Thermochimica Acta, 47 (1981) 121—123
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMOGRAVIMETRIC ANALYSIS OF OIL SHALES

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(Received 29 January 1981)

As a result of the world energy situation, research on oil shales is on the increase in many countries. The basis of most assaying procedures is the pyrolysis of kerogen (insoluble organic matter) into oil, gas, water and a char-containing spent shale under controlled temperature conditions. The modified Fischer assay [1] and ISO Recommendation R647 [2] are widely used, but require 100 and 50 g of shale, respectively, for each determination. For research purposes it is often desirable to compare the thermal behaviour of much smaller samples or fractions separated from oil shales. Modern thermogravimetric analysis (TG) equipment is ideally suited to such comparisons, and in this note a novel yet simple procedure, developed and used at CSIRO, is described. The application of TG to oil shales and demineralized kerogens is an extension of similar methods applicable to coals [3].

EXPERIMENTAL PROCEDURE AND RESULTS

The method consists of heating samples in a series of steps and varying the atmosphere in a single run. Details of the programme and other parameters are given in Fig. 1. Oxygen-free helium or nitrogen are suitable gases for the initial pyrolysis under inert conditions. The exact sample size depends on the organic content of the shale. The isothermal periods are designed to briefly decrease the rate of evolution of volatiles so that losses from different samples during particular temperature intervals can be compared. A second pen can be used to record either temperature or the derivative of the weight loss curve. The time taken for a complete run is less than 40 min.

Comparative data for a number of Australian oil shales, demineralized kerogens resulting from HCl/HF treatment of oil shales, coals and tar sands are given in Table 1. The volatile matter is divided at 500°C into an oil-rich fraction (150—500°C) and the high temperature gas (500—900°C). The maximum temperatures used in the modified Fischer assay and ISO methods are 500 and 520°C, respectively. In some cases the TG curves obtained on whole oil shales are greatly affected by inorganic minerals (clays, carbonates, pyrite, etc.). For these shales TG of demineralized samples gives much more accurate data on the kerogen breakdown into shale oil.

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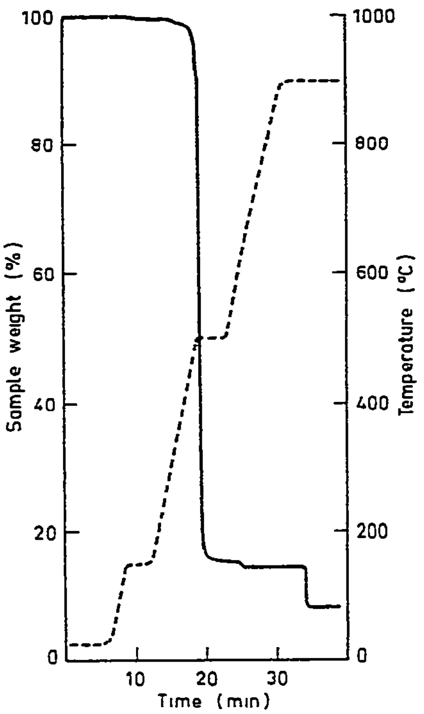

Fig. 1. Programme and parameters for TG of oil shales. TG curve (————) and temperature curve (- - - - -) are for the torbanite sample of Table 1. Sample size: 5—50 mg. Heating rate: 50°C min^{-1}. Programme: 25°C, air removed by vacuum; 25—150°C, under He; 150°C, 3 min under He; 150—500°C, under He; 500°C, 3 min under He; 500—900°C, under He; 900°C, 3 min under He; 900°C, 5 min under O_2. Flow rates: He, 40 ml min^{-1}; O_2, ~100 ml min^{-1}.

The procedure outlined above is flexible, allowing the study not only of small samples but also of variations in heating rates, retorting temperatures and inert (or reactive) gas purge rates. The method also provides a preliminary assessment of samples prior to the application of more advanced thermal and kinetic techniques (see for example ref 4). The shale oil, gases

TABLE 1

Comparative TG results for oil shales and other related samples

	Moisture (to 150°C) (%)	Volatile matter (150—500°C) (%)	Volatile matter (500—900°C) (%)	Char (%)	Ash (%)
Torbanite	0.2	84.7	0.7	6.3	8.1
Rundle	11.8	19.8	5.2	7.0	56.2
Demineralized Rundle	2.8	54.9	13.3	19.4	9.6
Julia Creek	1.0	9.0	25.0	0.0	65.0
Demineralized Julia Creek	0.8	42.0	15.9	26.1	15.2
Brown coal	9.4	26.4	17.1	43.2	3.9
Bituminous coal	3.8	18.9	10.1	49.1	18.1
Tar sand	1.0	7.7	1.5	0.9	88.0

and water from any pyrolysis step can, if required, be trapped or run directly into a GC or GCMS for detailed chemical analysis.

REFERENCES

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2 International Organization for Standardization, ISO Recommendation R647 (1974)
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