

Review

THERMAL ANALYSIS OF COALS, OIL SHALES AND OIL SANDS

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ABSTRACT

Instances where differential scanning calorimetry and thermogravimetry have been applied to the study of coals, oil shales and oil sands are reviewed. Work carried out in this laboratory and model studies culled from the literature are used as examples to illustrate a particular application. The topics covered include characterization, assay, thermal stability determination and simulation of processing conditions.

INTRODUCTION

It is now clear that world production of conventional fossil fuels (mainly oil and gas) will be declining by the end of the century. Energy demands for the future, therefore, will have to be met, at least partially, by alternative fuel supplies. One near-term option is coal. Coal supplies in the United States are substantial and are projected to far surpass the future requirements on the assumption of a 5% increment in energy consumption per annum [1]. In this respect, future applications of this material are expected to extend beyond the present major uses for power generation, metallurgy and chemicals manufacture. The extent to which such an extension will become feasible will depend to a large extent on the success of current research and development on developing energy efficient, economical and non-polluting means of converting coal to gases and liquids.

In addition to coal, specific geographic areas in the North American continent have substantial oil shale and oil sand resource bases which may be profitably tapped. The equivalent of over 8 trillion barrels of oil is estimated to lie in the tri-state area of Colorado, Utah and Wyoming of which some 400 billion barrels are recoverable by existing technology [2]. The Athabasca formation is estimated to contain over 700 billion barrels of bitumen [3]. This resource base is equivalent to about 1/6 of the U.S. shale oil and coal resources.

Coals, oil shales and oil sands all represent one form or another of

fossilized carbon. In this sense, they can be broadly classified under one heading as “unconventional fossil fuels”. While the enormity of the resource base for these materials is beyond question, it is the cost at which this base can be exploited that will determine its ultimate future. Aside from economic considerations, however, it must be pointed out that increasing reliance on fossil fuels for energy and chemical feedstock has environmental impacts, the adverse effect of which are only now being gradually recognized. Climatic changes resulting from CO₂ build-up and the carcinogenic nature of some fossil-derived chemicals are two such effects receiving intense scrutiny.

The majority of state-of-the-art conversion technologies for processing coals, oil shales and oil sands utilize the application of heat in one form or the other. Thus, in the case of coals and oil shales, pyrolysis and combustion are the primary routes employed for the conversion of the energy-rich organic constituents to gases and liquids. In the case of oil sands, heat is applied initially to lower the viscosity of the indigenous bitumen and thereby permit its subsequent extraction (e.g. via the hot water process [3]). The product bitumen is upgraded in a subsequent thermal cracking step. In all three cases, namely coals, oil shales and tar sands, in situ recovery processes are also suitable candidates wherein the indigenous organic matter is subjected to combustion, pyrolysis and combination of the two. Unanswered questions, however, still remain with this technology.

From the preceding discussion, the question arises as to how thermal analysis (TA) techniques can play a key role in the technology of coals, oil shales and oil sands. It is the purpose of this article to provide a survey of TA applications in the study of these materials. Areas for further application extending beyond the scope of current use are also highlighted.

SCOPE OF THE REVIEW

Only “primary” TA techniques, namely thermogravimetry (TG) and differential scanning calorimetry (DSC), are considered here. It is further assumed that readers of this journal have familiarity with these techniques. Basic aspects dealing with instrumentation, etc. are, therefore, omitted except in their relevance to the specific case of fossil fuels. The reader is referred to monographs in the literature [4–6] for further details on TA methodology. The literature cited in this article is not meant to be a comprehensive compilation of all the TA work that has been attempted on coals, oil shales and oil sands. Rather, the approach we have adopted is one wherein a particular application is highlighted using some typical model studies.

A definition of coals, oil shales and oil sands, details of their properties, and a discussion of their overall thermal behavior (beyond aspects which

directly influence TA applications) are considered to be beyond the scope of this review. These topics have been addressed by other authors [2,3,7-9].

GENERAL CONSIDERATIONS

One factor common to coals, oil shales and oil sands, which has a significant bearing on their amenability to TA techniques, is sample heterogeneity. In order to ensure a satisfactory degree of reproducibility, sample selection must be made with particular care. Where the use of a single sample piece is practical, it is desirable to make replicate measurements on samples obtained from adjacent locations in one massive block. In this manner, any heterogeneity or non-uniformity in the distribution of organic matter will manifest itself as variations in the measured parameter (e.g. enthalpy, weight loss) along the sample suite. A striking example of the type of variations that could be expected is found in work conducted at the Laramie Energy Technology Center (LETC), Wyoming [10]. This study comprised a DSC examination of 18 alternating rich and lean oil-yield zones on an oil shale core from the Colorado C-a tract. Mineral to organic enthalpy ratios varied from a high of 10 to 1 to a low of 2 to 1. The Mahogany zone was characterized by the lowest value of this ratio. Other examples where compositional heterogeneity exerts an effect will be given below. Suffice here to point out that such effects, while often not entirely controllable in spite of judicious sample selection, will have to be recognized at least in data interpretation. Deleterious effects of sample heterogeneity may be minimized by employing a spin-riffling arrangement for sample preparation [11].

Sample geometry is another important variable in TA studies of fossil fuels. Very often, the data are clouded by artifactual effects introduced by non-optimal choice of this variable [12]. A specific example of this complication is found in the widely varying kinetics parameters and overall rate behavior reported for Green River oil shales by different authors [12]. Very low values for the activation energy, observation of a varying mechanistic fit with temperature of conversion vs. time curves and a strong dependence of kinetics parameters on particle size, are all evidence that physical limitations on reaction rate (e.g. product diffusion) or on the effectiveness of heat transfer are clouding the measured kinetics. A detailed discussion and mathematical models of such effects are available [13]. It should be noted, however, that coals, oil shales and oil sands all have rather poor thermal conductivity. A thin, uniform layer of the sample should therefore be employed when it is available in powder form. If, on the other hand, a single piece of sample is used, its dimensions should be small enough such that supply of heat to the reacting sample interior will not be a serious restriction. There is obviously a trade-off here, since too small a sample will lead to a

loss of representability. In this respect, ground samples are preferable since they can be subsequently “quartered” (see above). The grinding procedure, however, must be done with care, especially in view of the susceptibility of these materials (especially coals) to structural (irreversible) alterations as a result of such procedures. Another example of irreversibility concerns sample drying prior to a TA “run”. It has been observed that, while the water content of Illinois no. 6 bituminous coal can be reversibly displaced by suitable temperature cycling, only ~ 60% the water can be replaced in Rawhide sub-bituminous coal and even less (~ 35%) in the Arkansas lignite [14]. This loss of water capacity has been attributed to irreversible pore structure changes on thermal pretreatment [14]. Obviously, in routine TA examination of coals, oil shales and oil sands it is preferable that minimal pretreatment is carried out in order that the original features may be retained. Sample storage prior to testing also plays a critical role in this respect. In order to minimize “weathering” effects, test samples must be stored in sealed bags, preferably under a positive pressure of inert gas.

Ambient atmosphere around the sample undergoing a TA experiment is yet another factor, the control of which is essential. This factor is related to a degree to the sample geometry effects discussed in the preceding paragraph. Samples contained in deep cavities (as, for example, in some early DTA and TG studies) are subjected to self-generated atmospheres [15] because of non-optimum contact with the ambient. This often results in a distortion of peak shapes (in the case of DSC or DTA) or an “anomalous” peak shift for the pyrolysis reaction (for DSC, DTA and DTG). In the extreme case, when the reaction is carried out in an oxidative atmosphere (leading to combustion), limitations in the rate of O₂ supply to the reacting particles will alter the overall energetics from exothermicity to an endothermic behavior. Again, these problems may be alleviated by employing a thin layer of the test sample. Some of the disagreements in the early DTA data on the nature of the thermal effects in coal (see, for example, ref. 16) are undoubtedly due to such (poorly reproducible) effects.

In all the cases described above, a key factor is the ease of product effusion from the reaction zone. The residence time of products is determined by a combination of factors involving sample geometry, particle size, sweep gas flow rate and, in the case of non-isothermal TA work, by the heating rate. The longer the product residence time, the greater will be the complicating effects of recondensation [17] and secondary reactions. A high sweep-gas flow rate and a not-too-slow heating rate ($\geq \sim 10^{\circ}\text{C}$) will minimize these spurious effects. Heating rate effects are discussed in further detail in a subsequent section.

Specific TA applications and data for coals, oil shales and oil sands are discussed in turn below.

COALS

Much of the early work on the DTA of coals was directed towards correlation between thermal behavior and rank or towards characterization of various stages in the carbonization process. These studies have been reviewed elsewhere [16].

Differential scanning calorimetry at elevated pressures (5.6 MPa) has been used to characterize twelve U.S. coals of varying rank from anthracite to lignite [18]. An interesting aspect of this study is the use of TG in conjunction with DSC to correct for baseline variations due to weight loss from the pyrolyzing coal sample. Thermal effects were found to be endothermic for all coals ranging in rank from anthracite to HVC. Sub-bituminous and lignitic coals, on the other hand, exhibited exothermic effects.

A study of exothermic effects in HVB and sub-bituminous coals has been made by DSC in a nitrogen environment [19]. In contrast with the study referred to in the preceding paragraph, substantial exothermic effects were often observed in the temperature range 400–500°C. The appearance and magnitude of these exothermic effects did not appear to be correlated with rank, again contrasting with the results of previous authors [18]. The amplitude of the exothermic peak, however, was strongly dependent on heating rate, sample mass and particle size. In the former case, the peaks showed the rather usual diminution in peak amplitude with reduced heating rate. Smaller particle size and sample mass were also observed to cause a reduction in the magnitude of this exothermic effect.

By way of contrast with these results, a recent DSC study in this laboratory on a suite of 21 Ohio bituminous coal samples revealed no exothermic effects in an inert atmosphere [20]. Traces of O₂ when admitted into the DSC cell, however, caused a sharp transition from endothermicity to exothermic effects.

The specific heats (C_p) of bituminous and sub-bituminous coals have been measured by DSC over the temperature range 300–360 K [21]. While the C_p values were sensitive to parameters such as particle size, moisture content and nature of pretreatment (whether wet or dry screened), only minor differences were observed between bituminous and sub-bituminous samples.

An interesting application of DSC specific heat measurements on coals concerns elucidation of pore network structure in the latter [14,22]. Differences observed in the C_p vs. T behavior for bulk water and water molecules in coal have been thus utilized to gain information on structural details.

Combustion of coal is conveniently studied by DSC in an oxygen atmosphere. The enthalpy computed from the net area under the two-stage exotherm usually observed under these conditions, accords well with ASTM values for the calorific content of coal [23]. No clear correlation, however, could be established between the volatile matter content of Ohio bituminous

coals and the DSC endotherm areas under conditions (inert gas purge) wherein pyrolytic reactions proceeded [20]. The absence of such an expected correlation underlines the complicating effects introduced by the heterogeneity of coal. By way of contrast, an opposing school of thought believes that differences in total mineral matter content and composition have only negligible influence on DTA and DSC behavior [18,24].

Turning to TG studies, bituminous and lignitic coals from four locations have been examined over the temperature range 20–1000°C [25]. These authors have used the location of the DTG peak as a measure of relative reactivity. In an inert gas environment, differences in reactivity were negligible for the four coals. A reactivity sequence, however, was established for combustion in air using the ignition temperature as a criterion. Kinetics analyses were also carried out using a distributed-activation energy model (cf. ref. 26).

Non-isothermal TG was used to study the kinetics of pyrolysis and hydrogasification of Hanna (Wyoming) coal and char [27]. Both raw samples and those mixed with K_2CO_3 catalyst were examined. The kinetics parameters were observed to vary with the degree of conversion in all cases. Such variations are diagnostic of structural variations in the samples while pyrolytic and combustion reactions proceed [12].

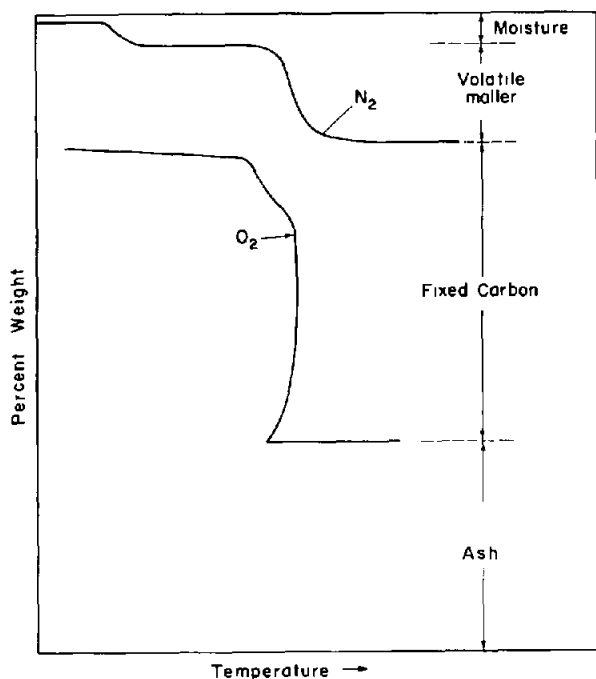


Fig. 1. Proximate analysis of coal using non-isothermal thermogravimetry (TG).

Proximate analyses of coal are conveniently and rapidly carried out by TG techniques [20]. Either a combination of non-isothermal and isothermal TG [23] or two consecutive non-isothermal experiments [20] may be used for proximate analyses. In the former, O₂ is bled into the system after a preliminary programmed heating in an inert gas environment whereby the coal is first freed of water and volatile matter. The combustion of fixed carbon is carried out under isothermal heating at 950°C for 7 min. This method closely parallels the conditions prescribed by the ASTM method. Alternatively, non-isothermal conditions may be employed in both the pyrolysis and combustion steps. This analysis procedure, illustrated in Fig. 1, has been employed for the analysis of Ohio bituminous coals [20].

General discussion on TA of coal

Obvious from the preceding review is the conflict in DSC data on the nature of thermal effects in coal (i.e. whether endothermic or exothermic). A similar discrepancy exists in the earlier DTA data [16]. The extreme sensitivity of the thermal effects to ambient atmosphere is undoubtedly a contributing factor here. In this respect, the observed dependence of features associated with DSC exotherms on experimental parameters [19] is significant. The anomalies introduced by non-optimal choice of experimental parameters (see previous section) are particularly well illustrated for the case of coal. Apart from oxidations induced by traces of O₂ in the ambient atmosphere, auto-oxidation of the reacting sample by the products evolved in an initial stage in the pyrolysis can also give rise to "spurious" exothermic effects. The extent of the occurrence of such reactions is expected to be influenced by sample mass, particle size and heating rate as is indeed observed (cf. ref. 19).

Kinetics parameters derived from TG methods for the pyrolysis and combustion of coal, are fraught with the same uncertainties as those associated with reactions in condensed phases (cf. ref. 28) and must therefore be interpreted with caution. Interpretation is greatly facilitated by carrying out *both* isothermal and non-isothermal experiments on the same suite of samples while systematically varying reaction and sample parameters. Corresponding variations (if any) in the measured kinetics parameters will then give a clue to the reaction mechanism (e.g. whether diffusional effects are important) and also establish the validity of a proposed kinetics model. Such an approach seems to have not been undertaken thus far in kinetics studies on coal.

OIL SHALES

Work on the TA of oil shales up to ca. 1978 was reviewed in a previous article [12]. The present treatment therefore focuses on more recent studies,

except in instances wherein a specific application is highlighted using earlier work as illustrative examples.

Perhaps the most widespread use of TA methods has been for the study of the decomposition kinetics of oil shale kerogen. An early TG study utilized quasi-isothermal conditions to establish the reaction sequence in oil shale pyrolysis [29]. In studies of this type, however, the influence of prior thermal history on its subsequent weight loss pattern will have to be recognized since the same sample is used throughout the experiment (cf. ref. 12). In a later study, the same author has again used TG techniques to elucidate the devolatilization behavior of Green River oil shale kerogen in CO₂ and water vapor [30]. In this manner, he was able to show superior product yields and product quality when "pyrolysis" was carried out in the reactive atmosphere of water vapor.

A mathematical model for oil shale pyrolysis has been developed using TG data on well-defined oil shale blocks [31]. Both isothermal and non-isothermal conditions were employed for heating these blocks. Mathematical modeling of the pyrolysis of single particles of Green River oil shale (~ 12.7 mm diam. spheres and cylinders) was again facilitated by isothermal TG [32].

Good agreement in the measured kinetics parameters has been reported on Green River oil shale kerogen using non-isothermal and isothermal TG [33]. These authors advocate non-isothermal analyses on the basis that they provide a more realistic simulation of actual processing conditions, particularly in situ extraction schemes.

Non-isothermal TG using a variety of heating rates has been applied to the determination of kinetics parameters for Green River oil shale pyrolysis [34]. Four different methods were employed for kinetics analyses and the results appear to be in fair agreement. The same group has employed non-isothermal TG for studying the oxidation kinetics of oil shale char under conditions wherein diffusional and mass transfer effects were claimed to be unimportant [35]. To ensure the existence of conditions for the latter, particles of fine mesh (- 200 U.S. standard sieve) were spread in a thin layer and a high O₂ flow rate was employed (see above).

Non-isothermal TG has been employed in this laboratory for the study of pyrolysis kinetics of Green River oil shale [36]. Some of the discrepancy in the earlier kinetics data (cf. ref. 12) could be rationalized by optimal choice of experimental variables. The TG results could be adequately represented by a scheme of two consecutive first-order reactions.

While the bulk of the kinetics studies have dealt with oil shales from the Green River formation, perhaps understandably considering the importance of this resource base, shales from other locations have been also studied by TA methods. Thus, the effect of heating rate on the pyrolysis kinetics of Chattanooga black shale has been studied by non-isothermal TG [37,38]. Non-isothermal TG along with DTA have been used for the study of

pyrolysis kinetics of Jordanian shale [39]. Samples of Israeli shale have been subjected to TG (both isothermal and non-isothermal techniques were employed) and the effect of mineral leaching on kerogen pyrolysis kinetics has been investigated [40]. An acceleration of pyrolysis kinetics, which is facilitated by the enhanced mass diffusion in the leached samples, has been observed in this manner [40]. The kinetics of gasification of shale char from the Swedish Ranstad deposit have been studied by isothermal TG [41]. A comparison of pyrolysis kinetics of both raw shale and kerogen concentrate has been presented for samples from the Green River and Devonian formations [42].

Shale mineral analyses represent another area where TA techniques can be profitably employed. The use of combined TG–DTA techniques for mineral analysis is well illustrated by studies conducted at LETC [15,17]. An interesting aspect of these studies is the manner in which TA helped identify a previously unsuspected mineral in dawsonite-bearing Green River oil shales. A mineral form of $\text{Al}(\text{OH})_3$, which is distinct from the known modifications, gibbsite and bayerite, was assigned to the observed thermal effects at 500°C [43]. The thermal properties of gaylussite, a mineral which is found in Wyoming shales, was studied by the same group using simultaneous TG–DTA–evolved gas analysis (EGA) [44]. An increase in energy requirements over those normally required for oil generation from shale is caused by endothermic heat effects (e.g. dehydration, thermal dissociation, phase transformation) in certain oil shale minerals. One of these is analcime, the presence of which was reported to cause an $\sim 6\%$ increase in the enthalpy for retorting Green River oil shale [45]. The thermal characteristics of this mineral were again studied by combined TG–DTA–EGA. Methods for quantitative analyses of dawsonite, nahcolite and nordstrandite in oil shales by combined use of DTA and TG techniques have also been reported by the same group [46]. In yet another study of dolomite by DTA and TG methods, these authors propose criteria wherein the extent of atmosphere control and the degree of prevalence of self-generated atmospheres in the TA apparatus can be established [47].

We have used TA probes in our laboratory for comparing Green River and Israeli shales and for gauging the extent of mineral leaching by acid treatment of these materials. Illustrative examples are shown in Fig. 2. Israeli shales, unlike their Green River counterparts, contain mostly calcite in the carbonate mineral matrix. The absence of significant amounts of dolomite in these materials (unlike the case of Green River shales) is reflected in the observed differences in TA traces at temperatures $\geq \sim 500^\circ\text{C}$ [Fig. 2(a)]. In fact, the calcite content of the Israeli shale is directly given by the TG weight loss observed between 700 and 900°C . Values obtained in this manner show good agreement with the calcite content as determined by X-ray analyses. Pronounced differences also exist in the thermal stability of the organic matter in the two shales. Data such as those in Fig. 2(a), illustrate the utility

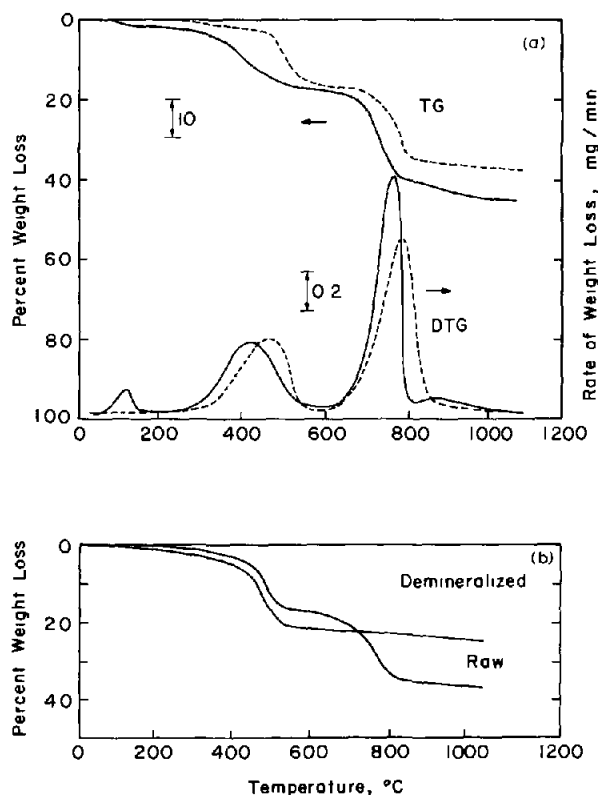


Fig. 2. (a) Comparison of non-isothermal TG and DTG traces for a Green River oil shale and an Israeli shale sample. The latter originated from the Ef'e deposit. Both samples had an organic content of $\sim 12\%$ by volume. Heating rate: $20^\circ\text{C min}^{-1}$; atmosphere: flowing N_2 . - - - - -, Green River sample; ———, Ef'e sample. (b) Comparison of TG traces for raw Green River oil shale and a demineralized sample. Conditions same as in (a).

of TA methods for “fingerprinting” shales from different locations.

In Fig. 2(b), TG results are compared for a Green River oil shale sample and one wherein the carbonate minerals were selectively removed by HCl leaching. The TG curves for the demineralized sample show a pronounced attenuation of the high temperature weight loss caused by carbonate mineral decomposition.

Another important application of TA probes from a practical standpoint concerns assaying of shale organic content. Obviously, estimation of this parameter is important since all of the useful energy content of the shale resides in the organic matrix [12]. Both DSC [48] and non-isothermal TG [49,50] can be used for this purpose, wherein the area of the pyrolysis endotherm and the weight loss in the $400\text{--}500^\circ\text{C}$ temperature range, respectively, yield a direct measure of the shale oil yield. These oil yields can be then expressed in terms of a Fischer assay equivalent using correlation tables

[48–50]. The main advantage of TA methods for assaying oil shale vis-à-vis the conventionally adopted Fischer assay method lies in their inherent simplicity and amenability to routine use. For routine assay applications, moreover, TG has a slight edge over DSC in terms of ease in data acquisition. (This arises primarily because enthalpy estimates via the latter require calibration “runs” with standard samples, whereas the organic content is *directly* estimated via TG from the measured weight loss, cf. refs. 5, 49, 50.) Use of computer-assisted TA, however, should enable the routine use of *both* DSC and TG for these applications. A further point regarding the use of TG and DSC for oil shale assay needs to be noted. These tools are sensitive only to the *overall* pyrolysis reaction and do not reflect the extent of partitioning of the volatile products between oil and gas. Any differences in partitioning among a suite of samples (caused, for example, by varying C/H ratios) from those employed for the calibration curve will yield spurious values for the oil yield.

Similar to the case of coal, DTA or DSC can be employed for measuring combustion enthalpies. Samples of Green River [51] and New Zealand shales [52] have been analyzed in this manner. In the former study, the samples were mixed with an equal amount of benzoic acid to ensure complete combustion.

OIL SANDS

The main application of TA in studies on oil sands has been for the elucidation of features associated with pyrolysis of the indigenous bitumen. The use of TG techniques seems to have been preferred to either DSC or DTA in these studies.

The pyrolysis of asphaltene and maltene fractions in Athabasca oil sand bitumen has been studied by non-isothermal TG [53]. The maltene fraction was determined to be thermally less stable than asphaltenes. Similar conclusions have been reached by other authors [54] who attribute the two peaks in the DTG traces for oil sand bitumen to maltene devolatilization and asphaltene decomposition, respectively. By using TG techniques coupled with pyrolysis–gas chromatography, these authors conclude that, under conditions typical of in situ processing, only distillation of the maltene component obtains [55]. Temperatures upward of 500°C were believed to be necessary for asphaltene decomposition.

Both isothermal and non-isothermal TG in an inert atmosphere were employed for the study of the pyrolysis of pitch derived from hydrocracked Athabasca bitumen [56]. Knowledge of the thermal behavior of pitch (which is produced in amounts as much as 10–15% in hydrocracking processes) is important in that it reveals possibilities of conversion routes not hitherto considered to be of practical significance. For example, gasification of pitch

is an obvious route. Pyrolysis, however, may be more attractive, especially since the conversion can be carried out at much lower temperatures ($< \sim 500^\circ$). The relative product yields in pyrolysis vis-à-vis combustion play a role in the choice of conversion routes. Methods such as TA help in assessing the efficacy of each conversion route by direct measurement of product yields (see below).

Kinetics measurements have been carried out on pitch materials by TG methods [56,57]. The occurrence of a kinetics compensation effect [58] is implicated in both these studies.

A suite of five oil sand samples and bitumen extracts from the Athabasca and Utah deposits has been examined by DSC and TG in this laboratory [59,60]. The parameters and property in these experiments measured were C_p , pyrolysis enthalpy and thermal stability. A two- to threefold increase in C_p was observed for the bitumen extracts relative to the parent oil sand samples [59]. The TG and DTG traces for the various bitumen extracts were essentially similar, suggesting that differences in depositional history (and location) had only a minor influence on thermal stability. This, in turn, suggests that no major modification in in situ extraction technology over that presently developed for the Athabasca formation would be necessary for U.S. tar sands. It is emphasized that such a conclusion would be valid only for those extraction methods which rely on the pyrolysis and thermal cracking of oil sand bitumen. (On the other hand, the solvent extraction technology developed for Athabasca oil sands is thought not to be entirely applicable to U.S. oil sands because of intrinsic structural differences at the sand-oil-water interface, cf. ref. 61.)

Pyrolysis enthalpies of a few hundred J g^{-1} have been measured for these bitumen extracts by DSC [60]. Our results for Athabasca samples show good agreement with values reported recently by other authors [62]. Our C_p values [59] are also in accordance with those determined by another group via a different measurement technique [63]. It is encouraging to note the consistency in the data reported by different laboratories, especially in view of the complexity and heterogeneity of these materials and the extreme sensitivity of their thermal behavior to experimental conditions (see above).

As a final example of the utility of TA methods for oil sands characterization, Fig. 3 compares some results from isothermal TG on an Athabasca and a Utah (N.W. Asphalt Ridge Formation) bitumen extract. The relative volatile matter (VM) yields and their dependence on pyrolysis temperature are illustrated in this figure. The former were determined by extrapolation of the instantaneous isothermal TG weight loss values to infinity under conditions wherein the rate of weight loss approaches a linear, steady-state value. The inset in Fig. 3 shows an example of such a plot. One interesting aspect of the data presented in Fig. 3 is that the rate of increase of VM yield with temperature for the two samples is comparable (0.26 and 0.22% per degree rise in temperature for the Athabasca and Utah samples, respectively). This

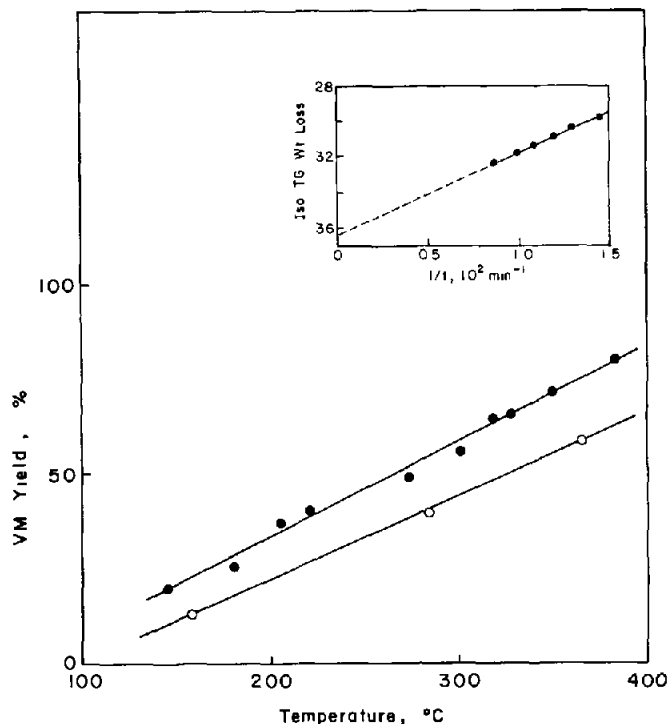


Fig. 3. Dependence of volatile matter (VM) yield on temperature for Athabasca (●) and N.W. Asphalt Ridge (○) bitumen. Inset: Representative plot of isothermal TG weight loss vs. $1/t$ (t = time of heating) for an Athabasca bitumen sample poised at $207 \pm 1^\circ\text{C}$.

result complements the conclusions reached from data in a previous study (cf. ref. 60; also, see above) on the relative insensitivity of the thermal behavior of these materials to depositional history.

CONCLUDING REMARKS

The preceding material was assembled in an attempt to illustrate the many-fold applications of TA techniques in studies on coals, oil shales and oil sands. These applications range from routine characterization and assay to simulation of actual processing conditions. A brief reference was already made on the suitability of non-isothermal TA techniques to simulation of processing conditions (cf. ref. 33). It seems pertinent here to amplify this point. Two key variables (sometimes coupled) which influence product yield and product distribution in thermal processing of coals, oil shales and oil sands are atmosphere and heating rate. The use of reactive atmospheres (e.g. H_2 , superheated steam) greatly enhances product yields under favorable

conditions. Combined use of a reactive atmosphere and a very fast heating rate can cause a dramatic shift in product distribution to lighter hydrocarbon species as, for example, has been observed for Athabasca oil sands [64]. Similarly, the percentage of acetylene produced during pyrolysis of coal increased significantly when laser pyrolysis and a H_2 atmosphere were used [65]. It is obvious that TA methods can play a crucial role in the elucidation of such effects, particularly with the availability of modern instrumentation which permit rapid heating of the test samples. In our opinion, this area in the application of TA methods remains little explored thus far.

A second application of TA methods for simulation of processing conditions, concerns retorting under elevated pressures. A pressurized DSC module may be conveniently employed to simulate such conditions. Green River oil shale samples have been retorted under elevated pressure in a recent bench-scale study [66,67]. Kinetics of pyrolysis [66] and product distribution [67] at various pressures in the range 78–765 kPa have been determined and compared with data at ambient pressure. A decrease in both the total oil yield as well as in the pyrolysis rate was observed with increasing pressure. These trends contrast those reported in a recent study on Athabasca oil sands using high pressure DSC [62]. An *increase* in the endothermicity and exothermicity was observed here for the pyrolytic and oxidation reactions, respectively, with increasing pressure. It would be interesting to probe the correlation between product yield/retorting rate on the one hand and the extent of attenuation or enhancement in the DSC and DTG peaks. Obviously, this is another area wherein much of the potential of TA methods remains to be exploited.

Finally, to weigh matters in a proper perspective, TA methods would be of limited applicability in studies on structural aspects of coals, oil shales and oil sands *unless* they are used in conjunction with other analytical tools such as mass spectrometry and gas chromatography. Such a limitation contrasts the extreme amenability of TA probes to *routine* characterization of these complex materials as exemplified by the examples listed in this review.

ACKNOWLEDGEMENTS

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