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Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/0016-2361\(83\)90026-1](https://doi.org/10.1016/0016-2361(83)90026-1)

Fuel, 62, 7, pp. 772-774, 1983-07

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Determination of residual organic matter in extracted oil sands using a low temperature ashing method*

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(Received 23 December 1982)

The application of a low temperature ashing method for estimating total residual organic matter (toluene insolubles) in oil sands is described. A linear correlation exists between organic carbon content and loss on ignition at $400 \pm 10^\circ\text{C}$ of solvent extracted oil sands. The ratio between total organic carbon and the weight loss on ignition (CT/LOI) owing to the removal of residual organic matter is much lower than that obtained for toluene soluble bitumen fractions, indicating very different chemical composition for the residual organic matter. The measured carbon content of the residual organic matter in oil sands suggests that this material could be a mixture of various fractions contained in resins, asphaltenes, asphaltic acids and humic acids.

(Keywords: oil sands; organic matter; low temperature ashing)

Toluene extraction using Soxhlet apparatus is an accepted standard for determining the organic content of oil sands. Although the technique gives a good measure of easily extractable bitumen, considerable quantities of organic matter remain associated with the solids, particularly when the fines ($< 44 \mu\text{m}$) content is high^{1,2}. Even combinations of solvents are incapable of extracting all of this residual material. However, the nature and quantity of unextracted organic matter is important when processing the sand and important to the quality of bitumen produced (solids content) and the environmental impact of waste disposal³⁻⁷.

There appears to be no direct method for estimating residual organic matter from solvent extracted oil sands. This report investigates the applicability, for this purpose, of a low temperature oxidation method, originally developed for coal analysis^{8,9}. These results, combined with organic carbon determinations, are useful in predicting the approximate nature of the residual organic matter without isolating it.

EXPERIMENTAL

A number of samples of different grades of oil sand were used in the study. The samples were first extracted with toluene, dried at 110°C to a constant weight (≈ 2 h), ground for homogeneity and then divided into two portions. One portion was used for carbon analysis and the other for loss on ignition studies (LOI).

Total carbon was determined using a Leco CR12 carbon determinator. Carbonate carbon was measured by titration after acid digestion. Carbonate carbon was then subtracted from the total carbon to obtain the amount of organic carbon in these samples.

Low temperature ashing (loss on ignition)

The low temperature oxidation procedure was essentially similar to the one used for coal⁸⁻⁹. The oil sands sample (≈ 10 – 20 g) was weighed into a pre-weighed porcelain crucible and then dried at 110°C for 3 h in a drying oven. After cooling in a dessicator the crucible was weighed to determine moisture loss. It was then placed in a well ventilated furnace (Blue M Company, Laboratory heat muffle furnace). The temperature was raised to 300°C and held constant for 2–3 h, before raising it to the final ashing temperature. Ashing temperatures used were $380 \pm 10^\circ\text{C}$, $400 \pm 10^\circ\text{C}$, $420 \pm 10^\circ\text{C}$ and $500 \pm 10^\circ\text{C}$. Times required for complete oxidation at these temperatures were 2–5 days at 380°C ; ≈ 20 h at 400°C ; ≈ 15 h at 420°C ; and ≈ 4 h at 500°C . After removal from the furnace the mineral residue was cooled and then equilibrated with moisture at 100% relative humidity at room temperature. This was accomplished by placing the samples in a closed vessel over water, to restore the reversible loss by the clay minerals of loosely bound water¹⁰. The sample was then dried at 110°C for 2 h, cooled in a dessicator and weighed. The organic matter content of the samples was calculated as follows:

Percentage of organic matter = $[100 \times \text{difference in wts of dried and ashed samples}] \div [\text{Total wt of the sample}]$

RESULTS AND DISCUSSION

Hydrated silicate minerals usually associated with oil sands are said to be generally stable up to temperatures considerably in excess of 400°C . The water of hydration lost by these minerals below 400°C is either reversible or only slight¹⁰⁻¹².

The carbonate minerals, calcite, dolomite and ankerite were found in small quantities in some of the oil sand deposits¹³. Differential thermal analysis studies indicate the general thermal stability below 400°C of these carbonate minerals¹⁴⁻¹⁷.

* Issued as NRCC No.21144

Table 1 Carbon analysis and loss on ignition data for various pre-extracted oil sand samples

Sample ^a no.	Total organic carbon (%)	LOI at 400 ± 10°C 20 h ^b (%)	CT ^d LOI	(LOI of oil sands) ^c – (Bitumen extraction)
1(77)	1.83 ± 0.27	2.57	0.712	3.08
2(55)	1.295 ± 0.22	1.83	0.708	1.72
3(49)	1.92 ± 0.14	2.59	0.741	2.66
4(46)	1.08 ± 0.08	1.52	0.711	1.49
5(35)	0.89 ± 0.11	1.28	0.695	1.37
6(19)	0.63 ± 0.18	0.89	0.708	0.87
7(12)	0.44 ± 0.30	0.59	0.746	0.39

^a Per cent of fines content in parenthesis^b After correcting for loss due to the decomposition of carbonates^c Before extraction of the bitumen^d CT = % total carbon **Figure 1** Loss on ignition as a function of total organic carbon

From this evidence it would appear that at temperatures <400°C the hydrated silicate minerals usually associated with oil sands could be expected to lose reversibly only loosely bound water, whereas carbonate minerals would not account for any loss in weight <400°C. A temperature of 380°C was therefore, initially selected for the low temperature oxidation of organic matter in oil sands in this study.

When establishing the optimum experimental conditions for the low temperature oxidation the temperature was held near 300°C for 2–3 h before raising it to 380°C. This reduces the total time required for the complete oxidation of organic matter probably because mild oxidation at 300°C prevents fusion and caking at higher temperatures¹⁸. It also reduces the risk of establishing exothermic luminescent oxidation (probably low-temperature ignition). Such occurrences could result in the minerals being subjected to temperatures considerably in excess of 380°C which would not be detected unless thermocouples were embedded in the sample⁹.

Carbonate carbon of all samples was measured both before and after ashing. No carbonate carbon was detected in the ashed samples, although it ranged from 0.08–0.23% in the samples before ashing. Corrections were, therefore, made for the loss of carbon dioxide from the total loss on ignition.

Complete oxidation of residual organic matter in oil sands at 380°C requires 2–5 days. To reduce the ashing time, temperatures higher than 380°C were also used. Results obtained at 400°C were found to be very nearly the same as obtained at 380°C with considerably shorter time required (≈20 h) for complete oxidation of the organic matter. Temperatures >400°C gave much higher values for the residual organic matter in oil sands which correlate poorly with the carbon content of oil sands. A temperature of 400 ± 10°C was, therefore, employed for the estimation of organic matter in oil sands.

The low temperature ashing method could be particularly useful for the estimation of the residual organic content of oil sand samples after solvent extraction. This residual organic matter is usually not extractable by conventional solvents such as benzene or toluene. Most of the organic matter in these samples is oxidized at 400°C in about 15–20 h.

Table 1 shows loss on ignition (LOI) and carbon analysis data for various pre-extracted oil sand samples. The values of the loss on ignition of unextracted samples minus the bitumen extracted are also shown. These represent the quantity of residual organic matter. These values should be equivalent to the LOI of pre-extracted samples. A good agreement can be seen between the two columns in Table 1. The small difference in some samples could be attributed to the heterogeneous nature of the samples.

A plot of the LOI at 400°C of pre-extracted samples versus their organic carbon content, shown in Figure 1, gives a good linear correlation. As the intercept of the straight line is almost zero (0.03), most of the loss on ignition appears to be the result of the oxidation of the organic content of these samples. Ratios of total carbon (CT)/LOI for the residual organic matter are much lower than those obtained for toluene-soluble bitumen fractions, indicating a very different chemical composition. The mean value for the ratio CT/LOI was 0.73 as determined from the slope of the plot of LOI versus organic carbon content.

The carbon content of various fractions extracted from oil sands are given in Table 2^{19–22}. A comparison of the measured carbon content of residual organic matter in oil sands, with the carbon content of various fractions in Table 2 suggests that this organic matter could be a mixture of various fractions contained in resins, asphaltenes, asphaltic acids and humic acids. Polar groups from asphaltenes and resins are thought to adsorb strongly on to clay particles present in oil sands and are difficult to remove²³. More work regarding the isolation and characterization by chemical and spectroscopic methods of the residual organic matter in oil sands is in progress.

Table 2 Carbon content of various fractions from oil sands

Fraction	Carbon (wt %) ^a
Bitumen	82.6 – 84.0
Oil	84.0 – 86.0
Resins	80.0 – 82.0
Asphaltenes	76.0 – 82.0
Water soluble	
Asphaltic acids	66.4
Humic acids	60.6

^a References 19–22

ACKNOWLEDGEMENTS

Carbonate carbon analyses were performed by V. Clancy of our analytical section, for which we are grateful. We are also indebted to Dr J. A. Ripmeester and Dr D. W. Davidson for some helpful suggestions.

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