Thermochimica Acta, 66 (1983) 373–376
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMOGRAVIMETRIC ASSAY OF OIL SHALE

KRISHNAN RAJESHWAR *, ROBERT J. ROSENVOLD and JOEL B. DUBOW **

Department of Electrical Engineering Colorado State University, Fort Collins, CO 80523 (U.S.A.)

(Received 1 February 1983)

The need to develop a rapid assay method for resource evaluation of an oil shale deposit is clearly becoming more critical now that the increasing role that oil shales are likely to play in future energy options has been fully recognized. The authors have previously presented a differential scanning calorimetry (DSC) technique for the estimation of the potential oil yield of Colorado oil shales [1]. This technique, although much more convenient than the conventionally adopted Fischer assay [2], still involves the tedium of accurate measurement of peak areas. Furthermore, the complexity of the pyrolysis mechanism requires that considerable care be exercised in the construction of base lines for peak area measurements. On the other hand, as we shall attempt to illustrate in this paper, the simplicity of data reduction in the thermogravimetry (TG) technique yields a significant advantage in this regard. Equally important, this technique offers all the attractive features of the DSC method relative to existing assay procedures. We note here, however, that the TG technique has been used previously for kinetic studies on oil shale, e.g. ref. 3.

EXPERIMENTAL

Samples of Green River oil shale were obtained from the Laramie Energy Technology Center (LETC) in Wyoming. These samples originated from the U.S. Department of Energy Mine at Anvil Points near Rifle, Colorado. Their Fischer assay values were determined at LETC by the pulsed NMR technique [4]. Prior to a TG determination, 10–20 mg batches of the shale samples were crushed to particles which passed 250-mesh sieves. A sample of kerogen concentrate which had been prepared by methods documented in the literature [5], was also obtained from the LETC.

* To whom correspondence should be addressed.
**Present address: School of Engineering, Boston University, Boston, MA 02215, U.S.A.

0040-6031/83/$03.00

TG measurements were carried out on a DuPont 990 thermal analysis system fitted with the 951 TG accessory module. All experiments were performed in a flowing atmosphere (nominal flow rate: ~ 300 l min^{-1}) of ultrapure N_2. The sample was spread in a thin layer on the TG sample pan to preclude product effusion effects from clouding the TG data, cf. ref. 3. A nominal heating rate of 10°C min^{-1} was employed and the experiments were replicated at least twice to establish the degree of reproducibility (vide infra).

RESULTS AND DISCUSSION

Figure 1 shows a representative set of TG data on oil shale samples ranging in oil yield from 52 to 520 l $tonne^{-1}$. Excellent reproducibility was noted in the weight loss data in that a second series of "runs" (carried out on a different day), yielded curves almost exactly superimposable on the data set shown in Fig. 1, the maximum deviation in the percent weight loss at any temperature being no greater than 1.5 in all cases. A typical correlation between the percent weight loss at 500°C and oil yield is illustrated in the inset in Fig. 1. Weight loss data averaged from replicate experiments were used in this linear plot.

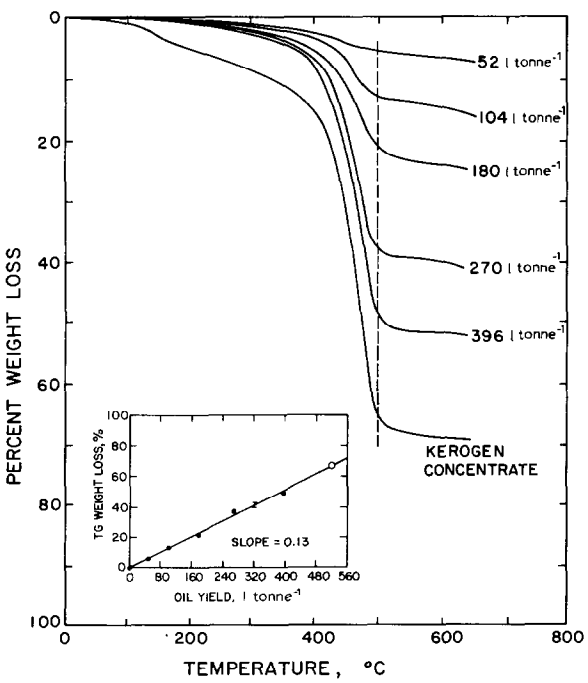

Fig. 1. Non-isothermal TG plots for Green River oil shale. Inset: Typical correlation between the TG weight loss at 500°C and the oil yield. I, Maximum mean deviation in the measured TG weight loss values; ○, sample of kerogen concentrate.

The efficacy of such plots for prediction of the oil yield of an unknown sample rests on the degree to which the following conditions hold: (a) the shale samples do not contain minerals that are thermally active at temperatures below ~ 500°C (e.g. nahcolite, dawsonite); (b) the ratio of gas yield to oil yield remains sensibly constant as a function of oil yield; and (c) the free moisture and bound water content of the sample is minimal or if appreciable is corrected for, in the computation of the percent weight loss at 500°C. In the first case, deviations from linearity arising from sample-to-sample variations in mineral content are to be expected, especially since these minerals often occur in the form of localized inclusions. The second factor is not likely to pose a significant problem for shale samples from the same formation since the organic matter that comprises kerogen should have comparable H/C ratios. In this regard, it is noted that TG responds to a net weight loss of the sample regardless of the physical nature of the pyrolysis products. Finally, oil shales usually contain very little free moisture ($\leq$ ~ 0.5 wt.%), although the water molecules bound to clays can amount to a significant fraction. Again, unless there is severe variability in bound water content in a sample suite, correlation plots such as those shown in Fig. 1 should accurately reflect the relative organic richness, other factors being equal. Interestingly enough, the curve for the kerogen concentrate (Fig. 1) shows an initial weight loss step around ~ 100°C corresponding to the loss of free moisture. This moisture was probably introduced in the sample during the leaching sequence associated with its preparation (cf. ref. 5). The percent weight loss data for this sample were corrected for this initial amount due to loss of moisture.

As diagnostic criteria, two factors, namely, severe distortions from linearity and a non-zero intercept, may be employed to assess the extent to which the foregoing factors preclude a straightforward correlation between the measured TG weight loss and the corresponding oil yield of the sample.

The gradual weight loss at temperatures above ~ 550°C in the TG plots (Fig. 1) corresponds to the thermal dissociation of carbonate minerals from the oil shale matrix. (Pyrite is also thermally active at these temperatures. Chemical analysis of the present samples, however, has revealed insignificant amounts of this mineral.)

In conclusion, a simple TG technique has been demonstrated for estimating potential oil yields of oil shale samples. The linear correlation that has been observed between percent weight loss at 500°C and oil yields is indicative of the potentially of the TG technique as an assay tool for rapid screening of oil shales. More importantly, this technique enjoys all the advantages of the DSC method (cf. ref. 1), plus added benefits associated with simplicity in data reduction (vide supra) and concomitant savings in time. However, master plots such as those illustrated in Fig. 1 (inset) should first be established for a suite of samples from each specific depositional area before further analyses on unknown samples are attempted.

REFERENCES

1 K. Rajeshwar, D.B. Jones and J.B. DuBow, Anal. Chem., 53, (1981) 121.
2 K.E. Stanfield and I.C. Frost, U.S. Bur. Mines, Rep. Invest. 3977 (1946).
3 K. Rajeshwar, R.N. Nottenburg and J.B. DuBow, J. Mater. Sci., 14 (1979) 2025.
4 F.P. Miknis, A.W. Decora and G.L. Cook, U.S. Bur. Mines, Rep. Invest. 7984 (1976).
5 W.E. Robinson, in Eglinton and Murphy (Eds.), Organic Geochemistry, Springer-Verlag, Berlin, 1969, p. 181.