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Isolation and characterization of humic acids from Alberta oil sands and related materials*

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Thirteen humic acid samples were isolated from a number of oil sand feedstocks using 0.5 N NaOH or a mixture of 0.1 N NaOH + 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. The feedstocks included three different grades of Athabasca oil sand, two samples of overburden, a sample of centrifuge tailings from the Syncrude Canada Ltd plant in Alberta and a heavy minerals fraction from oil sand tailings containing adsorbed organic matter. Based on the extraction efficiency of the two solvents it appears that the humic acids from oil sand and overburden feedstocks are strongly associated with calcium, while the humic acids from other feedstocks could be bound to non-silicate aluminum and/or iron. Comparison of analytical data for the various humic acid samples with corresponding data for humic acids from subbituminous coal, peat, soil and asphaltenes from bituminous feedstock, shows the similarity of these humic acids to those from subbituminous coal. Examination of the elemental analyses in terms of a van Krevelen diagram shows that most of the data either overlap or fall directly in the region of the recent and shallow kerogens. This kind of organic matter has very little potential for oil production, suggesting that the origin of this organic matter could be different from that of the greater part of the bitumen of the Athabasca oil sands.

(Keywords: humic acids; oil sands; solvents)

Athabasca oil sand is a complex, variable mixture of bitumen, sand, water and clays¹⁻⁵. The Athabasca deposit is the only one currently under commercial exploitation, and the hot water extraction process used⁶ results in very large volumes of tailings, consisting mainly of sand and a dispersion of various clays containing residual organic matter^{1,7-9}. The sand settles rapidly from the tailings and presents no real disposal problem¹⁰. It is the buildup of partially settled clay sludges or slimes that presents not only an environmental problem but also a significant repository for non-recycleable water.

The reason for the intractability of the clay slimes has been the subject of considerable study^{1,7,9,11-13}. Considerable quantities of insoluble organic material, as well as residual bitumen, are known to be associated with these clay slimes^{8,14,15}. Most of the organic material is strongly associated with mineral fines and is not soluble in the common organic solvents under mild conditions¹⁶.

It is generally believed that the interaction of organics with clay minerals is important in determining the nature of the oil sand slimes^{8,14,15}. The interaction is thought to provide a hydrophobic character to the clay particle surfaces allowing bridging through residual bitumen to set up a weak gel structure.

In previous work unextractable residual organic matter was successfully isolated from oil sand tailings using oil phase agglomeration and acid dissolution techniques^{8,16}. Characterization of this organic material¹⁷⁻¹⁹ led to the suggestion that the unextractable organic matter was mostly humic matter²⁰.

In the investigation described in this paper humic acids were extracted from various samples of oil sands, overburden and tailings streams. The analyses of the various samples of humic acids isolated have been discussed in terms of the geochemical significance of humic acids to the formation of oil sand deposits. Another objective of this study was to provide a better understanding of the nature of the oil sand slimes, which may eventually lead to a more acceptable solution for the sludge pond problem¹.

EXPERIMENTAL

Materials

Table 1 lists the various feedstocks that were used. Oil sands and overburden samples were obtained from Alberta Research Council sample bank. A sample of Syncrude centrifuge (SCT) tailings was provided by Syncrude Canada Ltd. Oil phase solids (OPS), the heavy metal minerals fraction containing unextractable organic matter, were isolated from Suncor sludge using oil phase agglomeration techniques reported elsewhere¹⁷.

Humic acid extraction

A 20-100 g sample of feed was treated with 200-500 ml of either 2 vol% aqueous NaOH or a mixture of 0.1 N NaOH and 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ at room temperature under N_2 for a period of 4-5 days, while stirring using a magnetic stirring bar²⁰. SCT, OPS and demineralized feedstocks containing very little clay minerals were extracted with NaOH alone, while a mixture of NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ was used to extract humic acids from

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Table 1 Sample description and analysis of feed materials

Sample no.	Description	Analyses (wt% of dry sample)			
		Fines ^a	Bitumen	Loss on ignition at 400°C	Organic carbon ^b
1	Low grade oil sands sample 1 (OS-1) ^c	32	3.5	1.30	1.0
2	Low grade oil sands sample 2 (OS-2) ^c	22	8.3	1.20	0.9
3	Beach sand (BS)	11	10.0	0.12	0.09
4	Overburden sample 1 (OB-1)	70	2.3	4.00	2.9
5	Overburden sample 2 (OB-2) ^d	64	3.6	2.10	1.5
6	Syncrude centrifuge tailings (SCT)	15	5.5	18.0	11.1
7	OPS ^e	0	—	32.5	19.3

^a Size < 38 µm (−400 mesh)^b Loss of toluene extracted dry feed^c Samples were from Suncor Mine sites, Section 23, Township 92, range 10, West of Fort Meridian. Sample 1 was 5% overburden bench while sample 2 was 7% mining bench^d Sample description: no. 86-17; Athabasca field; location 23-92-10-W4M; source Suncor Canada Ltd.; McMurray stratigraphic unit; overburden bench depth; sampled October 1986^e Oil phase solids. Heavy minerals fraction from oil sand tailings containing adsorbed organic matter, Ref. 17

feedstocks containing higher levels of clay minerals (samples of oil sand and overburden). The extraction was repeated several times with successive fresh portions of extractant, decanting the spent solution each time until the colour of the supernatant liquid became light brown. The alkaline solution was subsequently separated from the sand by centrifugation, and acidified to pH2 with 6 N HCl. The precipitated humic acids were recovered from the solution by centrifugation. The precipitate was washed several times with 1 vol% HCl. The washed precipitates were dried either under vacuum at 50°C or by freeze drying.

Elemental analysis

C, H and N analyses were performed using a CHN analyser and sulphur was analysed as total sulphur using X-ray fluorescence spectroscopy. Oxygen was determined either by difference or directly²¹. Heavy metal analyses were determined using the quantitative inductively coupled plasma atomic emission spectroscopic method (ICP-AES)²². Ash contents of humic matter fractions were determined²³ at 400 ± 10°C.

Instrumental analysis

Proton n.m.r. measurements were performed on samples of humic acid dissolved in deuterated NaOH, at a concentration of 50–500 mg ml^{−1}. The solutions were filtered using an n.m.r. sample filtering device before recording the spectra. A repetition time of 2 s was selected. Chemical shifts were determined using tetramethylsilane (TMS) as an external reference. Each spectrum was the Fourier transform of 20–50 free induction decay curves.

All solid state ¹³C n.m.r. spectra were obtained at 22.6 MHz or 45.3 MHz using the cross polarization (CP) technique with magic angle spinning (MAS), employing a contact time of 1 ms and a repetition time of 2 s. The magic angle spinning speeds were 3.0–3.4 kHz. Chemical shifts were determined by substitution relative to tetramethylsilane (TMS). Each spectrum was the Fourier transform of 3000–10 000 free induction decay curves. For a few samples, a dipolar dephasing technique²⁴ was also used to distinguish the quaternary carbons (except

groups in motion, e.g. CH₃) from those attached to hydrogens.

Some humic acid samples were dissolved in 0.5 N NaOD at a concentration of 50–500 mg ml^{−1}. ¹³C n.m.r. spectra of these solutions were obtained on a spectrometer, set to a sweepwidth of 50 kHz with inverse gated proton decoupling to suppress the nuclear overhauser effect. A pulse flip angle of 45° was used with a pulse repetition time of 2 s. As there were no sharp features in the spectra, the FIDs were truncated at 2 K datum points before zero-filling to 8 K. Between 20 000 and 50 000 transients were collected to obtain an adequate signal-to-noise ratio.

Infrared spectra were recorded as KBr pellet samples. These spectra were only used qualitatively, for quick identification of general features and the presence or absence of functional groups.

RESULTS AND DISCUSSION

It has been reported²⁰ that NaOH only extracts humic substances that are either free or associated with non-silicate forms of M₂O₃ (M = Al, Fe). A mixture of Na₄P₂O₇ and NaOH, on the other hand, extracts humic substances associated with calcium as well as with non-silicate forms of iron and aluminium. When the mixture of Na₄P₂O₇ and NaOH is used, calcium, iron and aluminium are replaced by sodium, so that soluble sodium humates and insoluble pyrophosphates of the corresponding cations are formed. The reaction may be represented as follows:

or

It may therefore be assumed that the humic acids extracted from oil sands and overburden samples were

associated with calcium in these feedstocks. The humic acids from other feedstocks could have been associated with non-silicate aluminium and/or iron.

Table 2 lists the yield of humic acids as a function of the total insoluble organic matter (IOM) content of the feedstocks. These results show that the amount of humic acid extracted from various feedstocks varies considerably and is not proportional to its IOM content. About 25–30 wt% of the total IOM of oil sands samples 1 and 2 consists of humic acid. The amount of humic acid extracted from BS, SCT and OPS ranged from 16 to 20 wt% of their total IOM content. The lowest amount of humic acid was obtained from overburden samples and amounted to about 3–6 wt% of the total IOM

content. This suggests that either the extraction of humic acid from overburden samples is much slower than from other feedstocks or that the humic acid content of IOM in these samples is low compared with other samples. Alternatively, being closer to the surface, IOM associated with overburden will be more susceptible to the changes brought about by the climatic conditions that could render the IOM insoluble. Having greater access to atmospheric air, it is also possible that this material has been rendered insoluble by air oxidation. Still another explanation could be that the IOM associated with overburden is of different geochemical age than the IOM from oil sands.

The amount of humic acid extracted from acid demineralized overburden sample 1 is about half the amount obtained from the untreated sample. This suggests interaction of acids with IOM rendering humic acids alkali insoluble. One of the possible reactions with acids could be decarboxylation. Since the organic matter associated with young sediments can be hydrolysed by HCl or HF as opposed to ancient organic matter²⁵, these results suggest that the IOM from overburden could be of a younger formation.

Elemental analyses

The elemental composition of various humic acid fractions is given in Table 3. The analytical data for coal, soil and marine humic acid samples are also listed for comparison. Interpretation of these data leads to the following conclusions. Carbon, nitrogen and oxygen contents of these samples are in the same range as for the coal humic acids³. The quantity of organic sulphur in these humic acid samples is considerably higher than

Table 2 Yield of humic acids as a function of the total insoluble organic matter content of the feedstocks

Feedstock	Insoluble organic matter (wt%) ^a	Yield of humic acid (wt% of insoluble organic matter) ^b
OS-1	1.3	25.4
OS-2	1.2	30.0
BS	0.12	16.7
OB-1	4.0	4.8
DOB-1 ^c	95.1	2.9
OB-2	2.1	6.2
SCT	18.0	16.1
OPS	32.5	20.9

^a Determined from the loss on ignition at 400±10°C of the toluene extracted dried feedstocks (Ref. 23)

^b Yield was calculated from the weight of the humic acid on an ash free basis

^c Demineralized overburden sample 1

Table 3 Elemental analyses of humic acids

Feedstock	Wt% (dry, ash free basis)					H/C atomic ratio	Ash (w/w%)
	C	H	N	S	O ^a		
UTOS-1	68.1	6.3	1.0	2.3	(22.3)	1.11	2.3
UTOS-2	66.6	6.0	1.2	3.2	23.0	1.08	7.4
TEOS-2	65.7	6.2	1.2	4.7	(22.2)	1.13	3.6
TEBS	64.6	6.1	1.3	3.0	(25.1)	1.13	21.1
UTOB-1	63.9	4.7	1.5	3.2	26.7	0.88	7.2
TEOB-1	65.7	5.0	1.3	3.1	24.9	0.91	n.d.
DOB-1	64.4	4.7	1.1	2.8	27.0	0.88	8.5
TEOB-2, 1st extract	64.9	4.5	1.5	2.9	26.2	0.83	5.6
TEOB-2, 2nd extract	65.1	4.7	1.4	2.7	(26.1)	0.87	7.5
TESCT, 1st extract	68.8	4.4	1.2	2.6	(23.0)	0.77	2.2
TESCT, 2nd extract	68.0	5.1	1.2	2.7	(23.0)	0.90	0.0
TESCT, 3rd extract	66.4	5.8	1.0	3.6	(23.2)	1.05	14.5
OPS	66.2	4.4	1.0	3.0	(25.4)	0.80	1.3
Mean value	66.0±1.5	5.2±0.7	1.2±0.2	3.1±0.6	24.5±1.7	0.95±0.13	—
Coal HA ^b	64.8	4.1	1.2	1.2	(28.7)	0.76	—
Soil HA ^b	55.7±1.6	4.0±0.4	2.8±0.5	0.8±0.1	36.8±2	0.87±0.07	—
Marine HA ^b	53.7	5.8	5.4	—	(35.1)	1.3	—

^a Experimentally determined values; values determined by difference are given in parentheses

^b From Refs. 3 and 4

UT=Untreated; TE=toluene extracted; D=demineralized; n.d.=not determined

	N/C	S/C	O/C
Humic acids from this study	0.016±0.002	0.017±0.003	0.28±0.02
Coal humic acid	0.016	0.007	0.33
Soil humic acid	0.04±0.01	0.005±0.007	0.49±0.04
Marine humic acid	0.086	—	0.49

Figure 1 van Krevelen diagram showing the elemental composition of humic acids from various feedstocks: ○, present study; ●, coal HA; □, soil HA; ■, marine HA

that in soil, coal and marine humic acids^{3,4,26}. However, the bitumen from these feedstocks also has a higher sulphur content, suggesting a common source for the two. The organic sulphur in the living organisms that led to the formation of humic matter and bitumen could not have been as abundant as in these samples, suggesting the incorporation of inorganic sulphur in humic matter during its formation²⁷.

Humic acids extracted from oil sands have a higher hydrogen content than humic acids extracted from other feedstocks. This is also reflected in higher H/C ratios. This is because the humic matter associated with overburden and tailings is more oxidized than the humic matter associated with oil sands. The presence of bitumen as a protective layer means that the humic matter from oil sands will be less susceptible to oxidation than the humic matter from other feedstocks.

Two classes of humic acids have been extracted from Victorian brown coal lithotypes²⁸: solvents extractable humic acids, and pseudo kerogen humic acids. Based on a comparison of the analytical data, it appears that humic acids from oil sands are similar to solvent extractable humic acids from brown coal, while humic acids from other feedstocks resemble pseudo kerogen humic acids from brown coal.

The generally low values for H/C in all samples suggest condensed aromatic ring structures, while the high O/C ratios may be indicative of the degree of oxygen substitution in these structures²⁸.

The van Krevelen diagram of atomic H/C versus O/C ratios provides a useful approach for the characterization of coals, kerogens and humic matter^{25,29}. Figure 1 is the van Krevelen diagram for all humic acid fractions listed in Table 3. The evolution paths of kerogens and humic coals are also shown for comparison. The data for marine and soil humic acids fall directly in the region of humic coals and humic acids, while the data from this study overlap with the regions of recent and shallow kerogens. This type of organic matter is usually derived from plants of terrestrial origin and is rich in polyaromatic nuclei and ketone and carboxylic acid groups²⁵. It is not considered to have potential for oil generation and usually matures to give coal. It appears to be of

comparable maturity to that of humic coals and is relatively immature on the basis of its oil generating potential.

The plots of H/C and O/C atomic ratios versus S/C and N/C ratios of various humic acid samples are shown in Figure 2. There is considerably more scatter of the data for S/C and N/C values than for the O/C values. However, there are correlations, although relatively poor, for S/C and N/C data with both H/C as well as O/C. Similar correlations have been reported for humic coals²⁷.

Proton n.m.r. spectra

Figure 3 shows typical proton n.m.r. spectra for humic acids. The samples were run in two solvents, deuterated DMSO and NaOD/D₂O. The spectra obtained in NaOD solution were broader than the spectra in deuterated DMSO. The spectra show three resolved signals in the aliphatic region. The signal at 0.8 ppm is the methyl ¹H resonance and the two peaks at 1.1 and 1.3 ppm are due to the methylene protons. A sharp and medium intensity peak observed around 2.4 ppm could be due to the protons attached to benzylic carbons³⁰.

Table 4 lists the proton aromaticities calculated by integrating peak areas assigned to aromatic hydrogens (6.5–8.0) and normalizing the total aromatic and aliphatic resonance areas. Also included are the proton aromaticities for soil and aquatic humic acids reported by Hatcher *et al.*³⁰. The following conclusions can be drawn from these data.

1. Humic acids extracted from oil sand tailings streams contain considerably more proton aromaticity (0.19–0.49) than humic acids extracted from oil sands and overburden feedstocks (0.2–0.3).
2. The proton aromaticity of humic acids from oil sands and related feedstocks is much greater than that of the aquatic humic acids. The values are comparable with those of the soil humic acids.

¹³C n.m.r. spectra

The solution ¹³C n.m.r. spectra of humic acids are

Figure 2 Elemental analysis of humic acids in an H/C versus S/C and N/C diagram

Figure 3 300 MHz ^1H n.m.r. spectra of: a, humic acid dissolved in NaOD; b, humic acid dissolved in DMSO- d_6 . The chemical shifts are reported as ppm downfield of TMS

Table 4 ^1H aromaticities of humic acids

Sample description	^1H aromaticity
Humic acid from oil sands 1	0.25
Humic acid from oil sands 2	0.30
Humic acid from overburden 1	0.20
Humic acid from Syncrude centrifuge tailings, 1st extract	0.49
2nd extract from above	0.49
3rd extract from above	0.19
Humic acid from OPS, 1st extract	0.48
2nd extract from above	0.24
Terrestrial humic acids ^a	0.17–0.35
Aquatic humic acids ^a	0.02–0.07

^a From Ref. 29

shown in Figure 4 and solid state spectra are illustrated in Figure 5. The solution spectra have an improved resolution especially for the aliphatic, acidic, aldehyde and ketonic peaks.

Although the basic features of the n.m.r. spectra of humic acids are similar, a few differences are noticeable.

1. The resolution in the aliphatic region of the solution spectrum of humic acid obtained from untreated overburden sample 1 is much better than for the spectrum of the humic acid from toluene extracted feedstock (Figure 4, spectra 3a and 3b).
2. Although there are distinguishable peaks in the carbohydrate region of the solution spectrum of the sample from untreated overburden-1, no such peaks are present in the spectrum of the sample from toluene extracted feedstock.
3. The solution spectra of the 1st and 2nd extracts from OPS (Figure 4, spectra 5a and 5b) are different in that the former has a much better resolution in the aliphatic

region and its aromatics carbon peak is sharper than in the latter spectrum.

The assignments are based on comparison with published spectra of humic acids and coals^{17,18,28,30–46}. The general features of all the spectra are similar to those found in the spectra of the coal humic acids. All spectra show a broad resonance extending from 10–50 ppm which is typical of methyl, methylene and methine carbons in a wide range of sterically hindered or highly branched environments. A considerable amount of fine structure in the 15–40 ppm region can be seen in the solution spectra of humic acids extracted from untreated oil sand sample 1, overburden sample 1, and OPS (Figure 4, spectra 1, 3a and 5).

The region from 50 to 110 ppm in the ^{13}C spectra is assigned to oxygen and nitrogen substituted carbons as in carbohydrates, ether, alcohols or amines. A broad area of resonance above the spectral baseline in this region is present in most of the spectra. A few spectra also show a small distinguishable broad resonance around 75 ppm. These resonances are predominantly due to carbohydrate carbons as in polysaccharides³³. However, the relative intensities of these peaks are very small indicating that polysaccharides are not major constituents. Carbohydrates are known to be far more susceptible to

Figure 4 ^{13}C n.m.r. spectra of humic acids in NaOD. Feedstocks: 1, untreated oil sands sample-1 (UTOSS-1); 2a, UTOSS-2; 2b, toluene extracted (TE) OSS-2; 3a, UT overburden-1; 3b, TE overburden-1; 4a, TE centrifuge tailings; 4b, as 4a, with solvent DMSO- d_6 ; 4c, as 4a, with 2nd extract; 5a, TEOPS; 5b, as 5a, with 2nd extract

Figure 5 CP/MAS ^{13}C n.m.r. spectra of humic acids. Feedstocks: a, TEOS-2; b, UTOB-1; c, TEOB-2; d, TE centrifuge tailings; e, as in d, with 3rd extract; f, TEOPS; g, OPS, 2nd extract

microbial degradation and hydrolysis than lignins and their minimal incorporation into these humic acid structures may reflect the greater age of the parent organic matter or a greater degree of decomposition²⁸.

The aromatic region extends from 110 to 160 ppm. Olefinic carbons also resonate in this region, but their contribution to the structure of humic substances remains unknown. All spectra show a broad peak in this region. The relative intensity of this peak centred around ≈ 130 ppm indicates that a large proportion of the aromatic rings are not substituted by oxygen or nitrogen.

Thus most of the resonance in this region is due to the proton bearing aromatic carbon, bridgehead and alkyl substituted carbon. The phenolic carbons in the humic acids are not resolvable as distinct peaks.

The humic acid sample extracted from toluene extracted overburden 1 (Figure 4, spectrum 3b), contains a very sharp peak at 168 ppm which is characteristic of the carbonate carbon. A distinct peak is observed at ≈ 175 ppm in all ^{13}C spectra of humic acids. This band represents carboxylic, amide and ester carbons, all of which have been identified as important functionalities of humic acids²⁶.

Table 5 lists the percentage composition of various regions calculated from the integrated area of the regions. The position of regional boundaries in spectra is a matter of definition, as no representative model compounds for these substances are available. The limits were chosen according to Verheyen *et al.*²⁸ and Ibarra *et al.*⁴². Interpretation of these data reveals the following.

1. Paraffinic carbons contribute from 20–55% of the total carbons in these humic acid samples.
2. Of the total carbon, 29–38% is aromatic.
3. The amounts of carbohydrate, phenolic, and carboxylic, amide, ester, aldehyde, and ketonic carbons also vary greatly among these humic acid samples. They range from 1.5 to 9%, 1 to 11% and 5.5 to 19%, respectively.
4. Humic acid extracted from untreated oil sands-2 has more paraffinic and phenolic carbon and less carbohydrate and carboxylic, amide, aldehyde, and ketonic carbon, than the samples obtained from toluene extracted feedstock.
5. The amount of paraffinic carbon increases with successive extractions.

The structural contribution of ethers and alcohols to the humic acids can be postulated as minor, because of the absence of distinguishable resonances attributable to these oxygen linkages. An insight into the significance of oxygen bonded carbon resonances in the aliphatic region can be made by comparing O/C ratios. If all the oxygen in the humic acid structure were present in carboxylic and phenolic functions, the O/C ratio calculated as a result of this assumption (see Table 5) should be comparable with that from elemental analysis (Table 3). The small contribution of carbonyl resonances to region D_1 should result in overestimation of the O/C ratio calculated by ^{13}C n.m.r..

The presence of ether oxygen linkages and alcohols can be confirmed by a comparison of the difference in the O/C ratios (Table 5). Despite the closeness of the values, the humic acid structures do contain oxygen which is not present as carboxyl and phenolic functions, as revealed by negative differences for O/C ratios in this table. The total contribution of these aliphatic oxygen functions to the humic acid structures cannot be defined further on the basis of these data or from the ^{13}C n.m.r. spectra themselves. However, it is a minor component compared with the proportion of carboxylic and phenolic functional groups.

Table 6 lists the aromaticities (f_a) calculated by integrating peak areas assigned to aromatic carbons (100–160 ppm) and normalizing to total area less the area of carboxyl carbons⁴¹. The values range from 0.4 to 0.69. These values are considerably higher than those reported for soil or aquatic humic acids. The higher values are closer to the ones reported for humic acids from Victorian

Table 5 Relative intensities for various regions of the ^{13}C n.m.r. spectra of humic acid fractions

Feedstock	Total intensity (%)					Atomic O/C ratio ^a	Δ^b
	0–50 ppm (A_1)	50–110 ppm (A_2)	110–145 ppm (B)	145–160 ppm (C)	160–220 ppm ($D_1 + D_2$)		
UTOS-1	35.3	—	41.7	6.9	16.1 ^c	0.32	0.07
UTOS-2	31.9	8.8	44.1	6.5	8.7	0.24	–0.02
TEOS-2	20.7	5.5	57.8	7.4	8.6	0.25	–0.08
UTOB-1	55.6	4.8	29.0	5.1	5.5	0.16	–0.08
TEOB-2	25.8	7.2	49.0	8.1	9.9 ^c	0.28	0.0
TESCT	27.1	2.7	45.8	9.7	14.7	0.28	0.03
TESCT, 2nd extract	30.2	2.8	41.6	11.1	14.3	0.29	0.04
TESCT, 3rd extract	42.5	5.6	36.4	4.6	10.9	0.13	–0.12
OPS	23.6	1.5	45.1	10.8	19.0	0.30	0.01
OPS, 2nd extract	34.8	2.0	55.1	1.4	6.7	0.13	–0.15

$$^a \text{O/C} = \frac{C + 2D_1}{100}$$

$$^b \Delta = \text{O/C } (^{13}\text{C n.m.r.}) - \text{O/C (elemental analysis)}$$

^cExcluding the intensity of the carbonate peak
Table 6 Carbon aromaticities of humic acids

Feedstock/sample description	f_a
UTOS-1	0.57
UTOS-2	0.55
TEOS-2	0.54
UTOB-1	0.40
TEOB-1	0.64
TEOB-2	0.62
TESCT, 1st extract	0.65
TESCT, 2nd extract	0.62
TESCT, 3rd extract	0.46
OPS, 1st extract	0.69
OPS, 2nd extract	0.61
Subbituminous coal	0.59
Soil	0.35
Kerogen from New Brunswick oil shales	0.28
Oil sands bitumen	0.30
Asphaltenes from oil sands bitumen	0.42

Figure 6 Aromaticity versus H/C and O/C ratios for humic acids: ○, data for H/C ratios; ●, data for O/C ratios

brown coal lithotypes²⁸. Since high aromaticity is a characteristic of contribution from vascular plants⁴⁴, it is likely that the humic matter associated with oil sands has a large contribution from terrestrial sources.

Figure 6 is a plot of the aromaticity versus H/C and O/C atomic ratios. Considering the limitations of n.m.r. measurements and elemental analysis, a fairly good correlation between increased aromaticity and increased O/C and decreased H/C ratios is obvious when the data points for the 3rd extract from SCT and humic acids from UTOB-1 are excluded. This reflects the decreasing content of paraffinic carbons and increased ring polycondensation⁴⁷. Similar correlations have been reported for coal⁴⁸.

Successive extractions from tailings stream material result in a material of low aromaticity. This suggests that the outer layer of the organic matter associated with this material could be different from the inner layer.

Humic acid extracted from untreated overburden-1 has the lowest aromaticity of all the samples. However, the aromaticity of the sample obtained from the toluene extracted feedstock is in the same range as for the other

sample. The reason for this discrepancy is not understood.

Dipolar dephasing experiments

To distinguish carbon directly bonded to a hydrogen from carbons not directly bonded to hydrogens, a dipolar dephasing experiment was also carried out for humic acid samples from Syncrude centrifuge tailings and OPS^{17,49}. These spectra are shown in Figure 7: 1b, 2b and 3b are the dipolar dephased spectra, and 1c, 2c and 3c are the differences between the normal spectra (1a, 2a and 3a) and those obtained using a dipolar dephasing time of 40 μs . The dipolar dephased spectra generally show quaternary aliphatic carbons and carbons in the interior of the aromatic rings. The carbons of the rotating methyl groups can show about 60% of their intensity in the dephased spectra. The difference spectrum represents mostly methyl, methylene and methyne carbons in the aliphatic region and perimeter carbons in the aromatic region. The signals for the non-proton bearing carbons are noticeably downfield from the proton bearing ones.

Figure 7 Dipolar dephased spectra of humic acids: a, delay time 0.5 μ s; b, delay time 40 μ s; c, difference spectrum (a-b); 1, third extract from centrifuge tailings; 2, first extract from OPS; 3, second extract from OPS

The following conclusions can be drawn.

1. Most of the signals in the aliphatic region are due to methyl, methylene and methyne carbons. The proportion of the proton bearing carbons in the aliphatic region, as calculated from the integrated areas of the dipolar dephased and difference spectra, range from 65 to 80% of the total aliphatic carbons.
2. The distribution of the two different types of carbons in the aromatic region calculated from the integrated areas of the dipolar dephased and the difference spectra indicate that carbons directly bonded to hydrogen constitute 50-65% of the total aromatic carbons.
3. Phenolic and carboxylic carbon signals are better resolved in the dipolar dephased spectra.

In comparison with ^{13}C n.m.r. spectra for humic acids from subbituminous coal and peat, the spectra of oil sand humic acids show a resemblance between the oil sands and subbituminous coal humic acids. This suggests that oil sands humic acids are of comparable maturity to those from subbituminous coal.

Infrared spectra

Humic acid samples extracted from oil sands and tailings streams had similar infrared spectra, but the sample extracted from overburden-1 had a slightly different spectrum. Figure 8 shows infrared spectra for two humic acid samples: one from oil sands or tailings streams, and the other from overburden-1. The assignment of the various bands in the infrared spectra is based on the published work for coal, asphaltenes and humic materials⁵⁰⁻⁵⁷. The main zones of interest are as follows. A broad absorption band around 3200-3400 cm^{-1} , related to H-bonded OH groups (phenolic, alcoholic, carboxylic OH), with small contributions from N-H groups also being possible. A weak band around 3060 cm^{-1} attributed to aromatic C-H. This band occurs at considerably higher frequency than the $\approx 3030 \text{ cm}^{-1}$ found for asphaltenes, suggesting that the

Figure 8 Infrared spectra of: a, humic acid obtained from oil sands; b, humic acid from overburden-1

number of aromatic rings in humic acids is considerably lower than that for asphaltenes⁵³.

Weak to strong absorptions in the $\approx 2900\text{ cm}^{-1}$ region are attributed to CH_2 and CH_3 aliphatic groups, and a medium to strong intensity band around $1700\text{--}1730\text{ cm}^{-1}$ is related to various $\text{C}=\text{O}$ groups (ketones, acids, esters). A weak to medium intensity band centred at 1600 cm^{-1} can be attributed partly to conjugated $\text{C}=\text{C}$ bonds and partly to carbonyl of ketones and/or quinones, while varying intensity bands at 1450 and 1380 cm^{-1} are due to bending frequencies of asymmetric $\text{C}-\text{CH}_3$ bonds and/or methylene and symmetric $\text{C}-\text{CH}_3$ bonds, respectively.

A group of bands located in the $1300\text{--}900\text{ cm}^{-1}$ region is assigned to $\text{C}-\text{O}$ stretch in aromatic oxygenated compounds, such as aromatic ethers, sulphoxides and polysaccharides. A number of absorptions in the $800\text{--}500\text{ cm}^{-1}$ region are considered aromatic out-of-plane frequencies and are important with regard to the nature of the structure of aromatic clusters.

Stevensen and Goh⁵⁶ distinguished three types of infrared spectra in humic and fulvic acids depending upon the absorption in the $1600\text{--}1700\text{ cm}^{-1}$ region. The type I spectrum, which is typical of those generally shown by most humic acids, showed equal absorption at ≈ 1700 and 1600 cm^{-1} . Type II spectra, represented by some fulvic acid preparations, had a strong 1700 cm^{-1} band with only a shoulder at 1600 cm^{-1} . Type III, isolated from recent lake sediments and some Podzol soils had a broad band centred at $1620\text{--}50\text{ cm}^{-1}$ with only a weak shoulder at 1720 cm^{-1} . According to the above authors, type III spectra are indicative of humic compounds synthesized without the participation of lignin. Furthermore this type contained more peptide linkages as indicated by a strong shoulder in the $1520\text{--}40\text{ cm}^{-1}$ region.

In the present results, the infrared spectra resemble only the type I and type II spectra. Humic acids extracted from oil sands and tailings streams give type I spectra, suggesting that these samples could be structurally similar to typical soil and coal humic acids. The infrared spectrum of the humic acid obtained from overburden-1 is typical of a type II spectrum. The humic acids from overburden also contain considerably more oxygenated compounds, such as aromatic ethers and polysaccharides, as compared with the oil sands humic acids. These facts can be interpreted in terms of greater maturity of the oil sands humic acids than the humic acids from overburden.

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