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Heat capacities and enthalpies for some Australian oil shales from non-isothermal modulated DSC

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Abstract

The application of thermal analysis to Australian oil shales has been quite common, however, the results have been somewhat limited by experimental technique and advances in thermal analysis instrumentation. In this paper we present a novel approach to the thermal characterisation of Australian oil shale. This approach involves separation of the unique components of oil shale, the kerogen (organic component) and the clay minerals (inorganic components), using chemical and physical techniques. The heat capacity and enthalpy changes for the kerogen and clay minerals were measured using non-isothermal modulated DSC from 25 to 500°C. Heat capacity data was obtained over a temperature range spanning several hundred degrees in a single experiment. Heat capacity was also estimated by incorporating TG data during regions where thermal reactions involving mass loss occurred. Enthalpy data for dehydration and pyrolysis of kerogen were also determined. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Australia's increasing reliance on fossil fuels combined with its decreasing oil reserves has provided the impetus for research into alternate fuel sources, such as shale oil. Australian oil shale is a fine grained sedimentary rock which consists of organic and inorganic components. The organic matter in oil shale is derived from a wide range of precursors. The organic matter (kerogen) for Australian oil shales in this study is derived from hydrogen rich algae, from which a significant amount of oil can be extracted by pyrolysis.

A typical mineral composition of an Australian oil shale is shown below in Table 1.

In Australia the proposed processing method is the AOSTRA-Taciuk continuous flow retort processor which comprises three stages [1]. In the first stage partially dried oil shale is dried at approximately 250°C and surface and crystalline waters are liberated from the oil shale. The second stage is the retort stage and is carried out at approximately 500°C and the kerogen in the oil shale is pyrolysed to oil vapour and hydrocarbon gas. Other constituents in the oil shale may also undergo thermal reactions such as decomposition and dehydroxylation. The third and final stage involves combustion of retorted oil shale at 750°C and is coupled with hot solids recycle to heat the preceding stages.

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Table 1
Typical composition of an Australian oil shale

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

The continued development of this technology for oil shale processing in Australia has revealed the need for a process model based upon oil shale thermal behaviour. In a process that is dominated by thermal reactions [1–3] and heat transfer, a knowledge of oil shale heat capacity and enthalpy changes is important.

The overall heat capacity change during oil shale processing results from the heat capacity change of each component in the oil shale. Enthalpy changes during oil shale processing result from thermal reactions of particular oil shale components [2,3], these include, kerogen (organic component), clay minerals, carbonate minerals and pyrite. Previous workers have analysed oil shale as a whole substance and then estimated the heat capacity and enthalpy contributions of the individual constituents [4–6]. Difficulties have also been highlighted when attempting to thermally analyse oil shale as a whole substance, in particular the difficulty of measuring enthalpy changes in the temperature range of retorting [2,3]. For these reasons we have taken a new and novel approach to the thermal characterisation of Australian oil shale.

The novel approach reported here involves treating oil shale as a mixture of kerogen and minerals that have individual heat capacities and enthalpies which when summed represent the thermal characteristics of a whole oil shale. Table 1 shows the mineral composition of a typical Australian oil shale. The thermodynamic properties of most of the inorganic mineral components in Australian oil shale are well known and are available in literature databases [7–9]. However, the kerogen and clay minerals (smectite, kaoli-

nite, illite) are unique to the geology and organic precursors of Australian oil shale. For this reason the kerogen and clay components have been isolated from Australian oil shale by chemical and physical means. These isolated components were then analysed using the most modern calorimetric technique, modulated DSC, to determine heat capacity and enthalpy changes.

Heat capacity determination by modulated DSC with isothermal and non-isothermal methods has been described previously [10–14]. Application of modulated DSC to petroleum fuels for determination of heat capacity has also been presented [11,12]. However, there has not been any reported work on the application of modulated DSC to solid fossil fuels for heat capacity determination. The ability of modulated DSC to obtain a direct continuous measurement of heat capacity has important consequences for process models in which the thermodynamic data measured here will be used.

2. Experimental

Calorimetry was performed on a TA Instruments MDSC 2920 instrument. Samples were analysed in aluminium pans with lids, in an atmosphere of dry nitrogen flowing at 120 ml min⁻¹. Samples were equilibrated at 0°C for 5 min and then ramped at 5°C min⁻¹ to 600°C. The modulation amplitude was $\pm 1^\circ\text{C}$ with a period of 60 s. Temperature and enthalpy were calibrated using In, Sn and Zn standards. Heat capacity was calibrated with sapphire. For heat capacity measurements, samples were dried in the MDSC at 120°C for 10 min before the analysis.

A TA Instruments SDT 2960 instrument was used for thermogravimetry. The samples were analysed in open platinum pans at a heating rate of 5°C min⁻¹ from ambient to 600°C in an atmosphere of dry nitrogen flowing at 120 ml min⁻¹.

A number of oil shale samples were selected to represent typical Australian oil shale. Kerogen was isolated using a HF/BF₃ maceration technique [15] which was modified to suit our work [16]. This technique uses HF to destroy carbonate minerals and siliceous minerals. The destruction of siliceous minerals leads to the formation of fluoride salts which are destroyed by BF₃ formed by the addition of

excess boric acid to the HF solution. This technique should destroy the mineral and clay components in the original oil shale with the exception of pyrite and anatase. Both of these minerals were present in the original oil shale and are not destroyed by the HF/BF₃ method. The purity of isolated kerogens was checked using X-ray powder diffraction and the mineral inclusion concentrations quantified using Siroquant [17–20]. Siroquant confirmed the presence of pyrite and anatase in isolated kerogens and no other mineral inclusions where detected.

The clay components of oil shales were isolated using buffered acetic acid and hydrogen peroxide [21]. In this method the acetic acid destroys carbonate minerals and hydrogen peroxide destroys the kerogen. The result of this treatment is clay plus other silica type minerals. The heavier silica type minerals were separated from the clay by a centrifuging [21]. Again the purity of the isolated clays was checked using X-ray powder diffraction.

3. Results and discussion

Modulated DSC was used to measure heat capacity and enthalpy changes for a series of kerogen and clay samples isolated from Australian oil shale for the process temperature ranges of drying and retorting. Heat capacity of pyrolysed kerogen was also measured. The response of the sample to the periodic modulation (heat flow amplitude) was used to calculate heat capacity using the following expression, $(C_s - C_r) = A_\Delta / A_{T_s} \sqrt{(K/\omega)^2 + C_r^2}$. Where, C_s is the sample heat capacity ($\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$); C_r the heat capacity of reference ($\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$); A_Δ the heat flow amplitude (mW); A_{T_s} the maximum modulation amplitude (K); K the heat capacity constant; ω the modulation frequency (s). Measured heat capacities were fitted to a fourth order temperature polynomial of the type, $C_p = a + bT + cT^2 + dT^3$ with units $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$. Table 2 shows examples of heat capacity data for an isolated kerogen, pyrolysed kerogen and a 1:1:1 mixture of smectite, kaolinite and illite. The kerogen and pyrolysed kerogen heat capacities were corrected for the presence of mineral inclusions. At retort temperatures (500°C), the kerogen and clay components undergo pyrolysis and dehydroxylation, respectively. All of these thermal events involve significant mass

Table 2

Heat capacities for isolated kerogen, pyrolysed kerogen and 1:1:1 smectite, kaolinite and illite clay mix^a

Temperature ($^\circ\text{C}$)	Kerogen ($\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$)	Pyrolysed kerogen ($\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$)	Clay mixture ($\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$)
25	1.82	1.07	0.69
100	2.12	1.29	0.80
200	2.43	1.60	0.89
300	2.74	1.84	0.95
400	2.50	2.01	0.99
500	0.49	2.23	1.02

^aDenotes C_p during pyrolysis.

loss [3]: 8–30% for moisture loss; approximately 80–90% for kerogen pyrolysis; and 10–20% for clay dehydroxylation. These mass losses make measurement of heat capacity during these regions difficult because the calorimeter cannot cope with large changes in mass. Indeed, the equation for sample heat capacity calculation assumes a constant mass. As a result the measured heat capacities during these temperature regions are not meaningful. However, the heat capacity during these regions of mass loss can be estimated by incorporating TG data to model the heat capacity.

It was assumed that the change in heat capacity between the kerogen and pyrolysed kerogen would approximate the change in mass of kerogen during pyrolysis. Mass loss data for isolated kerogens and clay mixtures were measured by TG under the same temperature ranges and linear heating rate that was used for the modulated DSC experiments. Heat capacity was measured for kerogen up to the region where pyrolysis begins (350°C). Heat capacity was then measured for a pyrolysed kerogen sample to 500°C . The heat capacity in the region of pyrolysis was then calculated as follows. The heat capacity of kerogen at 350°C , 2.86 J g^{-1} (per gram of kerogen) was taken as an initial value. The heat capacity of pyrolysed kerogen at 500°C , 2.23 J g^{-1} (per gram of pyrolysed kerogen) was converted to 0.37 J g^{-1} (per gram of kerogen) based upon the mass loss measured by TG was taken as the final value. The difference between the initial and final value was 2.49 J g^{-1} (per gram of kerogen). This difference was then multiplied by the fraction of total mass loss at 1°C intervals between 350 and 500°C and then subtracted from the initial heat capacity value at 350°C . Example curves for kerogen

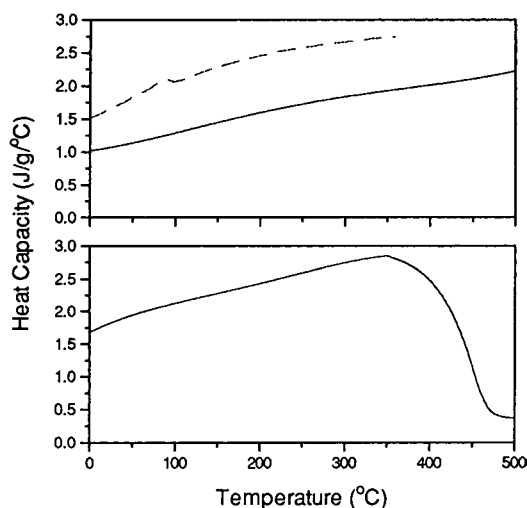


Fig. 1. Heat capacity curves for kerogen and pyrolysed kerogen (top) and estimated heat capacity for kerogen during pyrolysis (bottom).

and pyrolysed kerogen heat capacity and the calculated heat capacity for kerogen during pyrolysis are shown in Fig. 1. A similar estimate for the heat capacity during the region of clay dehydroxylation was also used.

In the drying temperature range (ambient to 250°C), all oil shales exhibited an endothermic loss of surface water and inter-Layer water from clay minerals [2]. The average enthalpy change here was approximately 2.5 kJ g⁻¹ at about 100°C. This enthalpy change is approximately equal to the latent heat of vaporisation for water.

The initial attempts to measure the enthalpies for kerogen pyrolysis gave results that were unexpectedly low. The reason for these initial low results are probably due to two factors, the large mass change for kerogen during pyrolysis and the difference in heat capacity between kerogen and pyrolysed kerogen.

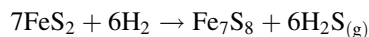
The very small volume of sample remaining in the sample pan after pyrolysis tends to dramatically lower the baseline on the heat flow curve making integration of the pyrolysis peak difficult. The downward trend of the heat flow curve after pyrolysis is expected given the difference in heat capacity of kerogen and pyrolysed kerogen shown in Fig. 1.

As well as changes in sample heat capacity, the intimate contact the sample has with the pan, and therefore, the instrument's thermocouple is somewhat

diminished as the mass of sample is now some 80–90% lower than the original sample mass.

To overcome the difficulties of measuring enthalpies for kerogen pyrolysis, the kerogens were diluted with freshly calcined high purity α -alumina. Kerogen was diluted in alumina to give kerogen concentrations of 30, 40, 50, 60, 70 and 80%. For kerogen concentrations lower than 30%, pyrolysis of kerogen was poorly resolved. Heat flow curves for the kerogen/alumina mixtures were measured and enthalpies of pyrolysis calculated.

As discussed above, pyrite and anatase inclusions were found in the isolated kerogens. At retort temperatures, anatase is inert whereas pyrite decomposes to pyrrhotite. Pyrrhotite is a non-stoichiometric substance with the approximate formula, Fe₇S₈. However, the extent of pyrite decomposition to pyrrhotite is limited by the concentration of reducing gases, residence time and temperature [5,22,23]. The most probable reaction is reduction by hydrogen from dehydrogenation of alkanes to alkenes during kerogen pyrolysis [5].



The enthalpy change for this reaction was calculated as 290.4 J g⁻¹, at a peak temperature of 475°C, using heat capacity and enthalpy data [9]. Analysis of pyrolysed kerogen revealed that the reaction of pyrite to pyrrhotite was only 54% complete. The measured

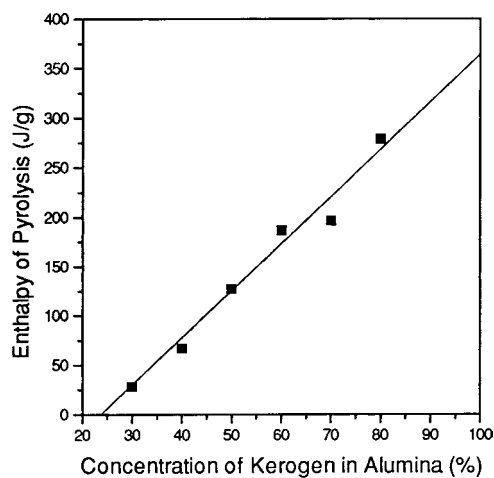


Fig. 2. Pyrolysis enthalpy versus concentration of kerogen in alumina.

pyrolysis enthalpies for kerogen were then corrected for the partial decomposition of pyrite.

The calculated enthalpies were then plotted versus concentration and a linear regression fitted and then extrapolated to give the pyrolysis enthalpy for 100% kerogen. This fitted curve is shown in Fig. 2. The extrapolated linear regression line to a concentration of 100% kerogen shows a value of approximately 360 J g^{-1} for the pyrolysis of isolated kerogen.

4. Conclusions

A novel approach to the thermal characterisation of Australian oil shale has been shown. This approach has involved the separation of the unique kerogen and clay components of Australian oil shale by physical and chemical means. Heat capacity and enthalpy changes for the kerogen, pyrolysed kerogen and clay minerals were measured using non-isothermal modulated DSC from 25 to 500°C . Heat capacity in regions of mass change was also calculated using modulated DSC and TG data.

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