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Characterization of Sulfur Compounds in Oilsands Bitumen by Methylation Followed by Positive-Ion Electrospray Ionization and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Sulfur compounds in Canadian oilsands bitumen were reacted with methyl iodide in the presence of silver tetrafluoroborate and converted to methylsulfonium salts. The methylsulfonium salts were characterized by positive-ion electrospray ionization (ESI) and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS). Heteroatoms were characterized by their class (number of nitrogen, oxygen, and sulfur heteroatoms), type [rings plus double bonds (DBE)], and carbon number distribution. The S_1, S_2, S_3, O_1S_1, O_1S_2, O_2S_1, and N_1S_1 sulfur-containing class species were identified in bitumen-derived methylsulfonium salts. The molecular weights of the sulfur compounds were varied from 200 to 700 Da. The S_x class species were the predominant heteroatom compounds. The S_1, S_2, and S_3 class species comprised 74%, 11%, and 1%, respectively, of the total identified species. As the sulfur atom number increased, the DBE of the abundant S_x class species shifted to a higher value. Sulfur species identified from the spectrum had a DBE value of less than 20. The potential molecular structures of heteroatom classes were inferred from the DBE distribution and carbon number data. Methylation followed by ESI MS is an effective technique for sulfur speciation of bitumen.

Introduction

Canadian oilsands are an important source of hydrocarbons, representing as much as two-thirds of the total world petroleum reserve.[1] Bitumen extracted from oilsands is a highly viscous hydrocarbon liquid with a high density and high concentrations of heteroatom compounds. As a result, processing bitumen into transportation fuels is technically challenging.

Hydrodesulfurization (HDS) is a commercial refinery process used in bitumen upgrading to produce ultralow sulfur transportation fuels.[2,3] Because of the requirements of increasingly stringent environmental legislation, work is being done on the catalyst and reaction system used in the HDS process. Information on the detailed composition of sulfur compounds in the feedstock is a key parameter required for catalyst development.

Although many techniques and equipment have been developed and used to characterize the composition of a petroleum feedstock, high-resolution mass spectrometry (MS) is the analytical tool most frequently used. Double-focusing MS (DFMS) provides in-depth compositional information on the distribution and elemental composition of hydrocarbon molecules.[4–7] However, the traditional high-resolution MS, DFMS, and time-of-flight MS have inadequate resolution power to distinguish individual mass peaks for the full mass range of a petroleum feedstock.

Fourier transform ion cyclotron resonance MS (FT-ICR MS) has been widely used in biological sciences. It has been successfully used for petroleum analysis, leading to a science of "petroleomics".[8–11] The ultrahigh-resolution power and mass accuracy of FT-ICR MS provides more precise elemental composition analysis of complex petroleum compounds. The data obtained from FT-ICR MS analysis have resolved many issues related to petroleum species, such as the molecular weight distribution of heavy petroleum[12] and the

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self-association of polar compounds in petroleum.[13,14] Combined with low-energy electron-impact ionization (EI),[15−17] and various soft ionization techniques, such as electrospray ionization (ESI),[18−22] atmospheric pressure photoionization (APPI),[23−25] atmospheric pressure laser ionization (APLI),[26] atmospheric pressure chemical ionization (APCI),[26] matrix-

assisted laser desorption (MALDI),[26] and field desorption/field ionization (FD/FI),[27−31] FT-ICR MS is capable of determining the composition of a wide range of complex species, such as crude oil,[18−21,32−34] coal,[35−37] and bitumen.[28,31,38,39]

The use of FT-ICR MS in analyzing sulfur compounds for petroleum products has been reported elsewhere.[23,26,40−43] To transform the neutral thiophenes into ions in solution so that they can be easily transferred into the gas phase in the ESI source, Muller et al.[40] converted sulfur compounds into methylsulfonium salts by reacting them with methyl iodide in the presence of silver tetrafluoroborate. The methylsulfonium

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salts were characterized using positive-ion ESI/FT-ICR MS. It was found that ESI MS with derivatization was highly selective toward sulfur species in the complex hydrocarbon matrix. Initially, it was suspected that the methylation discriminated against the polar aromatic sulfur hydrocarbons (PASHs) with rings plus double bonds (DBE) greater than 10.[23] A recent study[26] investigated phenylation and methylation procedures for the PASHs by ESI, MALDI, APCI, APPI, and APLI. It was concluded that methylation does not discriminate against polar aromatic sulfur compounds; variation in the MS data is dependent on the ionization technique.[26]

In this paper, a detailed elemental composition of sulfur species in oilsands bitumen was determined by methylation followed by ESI/FT-ICR MS analysis. The sulfur species in oilsands bitumen were characterized by the relative abundances for each class (number of nitrogen, oxygen, and sulfur heteroatoms), type (DBE), and carbon number distribution. The sulfur compound types were determined based on the DBE distribution, minimum carbon number, and other compositional information reported in the literature.
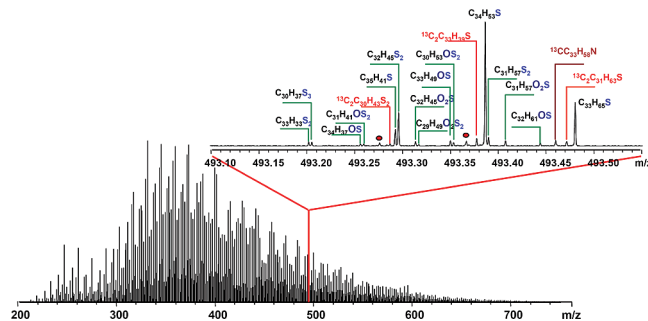
Experimental Section

Oilsands bitumen. Oilsands bitumen was obtained from a commercial mining oilsands plant in Fort McMurray, Alberta, Canada. The amount of sulfur and nitrogen in the bitumen was 4.5 and 0.4 wt %, respectively, measured by an ANTEK 9000 pyrofluorescence analyzer (ANTEK Instruments, Houston, TX) according to the ASTM D-5453 method.
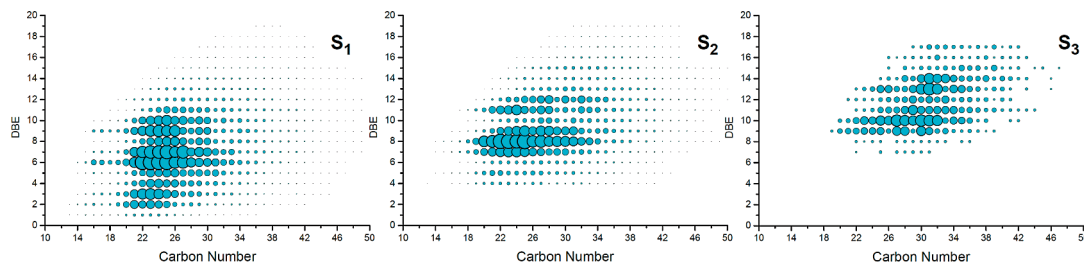
Methylation of Sulfur Compounds and Sample Preparation. Bitumen (200 mg) was diluted with 20 mL of dichloromethane (CH_2Cl_2). A total of 50 μL of methyl iodide and 2 mL of silver tetrafluoroborate in 1,2-dichloroethane (20 mg·mL^{-1}) were added to the bitumen solution. The mixture in a beaker was immersed in an ultrasonic bath for 5 min and allowed to react at room temperature for 48 h. The precipitate of silver iodide was removed by centrifugation and then rinsed with CH_2Cl_2. The methyl thiophenium salts and the unreacted oil were obtained by evaporating CH_2Cl_2 from the centrifuged solution.[26,40] A total of 5 μL of hexane was added to the mixture, and most of the unreacted oil was dissolved in the mixture and separated from the methyl thiophenium salts.

Thiophenium salts (10 mg) were diluted with 1 mL of CH_2Cl_2. A total of 5 μL of a thiophenium salt solution was diluted with 1 mL of a toluene/methanol/CH_2Cl_2 (3:3:4) solution. All solvents used were analytical-grade commercial products (from Beijing Chemical Reagents Company, Beijing, China), which were distilled twice and kept in glass bottles with ground-glass stoppers. Glassware was used for the solvent handling and transfer systems, except for the 10 μL Hamilton syringes with steel pistons.

FT-ICR MS Analysis. The thiophenium salt solution was analyzed using a Bruker Apex ultra FT-ICR mass spectrometer equipped with a 9.4 T superconducting magnet. The sample solution was infused via the Apollo II electrospray source at 150 μL h^{-1} by using a syringe pump. The conditions for positive-ion formation were −2.5 kV emitter voltage, −3.0 kV capillary column introduced voltage, and 320 V capillary column end voltage. Ions accumulated for 0.1 s in a hexapole with 2.4 V direct current and 300 Vp-p radio-frequency (RF) amplitude. The optimized mass for Q1 was 250 Da. Hexapole collision pool were operated at 5 MHz and 400 Vp-p RF amplitude, in which ions accumulated for 4 s. The transfer time was set to 1.2 ms to transfer the ions to an ICR cell by electrostatic focusing of transfer optics. The ICR mass spectrometer was operated at 11.75 db attenuation, 202−750 Da mass range, and 4 M acquired data size, and time-domain data sets of 256 acquisitions were coadded.

Figure 1. Broad-band positive-ion ESI/FT-ICR MS spectrum of the methylation-generated bitumen. The inset shows an expanded mass scale spectrum at *m/z* 493. Compounds were distinctly identified based on mass measurement except the two dotted peaks.

Figure 2. Heteroatom class (number of heteroatoms) and type (double bond equivalent) distribution for methylated bitumen derived from a positive-ion ESI/FT-ICR MS spectrum. The inset bar chart above shows the expanded scale relative abundances of all heteroatoms on the S_1 class species free basis. Note: Data are summed mass spectrometric intensities, not quantitative for the abundance of species in the sample.

Results and Discussion

Classes and Types of Heteroatoms in Thiophenium Salts. Figure 1 shows the broad-band positive-ion ESI/FT-ICR MS spectrum of the methylated bitumen. The data indicate that the molecular weight of sulfur compounds in oilsands bitumen varied from 200 to 700 Da. The inset in Figure 1 shows an expanded mass scale spectrum at *m/z* 493 for isobaric compounds. Certain peak pairs, such as $C_{33}H_{33}S_2$/ $C_{30}H_{37}S_3$ and $C_{35}H_{41}S$/$C_{32}H_{45}S_2$, have a mass difference of 3.4 mDa. This is due to the addition of a sulfur atom and four hydrogen atoms "in exchange" for three carbon atoms. These peak pairs were well-resolved throughout the entire mass range. The resolving power was greater than 400 000 ($m/\Delta m$ 50%) at *m/z* 493, ensuring accurate elemental composition assignment of equal magnitude at *m/z* 500. The peak identifications were obtained without subtraction of the mass of the derivatization group. There is an additional methyl on one of the sulfur atoms because of methylation of the sulfur compounds at the reaction conditions.

Figure 2 shows the class (number of heteroatoms) and type (DBE) analysis of the sample. Relative abundance is defined as the magnitude of each peak divided by the sum of the magnitudes of all identified peaks (exclude the isotopic peaks) in the MS spectrum. The data shown in Figure 2 are the summed mass spectrometric intensities but do not quantitatively reflect the abundance of species in the sample.
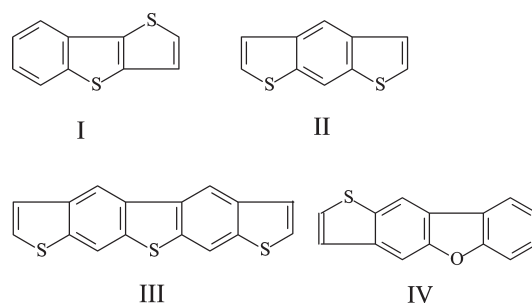
Figure 3. Plots of DBE as a function of the carbon number for S_x class species in methylated bitumen from positive-ion ESI/FT-ICR MS.

The relative abundances of the total identified peaks of S_1, S_2, and S_3 class species were 74%, 11%, and 1%, respectively. The inset bar chart shows the expanded-scale relative abundances of all identified peaks, which were normalized on an S_1 class species free basis. The S_1 class species, especially those with 2−12 DBE, were most abundant, followed by the S_2 class species. The order of relative abundances of sulfur class species is $S_1 > S_2 > O_1S_1 > O_2S_1 > N_1S_1 \approx O_1S_2 > S_3$.

S_x Class Species. Figure 3 shows the isoabundance map of DBE as a function of the carbon number for the S_x class species from the positive-ion ESI/FT-ICR MS spectrum of methylated bitumen. The most abundant S_x class species had 2−10 DBE and 20−30 carbon number. The carbon numbers along the *x* axis of Figure 3 include carbon atoms of the derivatization groups in methylated bitumen, which had one carbon atom more than those in the original bitumen sample. The S_1 class species, which was the most abundant species in the sample, varied over a wide range of DBE (1−19) and carbon number (10−50). A DBE value of 1 indicates that the alkyl sulfides did not exist or had very low concentrations in the species. The S_1 class species with DBE of 1 and 2 were sulfides with one and two cyclic rings. Thiophenes have a DBE value of 3. Figure 3 shows that the S_1 class species with 3 DBE had a high abundance. These compounds could be three cyclic-ring sulfides and/or thiophenes. Benzothiophene was the most abundant S_1 class species with 6 DBE. Some of the other compounds were benzo homologues of two cyclic-ring sulfides. The S_1 class species with a DBE value of 7 is referred to as either a benzo homologue of tetrahydrobenzothiophenes (one aromatic and one naphthenic ring) or phenylthiophene. The S_1 class species with 9 and 10 DBE were the benzo homologues with 6 and 7 DBE, respectively. The S_1 class species with carbon numbers fewer than 20 and DBE values of 6 and 9 had relatively high abundance. This finding is consistent with the gas chromatography (GC) analysis, which indicated that benzothiophenes and dibenzothiophenes were dominant in the sulfur-selective chromatogram.[44]

The upper limits of DBE values for S_2 and S_3 class species were similar to that of the S_1 class species; however, the minimum DBE value increased as the number of sulfur atoms increased. The sulfur atoms in S_2 and S_3 class species are likely in the form of cyclic sulfides or thiophenic compounds. If they were alkyl sulfides, the minimum DBE values for S_2 and S_3 class species would be lower than those shown in Figure 3. The S_2 class species with 8 DBE were most abundant. They are likely benzodithiophenes with a type I

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Scheme 1

and II core structure (Scheme 1). The 11 DBE species were the benzo homologues derived from 8 DBE species. The DBE values of S_3 class species varied from 7 to 17, with maxima at 10 and 13 DBE. Most of these species were likely conjugated benzothiophenes or dibenzothiophenes with two thiophenes with a possible type III core structure.
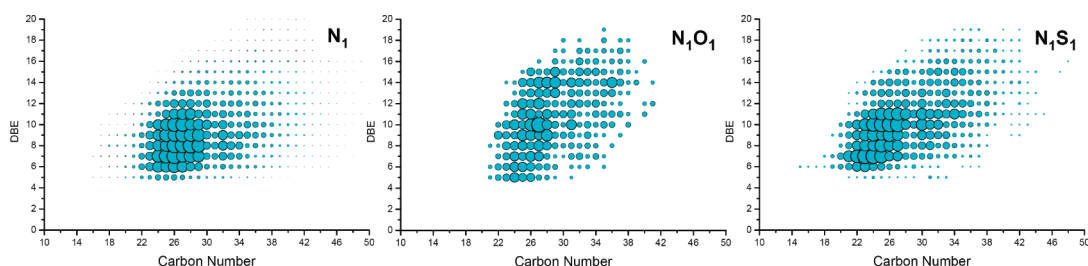
O_yS_x Class Species. Figure 2 shows that O_1S_1, O_2S_1, O_1S_2, and O_2S_2 were the abundant O_yS_x class species in the bitumen. Figure 4 shows the isoabundance map of DBE as a function of the carbon number for O_1S_1, O_2S_1, and O_1S_2 class species in methylated bitumen from the positive-ion ESI/FT-ICR MS analysis. The O_1S_1 class species were the most abundant class species among the O_yS_x species, with DBE varying from 2 to 19. The multimodal DBE distributions with maxima of DBE at 2−8, 11, and 14 suggest that O_1S_1 class species have various core structures. The O_1S_1 class species with a minimum DBE value of 2 are likely to have the core structure of two cyclic-ring sulfides with a hydroxyl group, or they are sulfoxides. A recent study[39] has showed that there is a higher abundance of O_1S_1 class species in the acid-free fraction of Athabasca bitumen-derived heavy vacuum gas oil than in bulk vacuum gas oil samples. This indicates that some of the O_1S_1 class species are not acid compounds. Most of the oxygen atoms present in the O_1S_1 class species are not in a hydroxyl form. The O_1S_1 class species with 11 DBE are likely to have a core structure of dibenzofuran flanked on a thiophene, which has a structure similar to that of type IV. The O_1S_1 class species with 14 DBE are likely benzo homologues with 11 DBE.

The O_2S_1 class species exhibit a bimodal DBE distribution with maxima at DBE of 3−4 and 7−8. The DBE distribution resembles that obtained from negative-ion ESI MS of bitumen distillation cuts.[31] This suggests that these compounds are acidic and the oxygen atoms exist in the form of a carboxyl functional group. The O_2S_1 class species with a minimum DBE value of 3 are likely to have a core structure of two cyclic-ring sulfides with a carboxyl group. The O_2S class species with 4 DBE were cyclic sulfides with carboxyl acid and/or thiophenes with a carboxyl group. The high
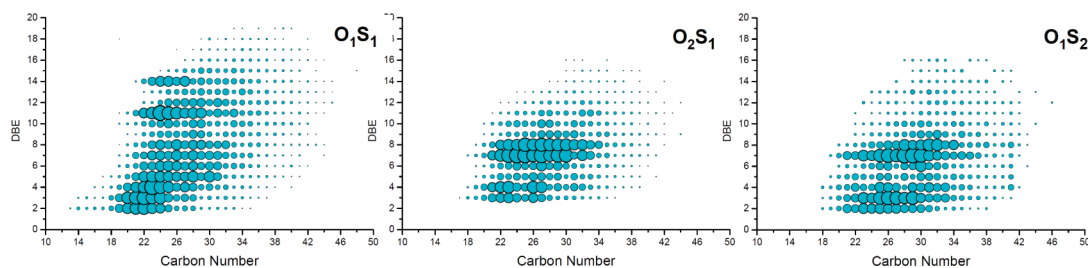
Figure 4. Plots of DBE as a function of the carbon number for O_yS_x class species in methylated bitumen from positive-ion ESI-FT-ICR MS.

Figure 5. Plots of DBE as a function of the carbon number for nitrogen-containing species in methylated bitumen from positive-ion ESI/FT-ICR MS.

relative abundance of two- and three-ring sulfides with carboxyl groups correlated with the high relative abundance of S_1 class species with two- and three-ring sulfides.

Figure 4 shows that the O_1S_2 class species with 3 and 7 DBE were in high abundance. However, the pattern of the distribution map was significantly different from that of S_2 class species shown in Figure 3. This indicates that the forms of the two sulfur atoms in O_1S_2 class species are not the same as those of S_2 class species. This suggests that sulfoxides are likely the key compounds of the O_1S_2 class species.

Nitrogen-Containing Species. Figure 5 shows plots of DBE as a function of the carbon number for N_1, N_1O_1, and N_1S_1 class species. The N_1 class species varied over a wide range of DBE values and carbon numbers. The relatively highly abundant N_1 class species were at 5–13 DBE and 22–33 carbon numbers. The lowest DBE value of the N_1 class species was 4, and the relative abundance increased at a DBE of 5. The N_1 class species with 4 DBE were alkylpyridines, which were in relatively low abundance. Species with 5–6 DBE were naphthenic pyridines, for which ESI MS exhibits a higher selectivity than an EI source.[45]

The nitrogen atom in the N_1S_1 class species exhibits either basic or nonbasic characteristics. The DBE value of abundant N_1S_1 class species was shifted one number higher than that of the N_1 species. This indicates that a cyclic-ring sulfide is attached to a mononitrogen species. The N_1S_1 class species with 7 and 10 DBE were the most abundant, consisting of thiophenoindoles and thiophenocarbazoles. The N_1O_1 class species had a very low abundance. The DBE distribution of N_1O_1 species resembles that of N_1 and N_1S_1 species.

Sulfur Species with DBE Greater Than 20. The results from this study show that the upper limit of the DBE value for the sulfur-containing heteroatoms in oilsands bitumen is 20. This finding is accurate for a number of reasons. ESI MS is a powerful technique used to detect trace amounts of polar

compounds in a complex petroleum matrix. However, for structurally diverse compounds, the relative magnitudes of ESI MS peaks of heteroatoms cannot be quantitatively correlated to the relative abundances of their neutral precursor compounds in the original sample for various ionization efficiencies.[22] Our data concur with those reported in other studies that used high-resolution magnetic MS[15] and FT-ICR MS,[17,27,31] with either FD[27,31] or EI[15,17] ion sources, which indicated that the DBE value varied from 0 to 20 for sulfur species in crude oil and bitumen. Moreover, the relative abundances of S_2 and S_3 to S class species in crude oil and bitumen obtained from FD, EI, and ESI are in agreement.[11,13,23,27] However, APPI analysis is biased toward high relative abundances of S_2 and S_3 to S class species.[23] Because the S_2 and S_3 class species have a more condensed core structure than the S_1 class species and APPI is selective toward ionization of highly condensed species, trace amounts of S_2 and S_3 class species can be detected by APPI in a limited dynamic range, even in the presence of abundant S class species.

For a mass spectrometer equipped with FD ion sources,[27,31,46] analysis results indicate that the DBE value of abundant species in petroleum hydrocarbons do not exceed 20. For example, coronene, which has the most condensed core structure among the thousands of species identified in crude oil analyzed by GC–MS, has 18 DBE. In theory, because of the low solubility of highly condensed species, low concentrations of high DBE species in crude oil or bitumen are expected in the analyte solvent. Another factor to be considered is that the dynamic range of FT-ICR MS is less than 10 000,[27] whereas the relative concentration of petroleum species varies over millions. Hence, the high DBE species would be masked by the low DBE species, which have a relatively high abundance within the dynamic range of the instrument.

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Conclusions

Various heteroatom classes, such as S_1, S_2, S_3, O_1S_1, O_1S_2, O_2S_1, and N_1S_1, were identified in oilsands bitumen by means of methylation followed by positive-ion ESI MS. The molecular weight of the heteroatom compounds varied from 200 to 700 Da. The S_x class species were the predominant heteroatom compounds. The relative abundance of S, S_2, and S_3 class species comprised 74%, 11%, and 1% of the total identified species, respectively. As the sulfur atom number increased, the DBE of the abundant S_x class species shifted to a higher value. Sulfur species identified in bitumen had less than 20 DBE. The possible forms of heteroatoms in the core structure of S_x, S_xO_y, and nitrogen-containing class species were inferred from the DBE distribution and minimum carbon number data, as well as information reported in the literature. Methylation followed by ESI MS is an effective technique for sulfur speciation of bitumen.