Journal of Thermal Analysis, Vol. 49 (1997) 737-743

THERMAL CHARACTERISATION OF AUSTRALIAN OIL SHALES

A. J. Berkovich, B. R. Young, J. H. Levy*[1]*, S. J. Schmidt*[2] *and A. Ray*[3]

Department of Chemistry, University of Technology, Sydney
[1]Division of Coal and Energy Technology, Commonwealth Scientific and Industriat Research Organisation, Menai Australia
[2]Southern Pacific Petroleum NL, Sydney
[3]Department of Material Science, University of Technology, Sydney, Australia

Abstract

There has been a significant research effort on the development of an oil industry based on Australian oil shales. However, to date the research has been based mainly on the processing aspects of oil shale. The thermal analyses of oil shales, while having been the subject of many studies, have been limited to some extent by instrumentation and analytical techniques. This paper reports on thermal analysis studies utilising traditional thermogravimetry/differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC). The application of modern thermal analysis techniques such as high resolution TG (HRTG) and modulated differential scanning calorimetry (MDSC) is also examined and compared to the traditional methods.

Introduction

Australia's increasing reliance on liquid fuels combined with its decreasing oil reserves has provided the impetus for research into alternate fuel sources such as oil shale. Although the existence of oil shale in Queensland has been known since last century, the level of exploration and processing research continues to be influenced by the world market price for crude oil.

The proposed processor is the AOSTRA-Taciuk rotary kiln process, which has been described elsewhere [1]. The process comprises three stages: drying the shale at approximately 250°C, retorting at approximately 500°C and combustion at approximately 750°C. The hot combusted solids are recycled to provide heat to the retorting and drying stages of the process. Given the nature of the process, it is of advantage to know the thermal characteristics of the oil shale. Thermal analysis allows mass loss and enthalpy data to be determined for the different types of oil shale processed. This study focuses on mass loss and enthalpy data for the retorting stage of processing, where several endothermic decomposition reactions are observed

---

* Author to whom all correspondence should be addressed.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

[2–4]. These reactions arise from various components in the oil shale such as the organic component, kerogen, as well as clays and other minerals.

The analysis of Australian and other oil shales by thermal methods has been the subject of many studies [5–9]. While the temperature ranges for the decomposition of minerals, clay dehydroxylations and kerogen pyrolysis are well known [2–4, 6], calorimetric data for Australian oil shale is quite sparse [9–12].

We report results from the thermal analysis of Australian oil shales using a variety of methods including DSC, TG, DTA and high resolution TG (HRTG). An introduction to the application of the most modern calorimetric method, MDSC is also presented.

Experimental

A sub-sample of shale was obtained from bulk shale samples received using a sample riffler. This sub-sample was then ground by hand in a mortar and pestle. The ground material was repeatedly sieved during grinding to achieve a particle size of <250 mm. The DSC analyses were performed on a heat flux Stanton Redcroft DSC 700 instrument, which has a working temperature range of –125 to 700°C. The TG/DTA analyses were performed on a Stanton Redcroft STA 780 instrument which has a working temperature range of 25 to 1500°C. Samples and calibrants were analysed in thin walled alumina crucibles. A heating rate of 12°C min^{-1} was chosen to coincide with the heating rate used in modified Fischer Assays [13, 14]. The nominal sample mass and reference (alumina) for DSC analyses was 5 mg. A larger mass of 10 mg was used for TG/DTA analysis to better fit the mass range of the thermobalance. The oil shales were analysed from 25–700°C in an atmosphere of dry nitrogen flowing at 40 mL min^{-1}.

HRTG analyses were performed on a TA Instruments TGA 2950 instrument, with a working temperature range of 25 to 1000°C. Samples were analysed in platinum pans in an atmosphere of dry nitrogen flowing at 50 mL min^{-1}. Dynamic rate analyses used a sensitivity setting of 4, a resolution setting of 4 and a heating rate of 20°C min^{-1}. The constant rate analyses used a sensitivity setting of 4, a resolution setting of –5 and a heating rate of 5°C min^{-1}. The nominal sample mass for HRTG analyses was 20 mg.

Preliminary MDSC analyses were performed on a TA Instruments MDSC 2910 instrument which has a working temperature range of –150 to 725°C. Samples were analysed in open platinum pans in an atmosphere of dry nitrogen flowing at 50 mL min^{-1}. The reference was an empty pan. The sample was equilibrated at 0°C for 15 min, followed by a heating rate of 5°C min^{-1} to 600°C. The modulation amplitude was ±1°C with a period of 60 s.

Discussion

Figure 1 shows the DSC and TG responses of an oil shale from the Stuart deposit. The DSC and TG analysis curves are representative of Australian oil shales.

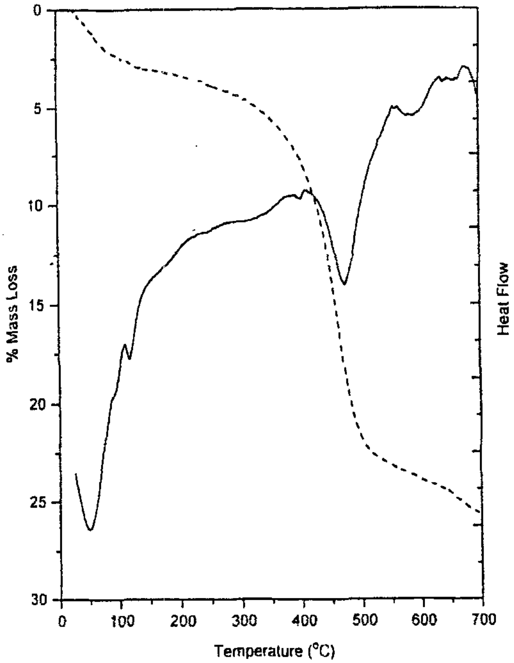

Fig. 1 DSC (—) and TG (- - -) of a Stuart oil shale

The initial mass loss and broad endothermic peak are associated with the loss of adsorbed surface moisture and the inter-layer water of the swelling clays [2, 4]. There is also a small sharp peak at approximately 120°C. This crystalline water peak is associated with gypsum [9, 15]. As can be seen in Table 1, gypsum is the only mineral present in the oil shale that has crystalline water.

Table 1 Typical composition of Stuart oil shale

Component	Concentration/ %
Kerogen	24
Smectite	27
Quartz	16
Kaolinite	6
Illite	5
Feldspar	5
Calcite	7
Mg-calcite	3
Mg-siderite	3
Pyrite	2
Gypsum	1
Opal	1

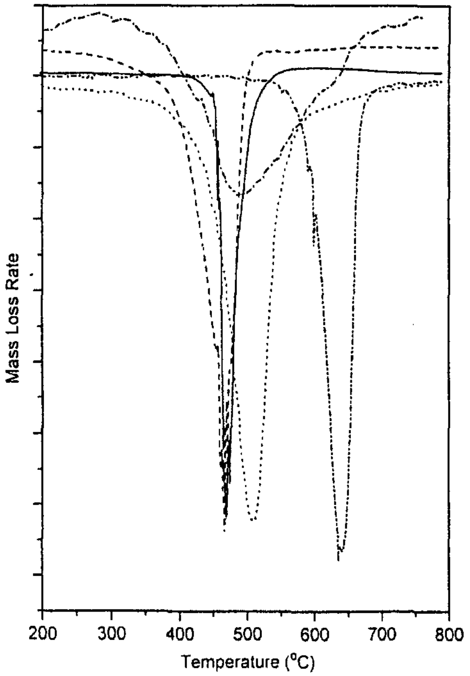

Fig. 2 DTG of — kerogen, - - - siderite, · · · kaolinite, - · - illite, - · · · pyrite

As the temperature of the sample increases it continues to lose moisture as indicated by a steady mass loss spanning approximately 200 degrees. The organic component of the shale, kerogen, also begins to lose carbon dioxide and light hydrocarbons [6]. The DSC curve shows a slight endothermic depression in this region. As the sample temperature approaches 400°C the kerogen begins to soften and pyrolyse. The siderite minerals in the oil shale also begin to decompose, and clay minerals such as kaolinite, smectite and illite begin to dehydroxylate. These reactions reach a peak rate at approximately 500°C: – denoted on the DSC trace as a broad endothermic peak which is indicative of the reactions and decompositions occurring during shale retorting. The overall enthalpy change and mass loss occurring is a combination of the reactions indicated above. This combination or overlapping effect is illustrated in Fig. 2, which shows DTG curves for some of the major components in the oil shale, kerogen, siderite, kaolinite, illite and pyrite.

The overlapping effect of the reactions and decompositions of the oil shale components makes quantifying the enthalpy change difficult. The nature of DSC analysis relies upon the determination of a peak onset, construction of a peak baseline and subsequent integration for enthalpy calculation. The overlapping of several decomposition reactions leads to a broad peak and therefore an ambiguous peak onset. Previous results [11, 12] show that the relative standard deviation for the quantification of five repeat analyses by DSC of relatively homogeneous sample was as high as 27%. This high variation is associated with the variability in determining

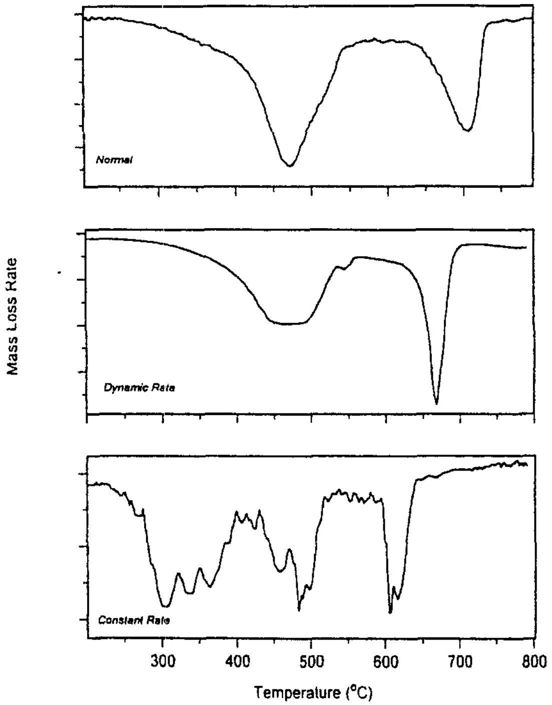

Fig. 3 Constant rate, dynamic rate and normal DTG of a Stuart oil shale

the peak onset and the construction of the DSC baseline. These effects have made DSC a rather difficult analysis to perform for whole shale.

HRTG has also been applied to the thermal characterisation of oil shales. HRTG has far superior sensitivity compared to the simultaneous TG/DTA used here. The HRTG is approximately 100 times more sensitive. The different analysis protocols available for HRTG take full advantage of its high sensitivity to enhance its resolving capability. Figure 3 shows how the different analytical techniques are able to resolve the different decomposition reactions that constitute mass loss during retorting. Normal (non-isothermal) HRTG shows a large peak at approximately 470°C. Dynamic HRTG also shows a peak at 470°C. However this peak is very broad, ranging between 300 and 500°C. This suggests that there are a number of overlapping peaks present. The constant rate HRTG resolves the overlapping peaks, clearly resolving at least four major peaks in the range of 300 to 500°C. The use of HRTG has shown that there are a number of thermal reactions occurring in the sample which are not resolved by DSC.

The HRTG analyses have also proved useful for determining the purity of individual components isolated from an oil shale. This is a useful analysis to perform before any heat capacity or enthalpy measurements are performed since the presence of trace amounts of impurities can then be corrected for in subsequent DSC analyses. HRTG is a relatively rapid analysis compared to other possible analyses

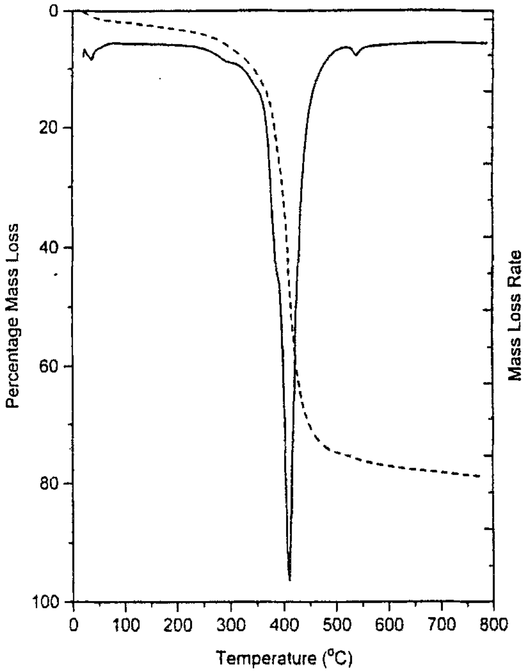

Fig. 4 High resolution DTG of isolated kerogen

such as X-ray diffraction. HRTG also has the advantage of being quantitative without the need for complex quantitative software as in X-ray diffraction.

The dynamic rate HRTG curve for a kerogen isolated from oil shale is shown in Fig. 4. The curve shows the decomposition of kerogen at approximately 420°C. The small peak observed at approximately 540°C is due to pyrite. Pyrite is not removed during the isolation procedure and hence would still be present in the kerogen. The presence of pyrite was confirmed by X-ray diffraction of the isolated kerogen. Simultaneous TG/DTA analysis of the kerogen did not reveal the presence of pyrite.

A new approach to oil shale thermal characterisation is currently being developed and is based upon treating each component in the oil shale separately. The separation of the unique components in the shale, particularly the kerogen and clays, allows individual quantification and hence overlapping and interfering effects can be overcome.

This new approach is also coupled with the application of a modern calorimetric method, MDSC [16], which has the ability to continuously measure heat capacity during enthalpic transitions or reactions, unlike traditional DSC. This feature is superior to traditional DSC, where heat capacity could only be determined before and after enthalpic events. This feature is also advantageous in terms of applying the calorimetric data into process models, where continuous knowledge of heat capacity is extremely important. To date only preliminary results have been obtained using MDSC whilst the methodology and approach to such analyses is developed.

Continuing work will analyse all major components in the oil shale, and allow a summation of heat capacity data. A thermodynamic model will also be developed, such that thermodynamic data can be generated based upon shale composition.

Conclusion

The determination of mass loss and enthalpy data for Australian oil shales is an important part in the development of an Australian oil shale industry. Improvements in thermoanalytical instrumentation and methodology development will lead to a wider knowledge of the thermal characteristics of oil shale and its unique components. The application of modern thermoanalytical techniques such as HRTG and MDSC have so far been successful. Work in progress will ultimately lead to a comprehensive database of the thermochemistry of oil shale and its unique components.

References

1 W. Taciuk and L. R Turner, Fuel, 67 (1988) 1405.
2 J. H. Patterson, H. J. Hurst, J. H. Levy and J. S. Killingley, Fuel, 69 (1990) 1119.
3 J. H. Patterson, H. J. Hurst and J. H. Levy, Fuel, 70 (1991) 1252.
4 J. H. Levy, Energy and Fuels, 4 (1990) 146.
5 R. H. McKee and E. E. Lyder, Journal of Industrial and Engineering Chemistry, 13 (1921) 678.
6 W. I. Stuart and J. H. Levy, Fuel, 66 (1987) 493.
7 K. Rajeshwar, R. Nottenburg and J. B. Dubow, Journal of Material Science, 14 (1979) 2025.
8 K. Rajeshwar, D. B. Jones and J. B. Dubow, Analytical Chemistry, 53 (1981) 122.
9 G. L. Corino and A. G. Turnbull, Proceedings of the Second Australian Workshop on Oil Shale, Brisbane Australia 6-7 December 1984.
10 S. C. Mraw and C. F. Keweshan, Fuel, 65 (1986) 54.
11 A. J. Berkovich, B. R. Young and J. Schmidt, Proc. 23rd Australasian: Chemical Engineering Conference and Exhibition, Adelaide, Australia 1995, p. 68-73.
12 A. J. Berkovich, B. R. Young, A. Ray and J. Schmidt, accepted (1997) to Fuel.
13 ASTM D 3904 - 90 "Standard Test Method for Oil from Oil Shale (Resource Evaluation by the Fischer Assay Procedure)."
14 M. A. Wilson, D. E. Lambert and P. J. Collin, Fuel, 64 (1985) 1647.
15 D. L. Hudson-Lamb, C. A. Strydom and J. H. Potgieter, Thermochim. Acta, 282/283 (1996) 483.
16 M. Reading, A. Luget and R. Wilson, Thermochim. Acta, 238 (1994) 295.