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## A THERMOGRAVIMETRIC ANALYSIS OF SOME OIL SAND FRACTIONS\*

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Organic matter, associated with the clays and heavy metal minerals present in the Athabasca Suncor Oil Sand Tailings has been recovered and then subjected to preferential dissociation by a series of acid treatments, followed by soxhlet extraction using benzene/methanol. The various fractions isolated have been studied by thermogravimetry (TG) and derivative thermogravimetry (DTG). Comparison of the data obtained in nitrogen with that obtained in air indicated the complex nature of the thermal degradation and thermal oxidative processes taking place on heating. The results indicate that TG is capable of providing information for the characterization of Oil Sand fractions which may contribute to an understanding of the refining process.

Thermal analysis techniques have been used extensively to study the thermal behaviour of coals, oil shales and oil sands and have been the subject of a recent review [1]. One of the main reasons for interest in this area of investigative research has been the evaluation of the fuel potential of indigenous bitumen present in these materials. Although both differential scanning calorimetry (DSC) and differential thermal analysis (DTA) have been employed in these studies, thermogravimetry (TG) seems to be the preferred technique. This arises since TG is not only capable of providing information on the fractions decomposable, but also data regarding rates of volatilization and decomposition. Although some TG curves may appear simple, the reactions responsible for the weight losses observed may be exceedingly complex such that derivation of meaningful kinetic data requires sophisticated mathematical calculations. Comparisons of derivative thermogravimetry (DTG) traces, on the other hand, are capable of providing characteristic data useful in the valuation of a series of comparable materials. In this paper we have used this comparative approach to determine the nature of the organic matter adsorbed by the mineral matter found in oil sands.

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### Experimental

The source of material for this study was aqueous tailings from the Suncor Athabasca oil sands plant sludge pond. The isolation of a heavy metal minerals concentrate containing approximately 20–30% of strongly adsorbed organic matter from these tailings is described in detail elsewhere [2]. This material was then subjected to a series of extraction procedures which are summarized in Fig. 1. In general, the

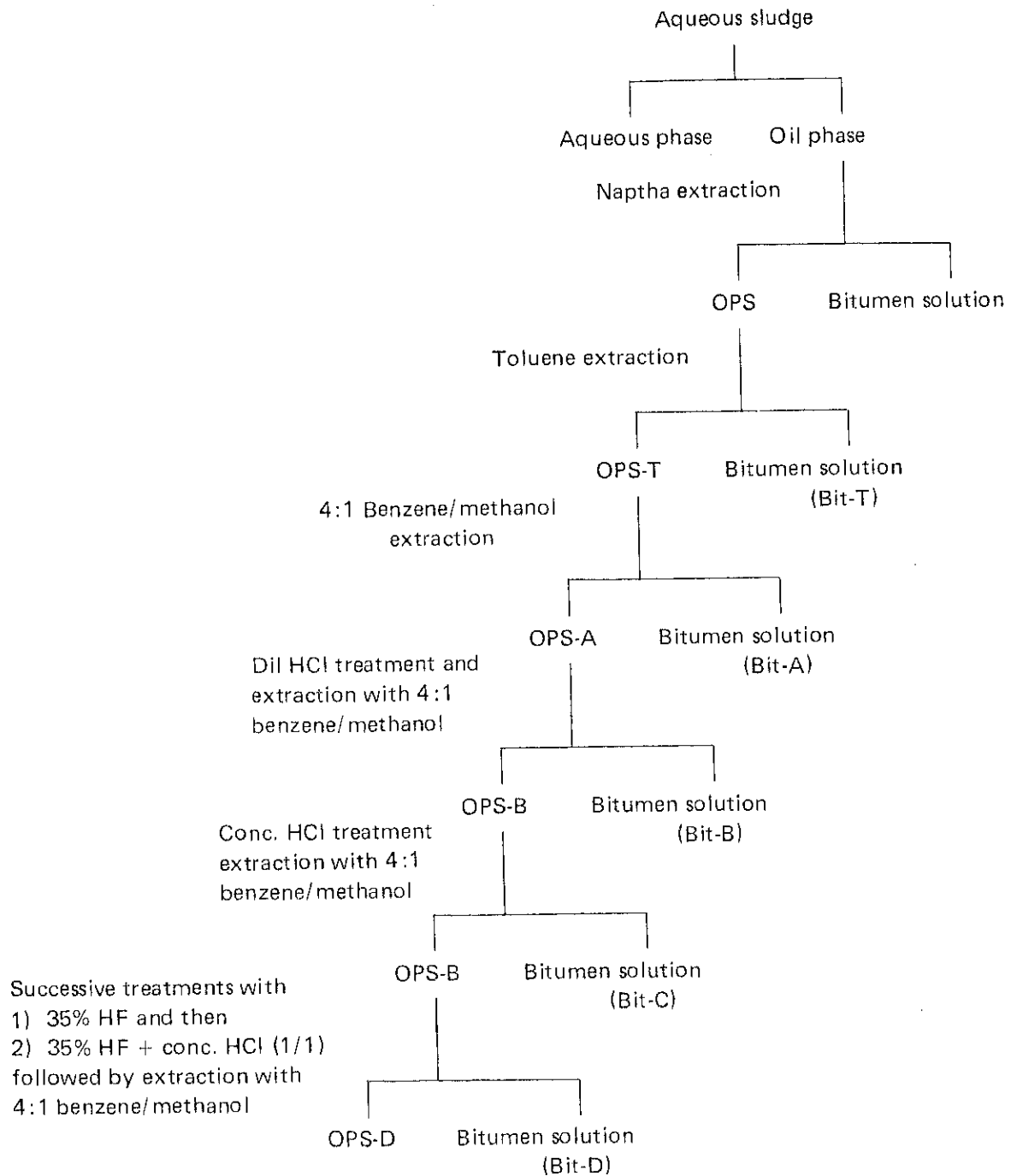


Fig. 1 Extraction flow sheet

solvent extractions were carried out by refluxing the appropriate oil phase solids (OPS) for 36 hours, after which the resultant suspensions were centrifuged and the liquids decanted off. The solid residues were then rinsed, centrifuged and decanted until colourless. The liquid bitumen fractions were filtered prior to isolation with a rotary evaporator at 100° operated under reduced pressure. These samples were further dried at 70° under vacuum for 18 hours. The solid residues were also dried in a similar manner prior to further processing.

The acid treatments were performed on OPS materials pre-wetted with methyl alcohol. The appropriate acid treatment solutions were always added dropwise and the resultant suspensions stirred for 36–48 hours to facilitate the treatment.

The thermogravimetric analysis were performed using a DuPont 951 instrument coupled to a 1090 Thermal Analyzer. Samples 15–20 mg were employed throughout using a platinum sample pan. The samples were examined employing both air and nitrogen purge gases at flow rates of 50 ml/min. The temperature programmed conditions employed involved a 30 minute hold at 30° and then controlled heating from 30° to 1000° at 10 deg/min.

## Results and discussion

The actual weight loss curves from all of the samples examined in this study are summarized in Figs 2–5. Figures 2 and 3 present the data for the OPS samples in nitrogen and air respectively, while Figs 4 and 5 illustrate the data obtained with the corresponding extracted bitumen samples. It will be noted that in general the early (low temperature) portions of the TG curves are very similar irrespective of the test purge gas employed. It is only at the higher temperatures (above 250°), that the

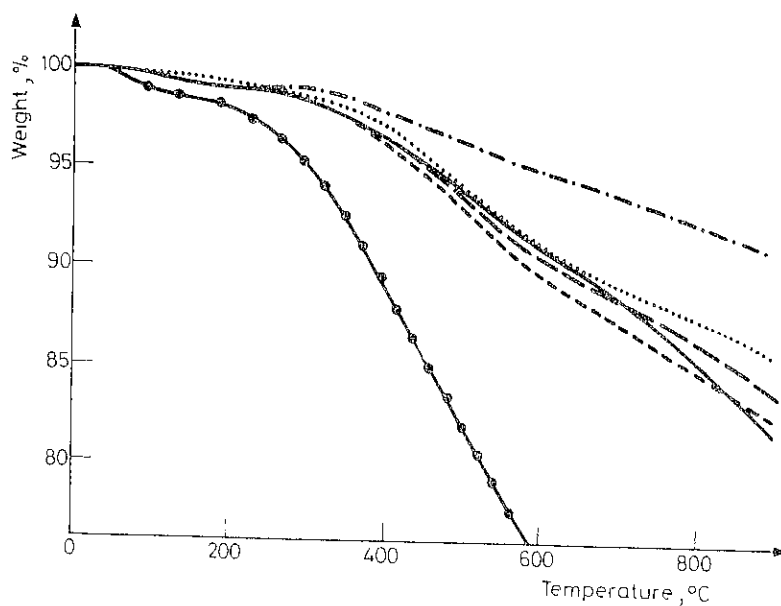


Fig. 2 Weight loss traces in nitrogen for OPS (—); OPS-T (— —); OPS-A (— —); OPS-B (. . . .); OPS-C (- . - .) and OPS-D (-●-●)

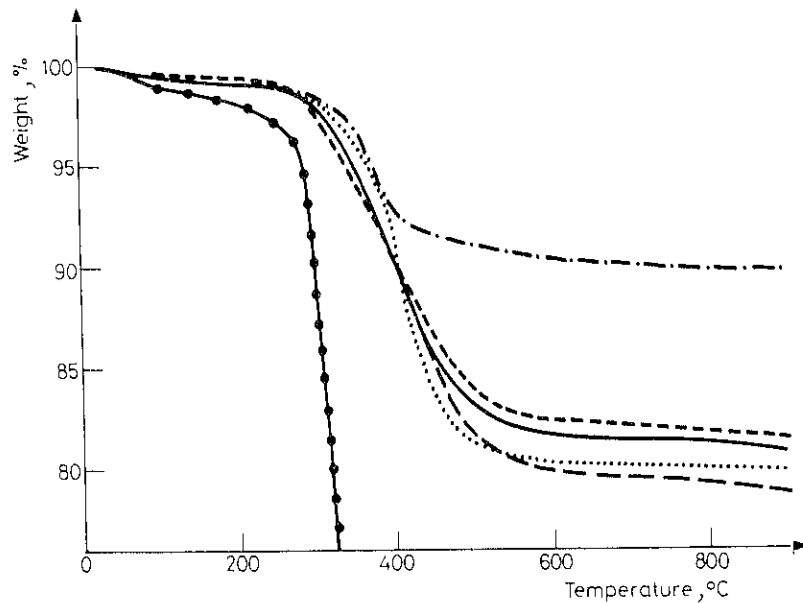


Fig. 3 Weight loss traces in air for OPS (—); OPS-T (— —); OPS-A (— — —); OPS-B (.....); OPS-C (- . - . -) and OPS-D (—●—●—)

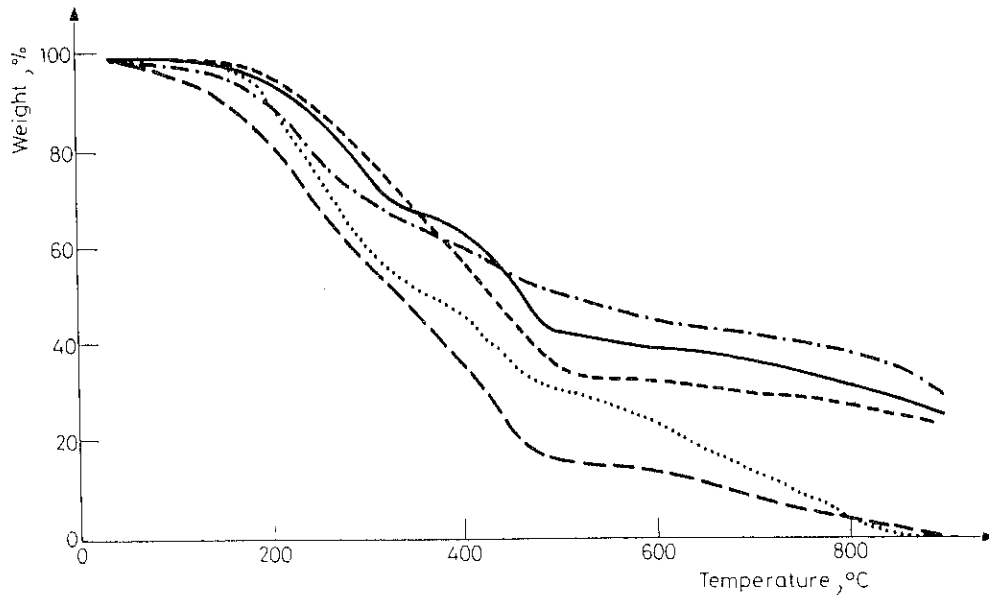


Fig. 4 Weight loss traces in nitrogen for Bit-T (— — —); Bit-A (— — —); Bit-B (.....); Bit-C (- . - . -) and Bit-D (—)

oxidative characteristics become evident. At these higher temperatures, much larger weight losses are detected which are assumed to be associated with the oxidative degradation process.

In the case of all the OPS samples, it will be noted that all the curves are very similar up to a temperature of about 250° for samples run in both nitrogen and air. Above this temperature, however, the rates of weight loss are much larger in air than in nitrogen and reach their residual weights at much lower temperatures.

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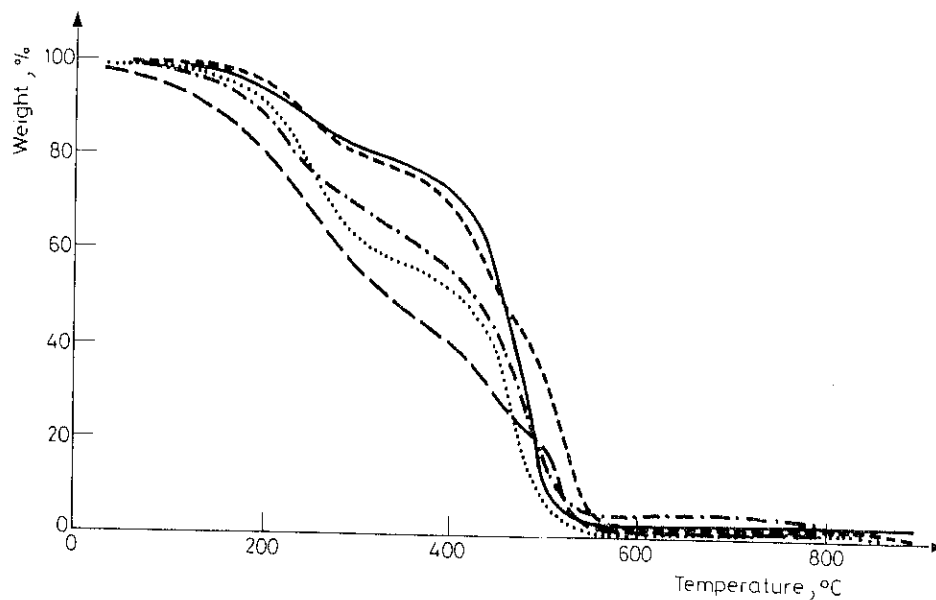


Fig. 5 Weight loss traces in air for Bit-T (—); Bit-A (---); Bit-B (....); Bit-C (-.-.-) and Bit-D (——)

The extracted bitumen samples show slightly different characteristics to those observed with the OPS samples. While the bitumen samples produce curves which are very similar in both nitrogen and air up to a temperature of about 250°, above this temperature there are noticeable differences observed in the curves obtained in the two environments. At temperatures between 250–400° the weight losses are faster in nitrogen than they are in air. However, above 400° the rates become faster in air than they are in nitrogen. The loss of weight in the low temperature region (250–400°) has been attributed to the loss of phenolic-OH groups and carboxylic acid groups based upon chemical and infrared analytical techniques [3]. This loss in weight being in addition to that due to the volatilization of light hydrocarbons [4, 5]. At temperatures above 400°, however, thermal breakdown and "cracking" of the "nuclei" occurs giving rise to further volatilization [5]. In air, meanwhile, it is possible for the oxygen to decrease the apparent weight loss at the low temperatures (250–400°) due to the formation of oxidative products in the condensed phase. Above 400°, however, oxidative degradation takes place enhancing the decomposition process and the actual rate of weight loss.

Although the weight loss curves presented in Figs 2–5 give some overall idea of the degradative processes taking place, the first derivative plot of the data facilitates the identification of the various degradative steps involved in the degradation process. These curves for the extracted bitumen samples are shown in Figs 6 and 7 for samples run in nitrogen and air respectively. These DTG plots clearly indicate the complex nature of the volatilization and degradation process taking place when these bitumen extract samples are being heated. However, irrespective of the test environment, it is possible to clearly identify a low temperature weight loss zone up to about 350° and a high temperature weight loss zone from about 350–550°. In the case of the oxida-

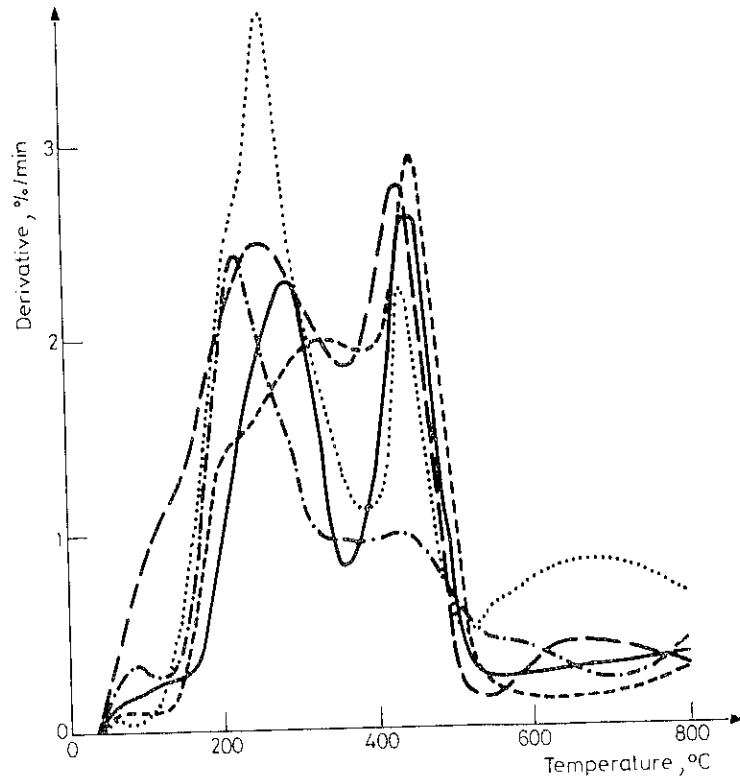


Fig. 6 Derivative thermogravimetric traces in nitrogen for Bit-T (— —); Bit-A (— —); Bit-B (.....); Bit-C (- . - .) and Bit-D (——)

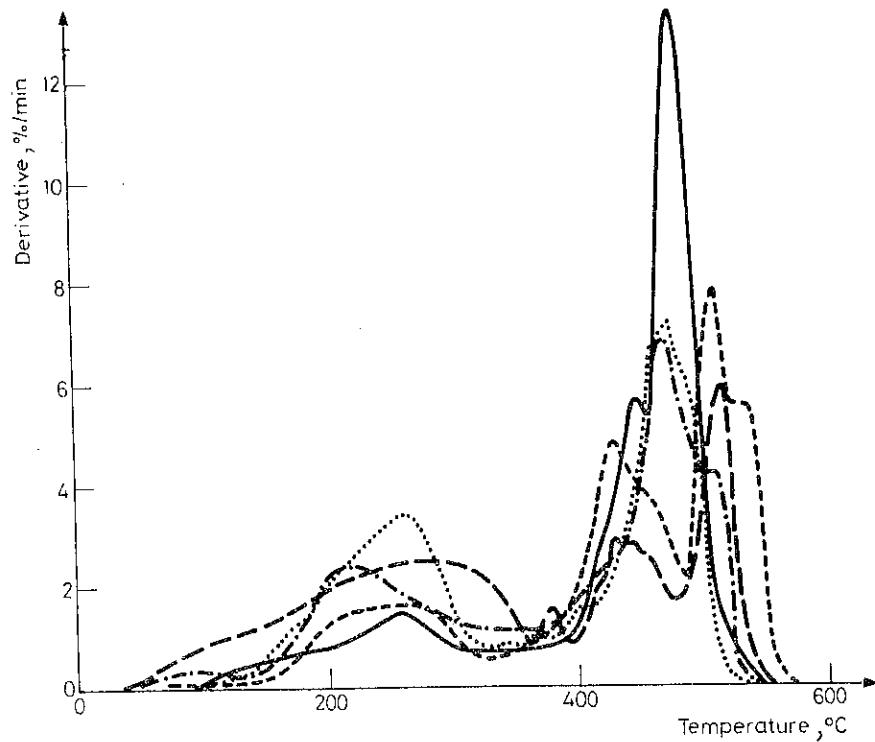
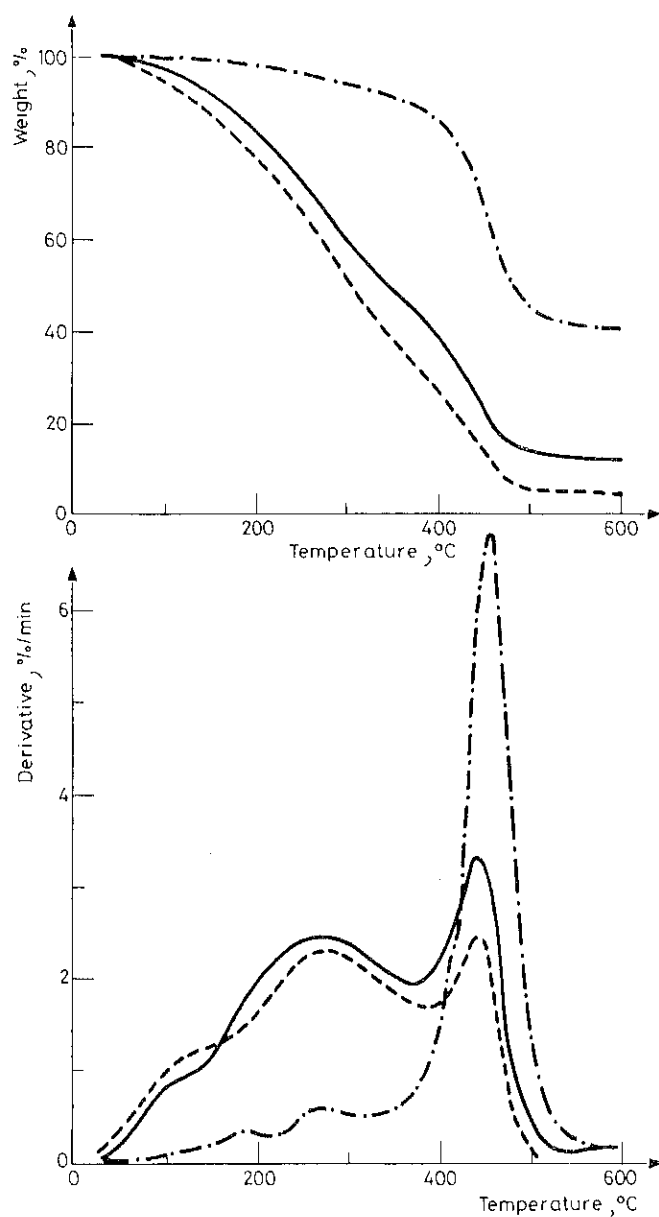


Fig. 7 Derivative thermogravimetric traces in air for Bit-T (— —); Bit-A (— —); Bit-B (.....); Bit-C (- . - .) and Bit-D (——)

tive environment, there is virtually no residue remaining at this temperature, whilst in the case of nitrogen, more thermal weight loss can be observed above this temperature. Earlier studies [5, 6] of the pyrolysis and oxidative degradation of Athabasca oil sands have identified the presence of these two regions by both DSC and DTG studies, and assigned to weight losses associated with species such as maltenes and asphaltenes. For comparison purposes it was therefore decided to examine samples of bitumen, maltenes and asphaltenes in our study using the same experimental conditions. The results of this thermogravimetry analysis are shown in Figs 8 and 9 for nitrogen and air respectively. Clearly, examination of the traces obtained in nitrogen (Fig. 8) reveals the bitumen to be composed of a peak centered at 277° associated with the



**Fig. 8** Weight loss and derivative thermogravimetric traces in nitrogen for bitumen (—); maltenes (---) and asphaltenes (- . - . -)

distillation of the maltenes fraction and a second peak centered at 445° due to the decomposition and subsequent volatilization of both the asphaltenes and the maltene fractions. In the case of the traces obtained in air (Fig. 9), whilst the two zones present in bitumen can be readily identified with the maltene and asphaltene fractions, the peak associated with asphaltenes is now no longer simple, indicative of the added complexities associated with the oxidative process.

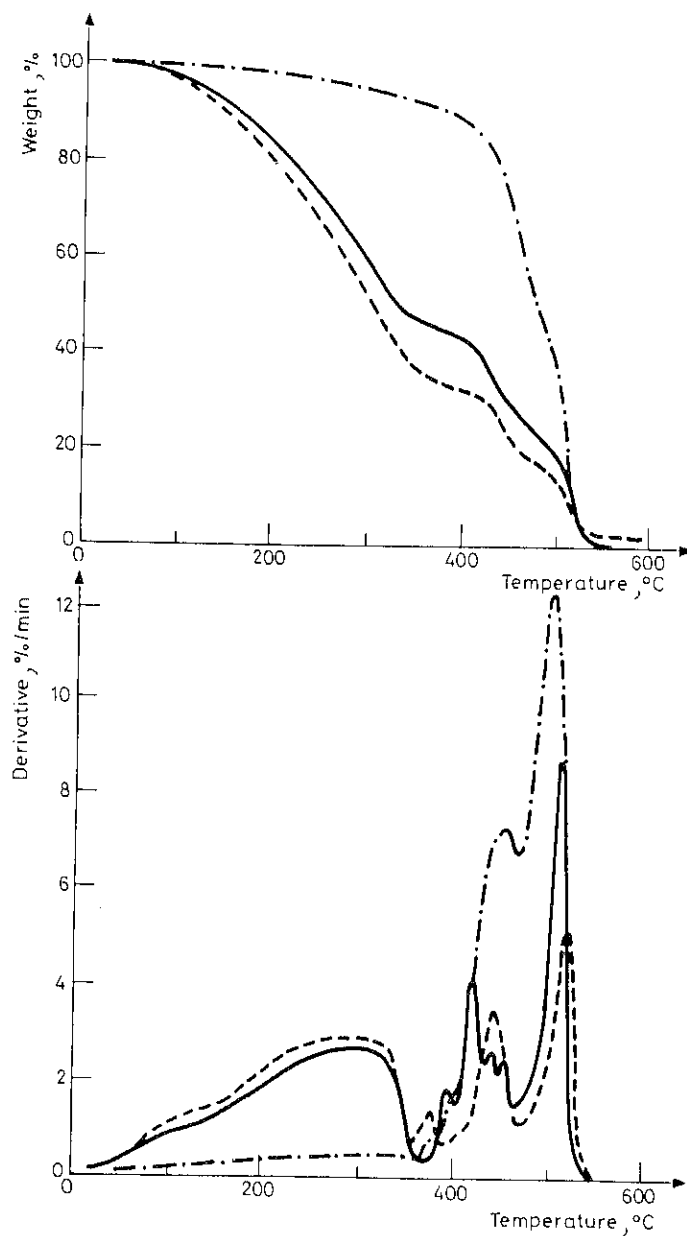
It is now possible to examine in more detail the data presented in Figs 6 and 7 in order to correlate structurally the fractions extracted from the oil phase solids with the bitumen fractions. For the sake of convenience and to facilitate the analysis of the data, the DTG curves can be divided into two regions. Region 1, between 30–350° in which low molecular weight species are volatilizing and functional groups are being eliminated along with light hydrocarbons. Region 2, between 350–550° in which cracking and degradation of the higher molecular weight species occur, such as decomposition of the aromatic nuclei. In the absence of air a considerable quantity of coke is to be anticipated, which in the presence of oxygen will be oxidized and subsequently lost as oxidative decomposition products. The actual composition of the bitumen extracts have been analysed based upon the above assignment and the results tabulated in Table 1.

The results obtained with the toluene extracted fraction Bit-T are very similar to those obtained with the standard bitumen shown in Figs 8 and 9. Thus the composition of this extract can be seen to be very similar to that of the standard bitumen sample, a result which was to be anticipated.

Further extraction of the OPS residue results in the Bit-A bitumen fraction. This sample, it will be noted, has a higher proportion of the more thermally stable high molecular weight fraction than the low molecular weight fraction. The sample also shows a relatively high amount of intractable matter as indicated by the high residual weight remaining during the nitrogen experiment. Under oxidative conditions, how-

**Table 1** Volatile product distribution from extracted bitumen samples, %

	Bitumen extract				
	Bit-T	Bit-A	Bit-B	Bit-C	Bit-D
Experimental results in N <sub>2</sub>					
Low molecular weight fraction (maltenes)	55.0	39.8	53.0	34.2	32.7
High molecular weight fraction (asphaltenes)	30.2	27.6	18.0	23.2	26.5
High temperature volatiles	11.7	10.7	28.1	14.2	15.7
Residue (Coke + Ash)	3.1	21.9	0.9	28.4	25.1
Experimental results in air					
Low molecular weight fraction (maltenes)	53.4	21.2	40.3	35.2	24.2
High molecular weight fraction (asphaltenes)	46.2	77.3	58.3	60.3	73.2
High temperature volatiles	0.1	—	1.0	1.6	—
Residue (Ash)	0.2	1.5	0.4	2.8	2.6



**Fig. 9** Weight loss and derivative thermogravimetric traces in air for bitumen (—); maltenes (---) and asphaltenes (- . - . -)

ever, the volatilization of the low molecular weight fraction is noticeably diminished in favour of two distinct weight loss zones associated with the high molecular weight fraction, both of which in themselves appear to be complex in nature. These two zones may be attributable to the thermal and thermoxidative degradation processes and subsequent volatilization of the products.

Treatment of the residual OPS with dilute hydrochloric acid prior to further benzene/methanol extraction results in the decomposition of the inorganic carbonates and liberation of carbon dioxide. The resultant Bit-B sample, unlike Bit-A has a relatively high proportion of low molecular weight material, similar to the Bit-T

sample. However, unlike the Bit-T sample, Bit-B evolved a relatively large amount of high temperature volatile material between 500–800° when heated in nitrogen. Consequently, the Bit-B showed the lowest residue in nitrogen of all the samples tested. The high low molecular weight fraction associated with Bit-B is also clearly evident in the air experiments. However, only one zone of decomposition appears to be present during the weight loss associated with the high molecular weight fraction under these conditions.

Further treatment of the OPS residue with concentrated hydrochloric acid dissolves most of the cations associated with the organic matter liberating such species as carboxylic acids, porphyrin complexes etc. These species such as the porphyrins and asphaltenes do not volatilize or degrade rapidly and thus are in part responsible for the large residues observed with the Bit-C extract in nitrogen. This observation is in keeping with the large quantities of coke known to be obtained from these species on thermal cracking [7, 8]. This residue observed in the nitrogen experiments was in fact

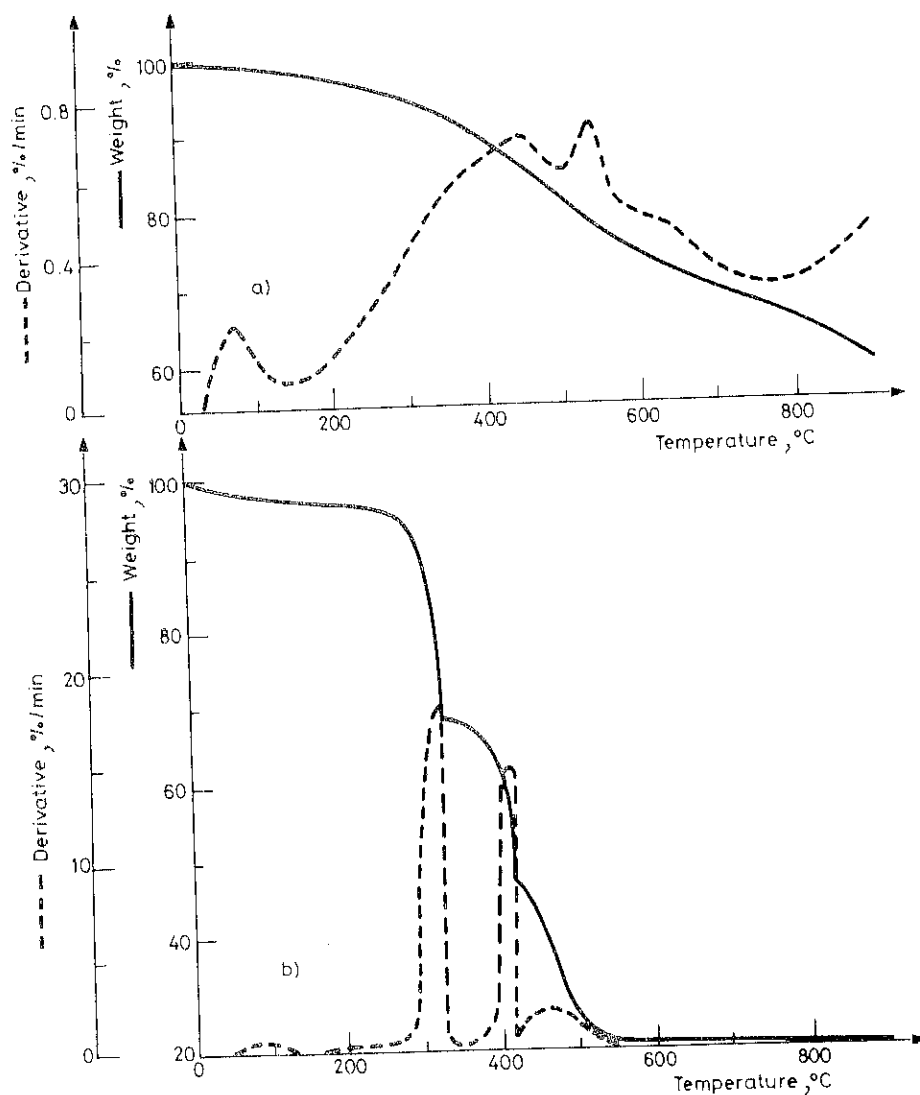


Fig. 10 Weight loss and derivative thermogravimetric traces for OPS-D in nitrogen (A) and air (B)

the largest of any of the bitumen extracts examined in this study. Under oxidative conditions the Bit-C sample was, however, found to behave very similar to the Bit-B sample, and have comparable low and high molecular weight fractions present.

The treatment and extraction process to obtain the Bit-D results in the dissolution and removal of the silica from the OPS. The resultant bitumen Bit-D when examined under nitrogen appears to be equal in low and high molecular weight fractions and yet has an appreciable high temperature volatile fraction and high residue. When examined under oxidative conditions, the very high fraction of high molecular weight material present becomes clearly evident. It should be noted that the shape of the DTG curve for the Bit-D sample (Fig. 7) shows a very close resemblance to that of the asphaltene sample shown in Fig. 9.

Because of the nature of the treatment in going from OPS-C to OPS-D, a large amount of non-volatile matter in the form of silica is being removed which consequently results in a material high in volatile matter in comparison to the other OPS samples studied as is evident by the traces shown in Figs 2 and 3. To fully appreciate the actual data obtained with the OPS-D sample, this has been presented in Fig. 10. It will be noted that under nitrogen conditions the weight loss curve is not very informative, apart from indicating the onset of a gradual decomposition at about 200°. Although the derivative curve does indicate two peaks between 400 and 600° and a shoulder just above 600°, these are not well resolved. This indicates that complex competing pyrolysis reactions such as polymerizations, condensations and molecular rearrangements producing higher molecular weight species could be taking place [8]. Under air conditions, however, the weight loss takes place in three distinct regions, which because of their sharpness in comparison to the nitrogen experiments must be assumed to be associated with oxidative thermal degradation processes.

## Conclusions

The use of thermogravimetric analysis has been shown to be a viable process for the evaluation and comparison of various fractions of organic matter extractable from mineral matter found in the Athabasca oil sands. The environment employed in the TG determination influenced the nature of the curves obtained, especially above 250°. Consistently, the extracted fractions lost weight faster between 250–400° in nitrogen while above 400° the weight lost rates became faster in air. The DTG curves clearly indicated that the extracted bitumen fractions could be divided into two regions. The first region between 30–350° has been assigned to the volatilization of low molecular weight species and the elimination of functional groups such as phenolic OH and carboxylic groups along with low molecular weight hydrocarbons. The second region between 350–500° has been assigned to the cracking and degradation of higher molecular weight species. These observations with the extracted samples suggest that they are structurally related to the maltene and asphaltene fractions of Athabasca

bitumen. This conclusion is based on comparisons of the TG and DTG results with various fractions and is consistent with previous studies concerning the interactions of asphaltenes and resins in mineral matter [9–12].

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**Zusammenfassung** — Die mit den in Athabasca-Suncor-Ölsandrückständen enthaltenen Tonen und Schwermetallmineralen assoziierte organische Substanz wurde abgetrennt, durch eine Reihe von Säurebehandlungen vorzugsweise einer Dissoziation unterworfen und anschließend mit Benzol/Methanol extrahiert. Die verschiedenen isolierten Fraktionen wurden thermogravimetrisch (TG) und differentialthermogravimetrisch (DTG) untersucht. Ein Vergleich der in Stickstoff und Luft erhaltenen Ergebnisse weist auf die komplexe Natur der thermischen Zersetzung und der beim Erhitzen verlaufenden thermisch-oxydativen Prozesse hin. Die Ergebnisse zeigen, daß durch TG Informationen zur Charakterisierung von Ölsendfraktionen erhalten werden können, die zum Verständnis der Raffinationsprozesse beitragen.

**Резюме** — Органическое вещество, связанное в глинах и минералах, содержащих тяжелые металлы, и находящееся в нефтеносных залежах, было извлечено и обработано кислотой после экстракции его смесью бензола метанола. Выделенные таким путем фракции были изучены методами ТГ и ДТГ. Сопоставление данных, полученных в атмосфере азота и воздуха, показали сложную природу процессов термической деградации и термического окисления, имеющих место при нагревании. Результаты показали, что метод ТГ дает информацию, которая может помочь понять процессы переработки нефти.