. The TG–DTG profiles suggest a strong dependence on the type of alginite maceral component comprising the organic matter in the shale specimen. The ash content as assigned by thermogravimetry may serve as an indication of the level of mineral matter present in the shale specimens. The physical relationship between the organic component in the shales and the mineral matter, as well as the composition of the mineral matter, may also affect the relative oxidative characteristics of the raw shales. Another important variable is the relative amounts of extractable organic matter in the shale specimens.

As was seen in some cases in this study, since the oxidation of the organic component(s) begins at much lower temperatures than the major kerogen pyrolysis event in inert atmospheres, the oxidation in the organic matter is often near enough to completion so that the decomposition and/or oxidation of mineral matter components may be observed in the 520–600°C temperature region. This has been found in this laboratory to be especially true with oil shale specimens containing much smaller amounts of organic component than those employed in this study. As in any comparative study of minerals by thermal analysis techniques, care must be exercised with respect to particle size distribution and instrument calibration.

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