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Characterisation of some Australian oil shale using thermal, X-ray and IR techniques

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Abstract

Thermogravimetric analysis (TGA), Diffuse Reflectance Infrared Fourier Transforms Spectroscopy (DRIFTS) and X-ray diffraction (XRD) were used in conjunction to characterise oil shale samples from an Australian Tertiary oil shale deposit. Results from these techniques were compared with conventional Modified Fisher Assay (MFA) data. DRIFTS and TGA results showed clear correlations with each other as well as with the MFA values. DRIFTS results indicated that most of the kerogen is in aliphatic hydrocarbon form. It was evident from TGA analysis that the weight loss in the 450–550 °C temperature region has a strong and direct correlation with the amount of oil in the samples, as determined by the MFA method. Calibration curves were generated in which oil content can be predicted from TGA and DRIFTS data. The combination of TGA and DRIFTS is mostly useful in examining organic matter in oil shale while DRIFTS and XRD combination is useful in examining the minerals phases. XRD and DRIFTS showed good agreement in identifying the presence of minerals such as quartz, clay and carbonates. Combination of these three techniques can provide an alternative and inexpensive method to the MFA analysis in determining the kerogen content, while overcoming the limitations of each other.

Keywords: Oil shale; TGA; DRIFTS; XRD

1. Introduction

The depletion of petroleum sources and the increase in oil prices urge the search for alternative energy sources. The use of renewable energy has a long way to go before they can match the present day energy requirements of the world that is adapted to depend mainly on the petroleum and its by products. Therefore, for the energy needs of the near future, it is essential to develop substitute fuel sources.

The production of shale oil from oil shale is one of the energy generation alternatives available in Australia. Oil shale is a sedimentary rock containing a complex organic substance called kerogen, which is a valuable source of energy as it can be converted to oil. Therefore, it is important to estimate the kerogen content and the possible oil yield in an oil shale accurately. The widely used industrial method of evaluating the oil yield from oil shale samples is the modified Fisher assay (MFA). This method is time consuming, destructive and expensive. Large number of oil shale samples is required to be tested in order to determine the validity and the feasibility of oil shale mining and processing.

Previous researches acknowledged the fact that the minerals in the oil shale influence the conversion of kerogens and the release of oil during oil shale processing (retorting). Berkovich et al. [1] discussed the effect of minerals on retorting enthalpies of some Australian Tertiary oil shales. Karabakan and Yürüm [2,3] studied the effects of mineral matrix in the reactions of oil shales using pyrolysis and oxidation reactions of Turkish Goynuk and US Green River oil shales. They reported the inhibition effects of silicate minerals and catalytic effects of the carbonate minerals on the pyrolysis reactions of the samples they studied. Patterson et al. [4–6] researched substantially on Australian oil shale from different deposits. Their main focus was on the mineralogy of Australian oil shale and its effect on oil shale retorting. They identified that smectite,

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kaolinite, calcite, pyrite and siderite have the largest effects on the processing of Australian oil shale [4]. Another important finding of Australian oil shale studies includes the prediction of the amount of siderite decomposition [7]. Therefore, when characterising the oil shales, it is imperative to know the mineral contents of the samples, accurately.

TGA/DTA instrument has been used previously to determine the characteristics of devolatilisation, effect of temperature on thermal degradation and kinetic parameters of oil shale [8–10]. While TGA does not provide direct measure of oil yields, many researchers reported shale oil yield and kerogen content based on TGA weight loss measurements [11–14]. The reported TGA operating conditions were 5–40 °C/min heating rates and final temperatures up to 950 °C.

TGA results were often presented according to the weight loss at different temperature regions. In general, oil shale weight loss at the lower temperature region recorded by TGA (40–200 °C) is attributed to the loss in moisture, interlayer water from the clay minerals and to the decomposition of certain minerals such as nahcolite and dawsonite [15,16]. The weight loss in the middle temperature range (200–600 °C) is attributed to the decomposition of kerogen into pyrolytic bitumen and later on to the decomposition of bitumen into gas and liquid products. The weight loss at the high temperature region (600–950 °C) is mainly attributed to the decomposition of carbonate minerals including calcite, dolomite and ankerite [10]. In this paper, in addition to comparing the data, attempts are made to identify the most appropriate TGA temperature regions to use in the prediction of the kerogen contents of oil shale.

DRIFTS has been suggested previously as a cheaper and faster way of evaluating oil yield and mineral contents of oil shale [17,18]. DRIFTS has an advantage of rapidly acquiring quantitative results of both shale organic and mineral matters in non-destructive manner. In the mid-IR region, kerogen content is associated mainly with the aliphatic peak intensity at 2935 cm^{-1} wavelength [17]. Snyder et al. [18] reported the bands that are associated with carbonate minerals for FTIR. They described characteristic band wave number for ankerite (876, 727, 713 cm^{-1}), dolomite (882, 729 cm^{-1}), siderite (873, 741 cm^{-1}), calcite (877, 713 cm^{-1}) and aragonite (856, 713, 700 cm^{-1}). Cronauer [19] reported the association of quartz and clay minerals to the bands 800 and 1040 cm^{-1}, respectively. However, overlapping of different bands of kerogen with those from other minerals, make the quantitative evaluation of kerogen complex.

Like in any mineralogical analysis, XRD plays a major role in identifying the mineral phases present in the oil shale. However, during the XRD data interpretation in oil shale, there are special considerations. Unlike in many other rocks, oil shale has a large amount of non-diffracting matter, mainly because of the presence of kerogen, which is amorphous. In this study, XRD is used mainly as a method to identify and quantify any crystallised mineral phases present in the oil shale. XRD is the only technique that can provide the quantitative data on crystallised mineral phases of a sample.

In this paper, three techniques, namely TGA, DRIFTS and XRD, are used in conjunction to characterise 10 Australian Tertiary oil shale samples. The results are compared with the MFA and kerogen values obtained from conventional industrial processes for the same samples with the intention to find a suitable methodology to predict the kerogen values without carrying out the MFA analysis. Also, this study aims at giving some insight on the Australian oil shale mineralogy.

2. Experimental

2.1. Samples

Oil shale samples were obtained from Southern Pacific Petroleum (SPP) Co. from their Stuart oil shale deposit in Queensland, Australia with measured MFA values in L T^{-1} and kerogen contents. Each shale sample was crushed and mixed thoroughly and about 50 g were separated and ground to a fine powder (<63 μm). The ground oil shale samples were then used for analyses.

2.2. TGA

Thermogravimetric analysis (TGA) of the shale samples was undertaken using a Perkin–Elmer TGA 7 thermogravimetric analyser connected to TAC 7/DX thermal analysis controller. The initial TGA temperature for all samples was 40 °C and the final temperature was 850 °C. The heating rate was 20 °C/min and the tests were carried out under nitrogen purging at a rate of 20 mL/min. In this work, 5–10 mg from each sample was thinly spread on platinum pan and used for TGA analysis.

2.3. DRIFTS

Oil shale sub samples were put in the diffuse reflectance cup (10 mm diameter, 3.3 mm depth) in which packing density was ensured by applying a constant mass (of 30 g) on the top surface of each sample. The instrument used was Perkin–Elmer Spectrum 2000 FT-IR spectrometer (Perkin Elmer, UK) fitted with a Praying Mantis diffuse reflectance attachment (Harrick Scientific, NY, USA). The spectra were obtained at 1 cm^{-1} resolution and collected in the mid-IR region from 4000 to 400 cm^{-1}. Stationary cell was used and measurements were taken at four different orientation positions for each sample.