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Mutagenicity testing and *in vivo* tests for skin carcinogenicity in mice are being carried out to assess whether the materials recovered at $<370^{\circ}\text{C}$ from the distillation exhibit any mutagenic or carcinogenic activity. If these biological tests are found to be essentially negative, as predicted from the analytical data presented here, then optimized process distillation should certainly warrant consideration as an option in the development of process modifications to produce safer coal-derived liquid fuels. Fuels obtained from an optimized distillation process step should be substantially less genotoxic than the full-boiling-range source materials from which they came.

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Comparative study of three laboratory methods for the extraction of bitumen from oil sands

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Measurements of total organic content and extractable bitumen for a number of different grade oil sands were used to obtain the extraction efficiency of several common bench-scale bitumen recovery techniques. The hot-water process was inefficient for feeds of moderate to high fines content. Soxhlet extraction and spherical agglomeration were found to be of similar efficiency for most grades of feed. For these two processes the efficiency is limited by the mineral fines content, probably because of surface absorption of bitumen components.

(Keywords: oil sands; bitumen; extraction)

The recent commercial development of the Alberta oil sands, based on the hot-water-separation process developed by Clark¹, is one of the major advances in the petroleum industry. The separation of bitumen is particularly straightforward for oil sands feeds which are substantially free from mineral fines ($< \approx 44 \mu\text{m}$, 325 mesh). Small quantities of these fines are, however, inevitably present even in high-grade oil sands feeds, and as recycle water for the hot-water process cannot contain more than $\approx 5\%$ fines, large volumes of non-settling tailings must be confined and stored indefinitely². Higher concentrations of fines cause an operational problem in the hot-water process³, leading to poor bitumen recovery.

For feeds with higher fines contents alternative processes, usually based on solvent extraction, have been investigated. A continuous, combined counter-current solvent extraction-spherical agglomeration process⁴ has shown promise in the ability to extract bitumen from such feeds. To establish the important factors which determine the extraction efficiency of different bitumen separation methods, the distribution of organic matter in the

residues, left after extracting bitumen from oil sands of different composition, was measured.

In industry, extraction with toluene or benzene using Soxhlet apparatus is employed to determine the bitumen content, even though extraction by combinations of solvents is not sufficient to remove all organic matter from high fines oil sand. Owing to this difficulty both carbon analysis and the simple loss on ignition methods were used here to assess the organic matter in both oil sands and fractionated extraction residues.

Different bitumen separation processes were tested on a bench-scale: the hot-water process, solvent extraction spherical agglomeration with toluene as the continuous phase, and Soxhlet extraction using toluene.

EXPERIMENTAL

Oil sands were obtained from the Oil Sand Sample Bank of the Alberta Research Council. All samples were broken into pieces $< \approx 0.5 \text{ cm}$ using a Comomill model No. 197-I-L (Quadro Engineering Co.) and were thoroughly mixed

to ensure homogeneity.

C, H and N analyses were carried out using a Perkin Elmer model 240 CHN analyser. Carbonate carbon was measured titrimetrically after acid digestion.

Extractable bitumen was measured using Soxhlet extraction with toluene as solvent for ≈ 24 h. Total organic matter contents were measured by carbon analysis or loss on ignition at 380°C ⁷ (after correction for carbonate content). All analyses were done in triplicate.

After extraction, the solids were dried at 110°C and dispersed in water using a high-speed blender. Particle size distributions were measured by wet screening, followed by drying to constant weight at 110°C .

Specific surface areas of a number of solid samples were measured by low-temperature nitrogen adsorption using a Ströhlein area meter. Prior to each measurement,

Figure 1 Extractable carbon content (calculated from bitumen extracted with toluene in a Soxhlet apparatus) as a function of total carbon content (after correcting for carbonate carbon)

Figure 2 Effect of fines on bitumen recovery. $\circ$, Total organic content (as calculated from carbon analysis); $\bullet$, bitumen extracted using batch agglomeration; $\square$, Soxhlet apparatus; $\blacksquare$, hot-water process

Figure 3 Effect of fines (surface area) on the residual organic matter in the tailings. Organic contents are average values derived from carbon analysis and loss on ignition. Surface area scale is derived from data in Table 1. $\circ$, Organic content of tailings after agglomeration; $\bullet$, organic content of tailings from Soxhlet extraction

Table 1 Analysis of oil sands

Oil sand sample no.	Fines fraction ^a	Specific surface area ^b ($\text{m}^2 \text{g}^{-1}$)	Loss on ignition at 380°C (wt %)	Carbon content (wt %)
1	0.77	26.6	5.0	4.5
2	0.55	14.8	7.0	6.1
3	0.46	15.0	7.9	6.2
4	0.35	12.9	7.6	7.2
5	0.19	2.6	13.6	11.4
6	0.12	0.3	13.3	10.8

^a $37 \mu\text{m}$ (<400 mesh)

^b After ashing at 380°C

samples were ashed at 380°C to remove adsorbed organic matter, mixed by gentle grinding in a mortar, so as to break up the lumps but not alter the surface area of the particles, and dried at $130 \pm 5^\circ\text{C}$ for several hours.

Procedures for the three extraction methods used in this study, carried out on a small scale, have been described previously^{5,8,9}.

RESULTS AND DISCUSSION

Analysis of representative samples

The organic matter and mineral fines contents vary over a wide range for the oil sands used in this study (Table 1). The organic content of the samples was measured using both carbon microanalysis and loss on ignition, and on assuming that the carbon content of Athabasca bitumen is 83 wt%,¹⁰ it is evident that the two methods are in good agreement. Two trends are apparent in Table 1. The first is the inverse dependence of organic content on the mineral fines fraction. Such a relation has been examined previously¹¹ although the study was concerned only with bitumen extracted with toluene. The second trend is the not unexpected dependence of surface area on mineral fines content.

Figure 1 shows the correlation between recoverable bitumen and the total organic content for the oil sands listed in Table 1. For feeds with $> \approx 8$ wt% organic matter, the bitumen recovered approaches the total organic content; however, from oil sands containing $< \approx 3$ –4 wt% organic material very little, if any, bitumen was recovered.

Evidently it is important to assess total organic content, in addition to recoverable bitumen, because these two quantities may differ considerably. Regardless of the bitumen separation method used, the difference has clear environmental implications in its effect on the nature of the tailings. In processing low-grade oil sands, difficulties in establishing a mass balance of organic matter can be envisaged unless total organic content is measured.

Comparison of extraction efficiencies

The percentage bitumen recoveries for the three bitumen separation techniques applied to the samples listed in Table 1 were calculated according to:

$$\text{wt}\% \text{ recovery} = \frac{\text{wt of bitumen recovered}}{\text{total organic content}} \times 100$$

The results are shown in Figure 2. It is evident that the hot-water process is not effective for feeds with moderate to high fines contents; however, the efficiency of the agglomeration method is essentially the same as that of Soxhlet extraction.

The significance of the mineral fines is also shown in Figure 2; both total organic content, as mentioned previously, and recoverable bitumen depend inversely on the fines content. The operational problems of feeds with high fines content in the hot-water-separation process have been described elsewhere². For the other two techniques, however, recovery appears to be related to the adsorption of bitumen components on mineral fines. This is in agreement with recent reports^{12,15} which suggest that bitumen components are strongly adsorbed on clays commonly found in oil sand formations.

Nature of the tailings

Sludge from the tailings ponds of the commercially operating, hot-water-separation plants is quite complex in nature, containing quantities of free and adsorbed bitumen and mineral fines suspended in water. Several reports have been published on this subject^{2,13,14,16}.

The tailings left after removal of bitumen using the

agglomeration process or Soxhlet extraction with toluene are similar in nature. Residual organic matter was determined for extraction residues fractionated according to particle size using both carbon microanalysis and loss on ignition at 380°C. It was found that residual organic matter is associated primarily with the 37 μm (<400 mesh) fraction. This is also shown in Figure 3, where the residual carbon content is plotted as a function of the 37 μm fraction present in the tailings. As surface area depends approximately rectilinearly on the 37 μm fraction (Table 1), a surface area scale is also shown in Figure 3.

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Determination of the stability of coal-oil mixtures (COM) by infrared analysis

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The stability of coal-oil mixtures (COM) may be assessed by using infrared (i.r.) spectroscopy. An i.r. spectrum of a COM has analytical bands at 540 cm^{-1} for coal and at 810 cm^{-1} for oil; these bands are used to determine the change in concentration of coal in a COM with time. The i.r. spectra provides information on the possible interactions between the two materials and an indication of the physico-chemical properties of such mixtures.

(Keywords: coal-oil mixtures; suspensions (chemical); instrumental methods of analysis)

As a result of the possible future exhaustion of the world reserves of crude oil and, therefore, the ever-increasing cost of fuel oil, the possibility of using coal in the electric and industrial power plants has aroused great interest.

As conversion of most of the gas- or oil-fired boilers to coal is associated with drastic modifications, high costs and also the inconvenience of long-term plant shut-down, with a consequent heavy loss of productivity, the importance of coal-oil mixtures (COM), which may avoid these problems, is emphasised.

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