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# Molecular Characterization of Sulfur Compounds in Venezuela Crude Oil and Its SARA Fractions by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Venezuela crude oil was separated into saturates, aromatics, resins, and asphaltenes (SARA) fractions. The sulfur compounds in the crude oil and its SARA fractions were reacted with iodomethane 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 mass spectrometry (FT-ICR MS). The $S_1$, $S_2$, $S_3$, $O_1S_1$, $O_1S_2$, $O_2S_1$, and $N_1S_1$ class species were identified in crude oil derived methylsulfonium salts. The molecular composition and mass distribution of sulfur compounds in the subfractions were distinctly different. Small amounts of $S_1$ class species (cyclic-ring sulfides) were present in the saturates fraction. Thiophenic sulfur compounds were dominant in the aromatics fraction. Complex multiheteroatoms ($N_1S_y$, $O_xS_y$, and $N_1O_xS_y$ class species) were present in the resins and asphaltenes fractions. The relative abundance plots of double-bond equivalence (DBE) versus the carbon number of $S_1$, $S_2$, $O_1S_1$, and $O_2S_1$ class species showed that as the molecular polarity of the fraction increased, the DBE values of the abundant $S_y$ class species increased. SARA fractionation isolates the highly aromatic sulfur species in the resins and asphaltenes fractions, which are not observed in the parent crude oil sample.

## Introduction

Sulfur-containing compounds are the most abundant of the heteroatom species found in petroleum. They must be removed in refining operations to produce clean transportation fuels. Hence, detailed characterization of sulfur compounds is needed to develop hydrodesulfurization catalysts and optimize refining processes.

In light distillate fractions, sulfur-containing compounds can be readily analyzed using gas chromatography (GC) with sulfur selective detection[1] or mass spectrometry (MS).[1−3] However, due to the complex nature of crude oils and limitations inherent in the analytical technique, it is difficult to characterize sulfur compounds that are present in low concentrations in the heavy fractions. Before analyses can be done, various fractionation techniques have to be used to isolate certain groups of compounds or to simplify the analyte composition.

Saturates, aromatics, resins, and asphaltenes (SARA) fractionation is a commonly used fractionation technique for petroleum samples.[4] Information on the thousands of species found in the saturates and aromatics fractions of petroleum has been successfully characterized by GC-MS.[5] However, the species in the resins and asphaltenes fractions are nonvolatile high-boiling materials, so GC-MS analysis is not suitable.[6] Most of the molecular information on resins and asphaltenes is derived from bulk properties, such as elemental composition. Recently, positive and negative ion electrospray coupled with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been applied to characterize the SARA fractions of crude oil and bitumen. These studies reveal detailed molecular composition and distribution of heteroatom class species in the subfractions of highly complex hydrocarbon mixtures.[7,8]

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(1) Schade, T.; Andersson, J. T. Speciation of alkylated dibenzothiophenes in a deeply desulfurized diesel fuel. *Energy Fuels* **2006**, *20* (4), 1614–1620.

(2) Depauw, G. A.; Froment, G. F. Molecular analysis of the sulphur components in a light cycle oil of a catalytic cracking unit by gas chromatography with mass spectrometric and atomic emission detection. *J. Chromatogr., A* **1997**, *761* (1−2), 231–247.

(3) Shi, Q.; Xu, C.; Zhao, S.; Chung, K. H. Characterization of heteroatoms in residue fluid catalytic cracking (RFCC) diesel by gas chromatography and mass spectrometry. *Energy Fuels* **2009**, *23* (12), 6062–6069.

(4) Kharrat, A. M.; Zacharia, J.; Cherian, V. J.; Anyatonwu, A. Issues with comparing SARA methodologies. *Energy Fuels* **2007**, *21* (6), 3618–3621.

(5) Waldo, G. S.; Carlson, R. M. K.; Moldowan, J. M; Peters, K. E.; Penner-Hahn, J. E. Sulfur speciation in heavy petroleums: Information from X-ray absorption near-edge structure. *Geochim. Cosmochim. Acta* **1991**, *55* (3), 804–814.

(6) Rudzinski, W. E.; Zhou, K.; Luo, X. Mass spectrometric characterization of organosulfur compounds using palladium(II) as a sensitivity-enhancing reagent. *Energy Fuels* **2004**, *18* (1), 16–21.

(7) Shi, Q.; Hou, D.; Chung, K. H.; Xu, C.; Zhao, S.; Zhang, Y. Characterization of heteroatom compounds in a crude oil and its Saturates, Aromatics, Resins, and Asphaltenes (SARA) and non-basic nitrogen fractions analyzed by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2010**, *24* (4), 2545–2553.

(8) Klein, G. C.; Angström, A.; Rodgers, R. P.; Marshall, A. G. Use of saturates/aromatics/resins/asphaltenes (SARA) fractionation to determine matrix effects in crude oil analysis by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2006**, *20* (2), 668–672.

FT-ICR MS[9] is an emerging technique which has been successfully used for petroleum analysis, leading to a new field of "petroleomics".[10–13] The ultrahigh resolution and mass accuracy of FT-ICR MS enables the assignment of a unique elemental composition to each peak in the mass spectrum of a petroleum sample. Different soft ionization techniques such as low voltage electron impact ionization (EI),[14–16] electro-

spray ionization (ESI),[17–23] atmospheric pressure chemical ionization (APCI),[24] atmospheric pressure photoionization (APPI),[25–28] atmospheric pressure laser ionization (APLI),[24,29] field desorption/field ionization (FD/FI),[30–32] and matrix-assisted laser desorption ionization (MALDI)[24] have been coupled to FT-ICR MS to characterize complex petroleum mixtures.[33–35]

Low-voltage electron ionization is used for the highly volatile compounds in these ionization techniques.[16] ESI is not suitable for relatively nonpolar compounds such as polycyclic aromatic sulfur heterocycles (PASHs).[36] Müller et al. developed a derivatization techniques for relatively nonpolar compounds such as thiophenes to facilitate ESI.[37] Initially, it was thought that methylation does not provide accurate sulfur speciation for petroleum samples that contain high double bond equivalence (DBE > 10) sulfur species.[26] Schrader et al.[29] demonstrated APLI FT-ICR MS as a novel tool for analyzing nonpolar aromatic heterocyclic compounds including the sulfur-containing compounds in crude oils. A recent study[24] investigated phenylation and methylation procedures for PASHs by ESI, MALDI, APCI, APPI, and APLI. On the basis of these studies, it was concluded that methylation does not discriminate against polyaromatic sulfur compounds; the

(9) Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. Fourier transform ion cyclotron resonance mass spectrometry: A primer. *Mass Spectrom. Rev.* **1998**, *17*, 1–35.

(10) Marshall, A. G.; Rodgers, R. P. Petroleomics: The next grand challenge for chemical analysis. *Acc. Chem. Res.* **2004**, *37* (1), 53–59.

(11) Rodgers, R. P.; Schaub, T. M.; Marshall, A. G. Petroleomics: MS returns to its roots. *Anal. Chem.* **2005**, *77* (1), 20A–27A.

(12) Rodgers, R. P.; Marshall, A. G. *Petroleomics: Advanced characterization of petroleum-derived materials by Fourier transform ion cyclotron resonance mass spectrometry* (*FT-ICR MS*); Springer: New York, 2005; pp 63–93.

(13) Marshall, A. G.; Rodgers, R. P. Petroleomics: Chemistry of the underworld. *P. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18090–18095.

(14) Guan, S.; Marshall, A. G.; Scheppele, S. E. Resolution and chemical formula identification of aromatic hydrocarbons and aromatic compounds containing sulfur, nitrogen, or oxygen in petroleum distillates and refinery streams. *Anal. Chem.* **1996**, *68* (1), 46–71.

(15) Fu, J.; Kim, S.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G.; Qian, K. Nonpolar compositional analysis of vacuum gas oil distillation fractions by electron ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2006**, *20* (2), 661–667.

(16) Fu, J.; Purcell, J. M.; Quinn, J. P.; Schaub, T. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. External electron ionization 7 T Fourier transform ion cyclotron resonance mass spectrometer for resolution and identification of volatile organic mixtures. *Rev. Sci. Instrum.* **2006**, *77*.

(17) Qian, K.; Robbins, W. K.; Hughey, C. A.; Cooper, H. J.; Rodgers, R. P.; Marshall, A. G. Resolution and identification of elemental compositions for more than 3000 crude acids in heavy petroleum by negative-ion microelectrospray high-field Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2001**, *15* (6), 1505–1511.

(18) Qian, K.; Rodgers, R. P.; Hendrickson, C. L.; Emmett, M. R.; Marshall, A. G. Reading chemical fine print: Resolution and identification of 3000 nitrogen-containing aromatic compounds from a single electrospray ionization Fourier transform ion cyclotron resonance mass spectrum of heavy petroleum crude oil. *Energy Fuels* **2001**, *15* (2), 492–498.

(19) Barrow, M. P.; Headley, J. V.; Peru, K. M.; Derrick, P. J. Fourier transform ion cyclotron resonance mass spectrometry of principal components in oilsands naphthenic acids. *J. Chromatogr., A* **2004**, *1058* (1–2), 51–59.

(20) Hughey, C. A.; Rodgers, R. P.; Marshall, A. G. Resolution of 11 000 compositionally distinct components in a single electrospray ionization Fourier transform ion cyclotron resonance mass spectrum of crude oil. *Anal. Chem.* **2002**, *74* (16), 4145–4149.

(21) Smith, D. F.; Rodgers, R. P.; Rahimi, P.; Teclemariam, A.; Marshall, A. G. Effect of thermal treatment on acidic organic species from Athabasca bitumen heavy vacuum gas oil, analyzed by negative-ion electrospray Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. *Energy Fuels* **2009**, *23* (1), 314–319.

(22) Barrow, M. P.; McDonnell, L. A.; Feng, X.; Walker, J.; Derrick, P. J. Determination of the nature of naphthenic acids present in crude oils using nanospray Fourier transform ion cyclotron resonance mass spectrometry: The continued battle against corrosion. *Anal. Chem.* **2003**, *75* (4), 860–866.

(23) Shi, Q.; Xu, C.; Zhao, S.; Chung, K. H.; Zhang, Y.; Gao, W. Characterization of basic nitrogen species in coker gas oils by positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2010**, *24* (1), 563–569.

(24) Panda, S. K.; Andersson, J. T.; Schrader, W. Characterization of supercomplex crude oil mixtures: What is really in there? *Angew. Chem., Int. Ed.* **2009**, *48*, 1788–1791.

(25) Purcell, J. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. Atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry for complex mixture analysis. *Anal. Chem.* **2006**, *78* (16), 5906–5912.

(26) Purcell, J. M.; Juyal, P.; Kim, D. G.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. Sulfur speciation in petroleum: Atmospheric pressure photoionization or chemical derivatization and electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2007**, *21* (5), 2869–2874.

(27) Qian, K.; Edwards, K. E.; Mennito, A. S.; Walters, C. C.; Kushnerick, J. D. Enrichment, resolution, and identification of nickel porphyrins in petroleum asphaltene by cyclograph separation and atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2010**, *82* (1), 413–419.

(28) Haapala, M.; Purcell, J. M.; Saarela, V.; Franssila, S.; Rodgers, R. P.; Hendrickson, C. L.; Kotiaho, T.; Marshall, A. G.; Kostiainen, R. Microchip atmospheric pressure photoionization for analysis of petroleum by Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2009**, *81* (7), 2799–2803.

(29) Schrader, W.; Panda, S. K.; Brockmann, K. J.; Benter, T. Characterization of non-polar aromatic hydrocarbons in crude oil using atmospheric pressure laser ionization and Fourier transform ion cyclotron resonance mass spectrometry (APLI FT-ICR MS). *Analyst* **2008**, *133*, 867–869.

(30) Schaub, T. M.; Hendrickson, C. L.; Quinn, J. P.; Rodgers, R. P.; Marshall, A. G. Instrumentation and method for ultrahigh resolution field desorption ionization Fourier transform ion cyclotron resonance mass spectrometry of nonpolar species. *Anal. Chem.* **2005**, *77* (5), 1317–1324.

(31) Stanford, L. A.; Kim, S.; Klein, G. C.; Smith, D. F.; Rodgers, R. P.; Marshall, A. G. Identification of water-soluble heavy crude oil organic-acids, bases, and neutrals by electrospray ionization and field desorption ionization Fourier transform ion cyclotron resonance mass spectrometry. *Environ. Sci. Technol.* **2007**, *41* (8), 2696–2702.

(32) Smith, D. F.; Schaub, T. M.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. Automated liquid injection field desorption/ionization for Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2008**, *80* (19), 7379–7382.

(33) Panda, S. K. *Liquid chromatography and high resolution mass spectrometry for the speciation of high molecular weight sulfur aromatics in fossil fuels*; University of Münster: Münster, Germany, 2006.

(34) Müller, H.; Pauchard, V. O.; Hajji, A. A. Role of naphthenic acids in emulsion tightness for a low total acid number (TAN)/high asphaltenes oil: Characterization of the interfacial chemistry. *Energy Fuels* **2009**, *23* (3), 1280–1288.

(35) Hughey, C. A.; Minardi, C. S.; Galasso-Roth, S. A.; Paspalof, G. B.; Mapolelo, M. M.; Rodgers, R. P.; Marshall, A. G.; Ruderman, D. L. Naphthenic acids as indicators of crude oil biodegradation in soil, based on semi-quantitative electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 3968–3976.

(36) Panda, S. K.; Schrader, W.; al-Hajji, A.; Andersson, J. T. Distribution of polycyclic aromatic sulfur heterocycles in three Saudi Arabian crude oils as determined by Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2007**, *21* (2), 1071–1077.

(37) Müller, H.; Andersson, J. T.; Schrader, W. Characterization of high-molecular-weight sulfur-containing aromatics in vacuum residues using Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2005**, *77* (8), 2536–2543.

variation in the MS data is dependent on the ionization technique.[24,38]

In this paper, Venezuela crude oil was separated into SARA fractions. The crude oil sample and its SARA fractions were subjected to methylation and characterized by ESI FT-ICR MS analysis. Sulfur species were characterized by class (number of N, O, and S heteroatoms), type (DBE), and carbon number.

## Experimental Section

**Materials.** A Venezuela heavy crude oil was used in this study. The sulfur content of the crude oil and its SARA fractions were measured with an ANTEK 7000 pyrofluorescence analyzer (ANTEK Instruments, Germany) in accordance with ASTM D-5453. The crude oil sample was subjected to SARA fractionation (Chinese industry standard method SH/T 0509-92, equivalent to ASTM D2007-93). To do so, 1 g of a crude oil sample was dissolved in 50 mL of *n*-heptane. The mixture was refluxed for 30 min and stored in the dark for 1 h. The *n*-heptane insoluble matter was obtained by filtration using ShuangQuan No. 202 quantitative filter paper ($\Phi$11 cm). The *n*-heptane insoluble matter on the filter paper was rinsed with *n*-heptane and then dried at room temperature. The dried *n*-heptane insoluble matter on the filter paper was washed with toluene. The asphaltenes were obtained by evaporating the toluene from the filtrate solution.

The maltenes, which are *n*-heptane soluble, were obtained by vacuum rotary evaporation of the *n*-heptane solution. The dried maltenes were redissolved in 6 mL of *n*-heptane. The maltenes solution was mixed with 3 g of activated alumina, in which maltenes were adsorbed onto the surface of activated alumina. The maltenes−alumina slurry was dried while being continuously stirred under a stream of nitrogen. A glass column (50 mm i.d. × 700 mm length) was packed with 40 g of neutral alumina adsorbent (100−200 mesh, activated at 450 °C for 6 h, 1 wt % water added). The maltene-adsorbed alumina was packed on the top of the neutral alumina adsorbent in the glass column. Saturates were obtained by eluting the packed column with 80 mL of *n*-heptane. This was followed by 80 mL of toluene to elute the aromatics. A total of 40 mL of a 50:50 (v/v) toluene/ethanol mixture, 40 mL of toluene, and 40 mL of ethanol were added sequentially to elute the resins. The solvent in each effluent was dried by vacuum rotary evaporation and weighed.

**Methylation Sulfur Compounds.** The procedure for the methylation of sulfur compounds was similar to that of Müller et al.,[37] except for the amount of regents used. The crude oil and its SARA fractions (100 mg of each) were diluted with 2 mL of dichloromethane ($CH_2Cl_2$). A total of 50 $\mu$L of iodomethane was added to each oil sample solution. The mixture in a beaker was immersed in an ultrasonic bath at room temperature for 5 min. While mixing, 2 mL of silver tetrafluoroborate (20 mg/mL) in 1,2-dichloroethane was added, resulting in the formation of a yellow silver iodide precipitate. The reaction mixture in the beaker remained in the ultrasonic bath for 5 min to allow the reaction to continue.

The reaction mixture solution in the breaker was stored in the dark for 48 h. A mixture consisting of methyl sulfonium salts, silver iodide, iodomethane, and unreacted oil was obtained. The silver iodide was removed by centrifugation followed by filtration. A nitrogen purge was used to remove excess iodomethane and 1,2-dichloroethane and dichloromethane from the solution. A total of 5 mL of toluene was used to wash the unreacted oil. The methyl sulonium salts were obtained by centrifugation followed by filtration.

Sulfonium salts (10 mg) were diluted with 1 mL of $CH_2Cl_2$. A total of 5 $\mu$L of sulfonium salt solution was diluted with 1 mL of toluene/methanol/dichloromethane (3:3:4 vol/vol/vol) solution. All solvents used were analytical reagent grade solvents, 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 100 $\mu$L Hamilton syringes with steel pistons.

**FT-ICR MS Analysis.** The sulfonium salt samples were analyzed using a Bruker apex-ultra FT-ICR MS equipped with a 9.4 T actively shielded superconducting magnet. The sample solution was infused via an Apollo II electrospray source at 180 $\mu$L/h by using a syringe pump. The operating conditions for positive ion formation were a −2.5 kV emitter voltage, −3.0 kV capillary column front end voltage, and 320 V capillary column end voltage. Ions were accumulated for 0.01 s in a hexapole with 2.4 V DC voltage and 300 Vp-p RF amplitude. The optimized mass for Q1 was 250 Da. An argon-filled hexapole collision pool was operated at 5 MHz and 400 Vp-p RF amplitude, in which ions accumulated for 0.2 s. The extraction period for ions from the hexapole to the ICR cell was set to 1.3 ms. The rf excitation was attenuated at 11.75 dB and used to excite ions over the range of 200−750 Da. Four M data sets were acquired. A number of 64 scans FT-ICR data sets were coadded to enhance the signal-to-noise ratio and dynamic range.

**Mass Calibration and Data Analysis.** The mass spectrometer was calibrated using sodium formate. Peaks with a relative abundance greater than 6 times the standard deviation of the baseline noise were exported to a spreadsheet. Data analysis was performed using custom software, which has been described elsewhere.[39,40] The data analysis was performed by selecting a two-mass scale-expanded segment in the middle of the spectra, followed by detailed identification of each peak. The peak of at least one of each heteroatom class species was arbitrarily selected as a reference. Species with the same heteroatom class and its isotopes with different values by DBE and carbon number were searched within a set ±0.001 Kendrick mass defect (KMD) tolerance.[23,41]

## Result and Discussion

**Heteroatom Class Distributions.** The yields of the SARA fractions were 19.0 wt % saturates, 33.7 wt % aromatics, 24.1 wt % resins, and 11.5 wt % asphaltenes. Total recovery amounted to 88.3 wt %. Since the crude oil contains a low boiling fraction, the unrecovered portion was likely volatilized along with the solvent during vacuum rotary evaporation. Moreover, once the strong polarity fraction was adsorbed on the activated alumina, it could not be eluted even with the use a polar solvent, such as ethanol, and resulted in a loss of the recovering rate. The sulfur content of the crude oil and its saturates, aromatics, resins, and asphaltenes fractions were 5.0 wt %, 0.65 wt %, 5.7 wt %, 5.5 wt %, and 6.6 wt %, respectively.

Figure 1 shows a comparison of the broadband positive-ion ESI FT-ICR mass spectrum of the methylated crude oil

(38) Shi, Q.; Pan, N.; Liu, P.; Chung, K. H.; Zhao, S.; Zhang, Y.; Xu, C. Characterization of sulfur compounds in oilsands bitumen by methylation followed by positive-ion electrospray ionization and Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2010**, *24* (5), 3014–3019.

(39) Shi, Q.; Zhao, S.; Xu, Z.; Chung, K. H.; Zhang, Y.; Xu, C. Distribution of acids and neutral nitrogen compounds in a Chinese crude oil and its fractions: Characterized by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2010**, *24* (7), 4005–4011.

(40) Liu, P.; Xu, C.; Shi, Q.; Pan, N.; Zhang, Y.; Zhao, S.; Chung, K. H. Characterization of sulfide compounds in petroleum: Selective oxidation followed by positive-ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2010**, *82* (15), 6601–6606.

(41) Hughey, C. A.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G.; Qian, K. Kendrick mass defect spectrum: A compact visual analysis for ultrahigh-resolution broadband mass spectra. *Anal. Chem.* **2001**, *73* (19), 4676–4681.
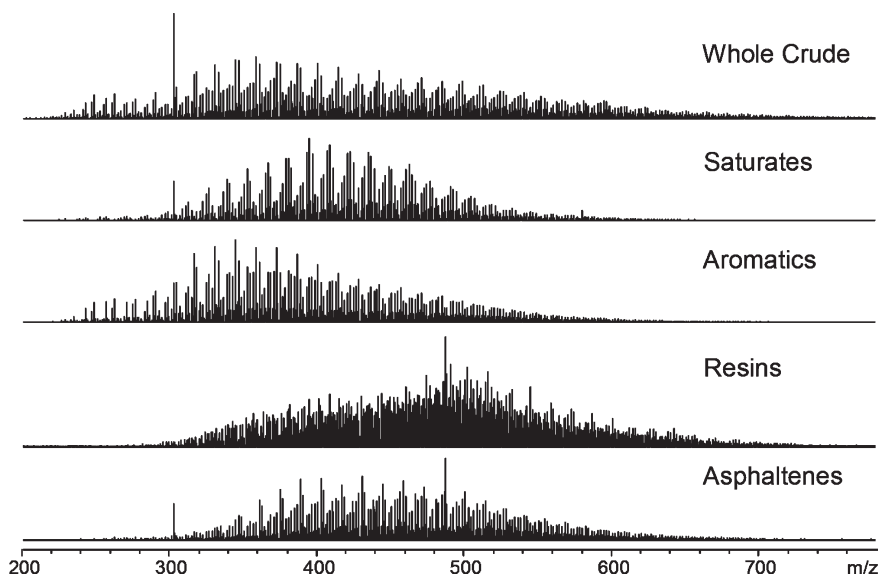
**Figure 1.** Broadband positive-ion electrospray ionization FT-ICR mass spectra of a Venezuela crude oil and its SARA-fraction-derived methyl sulfonium salts. The samples were analyzed at an approximate sulfur concentration and under the same instrumental conditions.
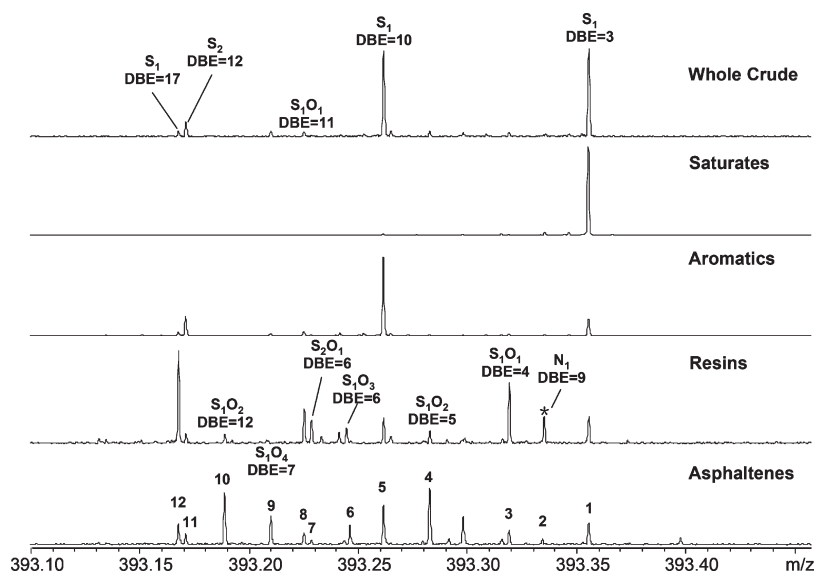


**Figure 2.** Narrow segment of the ultrahigh-resolution mass spectrum in Figure 1 at a representative odd mass, 393 Da. Asterisks denote ($*$) species containing one ^{13}C atom in place of [12]C. All 12 peaks resolved in the asphaltenes fraction in the 0.45 mass window are identified as listed in Table 1.

and its SARA fractions. The spectra show that the molecular weight distributions of crude oil and its SARA fractions were between $200 < m/z < 800$ Da. The mean molecular weights of the crude oil, saturates, aromatics, resins, and asphaltenes were at $m/z$ 350, $m/z$ 400, $m/z$ 350, $m/z$ 500, and $m/z$ 450, respectively. The sulfur compounds in the aromatics fraction had a lower molecular weight than those in the saturates fraction. Likewise, the sulfur compounds in the asphaltenes fraction had a lower molecular weight compared to those in the resins fraction.

Figure 2 shows the mass scale-expanded segments of the FT-ICR mass spectrum shown in Figure 1, at a representative odd mass of $m/z$ 393. The mass resolving power at $m/z$ 393 is greater than 400 000 ($m/\Delta m_{50\%}$, in which $\Delta m_{50\%}$ is the magnitude-mode mass spectral peak full width at half-maximum peak height). Elemental compositions of these compounds can be identified by accurate mass analysis (peak

identifications are listed in Table 1). In Figure 2, the various sulfur class species identified include $S_1$, $S_2$, $S_1O_1$, $S_1O_2$, $S_1O_3$, $S_1O_4$, $S_2O_1$, $S_2O_2$, $S_3$, $N_1S_2$, $N_1O_1S_1$, $N_1O_1S_2$, and $S_2O_3$. The major sulfur class species identified were similar to those found in Canadian oilsands bitumen.[38]

Unique elemental formulas were assigned to the spectral peaks on the basis of accurate mass values and the correspondence between homologue series. Figure 3 shows the class analysis (heteroatom content) by positive-ion ESI FT-ICR MS for the methylated Venezuela crude oil and its SARA fractions. Relative abundance is defined as the magnitude of each peak divided by the sum of magnitudes of all identified peaks (excluding the isotopic peaks) in the mass spectrum.

The crude oil had the highest relative abundance of $S_1$ class species, followed by $S_2$, $O_2S_1$, $O_1S_1$, and $N_1S_1$. It also contained less abundant multiheteroatoms such as $N_1S_1$,

**Table 1. Identification of Singly Charged Cations at Nominal Mass, 393 Da, Observed in the Methylated Asphaltenes Fraction of Venezuela Crude Oil (Figure 2)**

| peak no. | NOS | formula $[M + H]^+$ | observed mass (Da) | theoretical mass (Da) | error (ppm) | S/N | resolving power |
|---|---|---|---|---|---|---|---|
| 1 | $S_1$ | $C_{26}H_{49}S_1$ | 393.3551 | 393.3549 | −0.4 | 90 | 434 798 |
| 2 | $N_1$ | $^{13}C_1C_{27}H_{42}N_1$ | 393.3348 | 393.3345 | −0.8 | 23 | 503 415 |
| 3 | $S_1O_1$ | $C_{25}H_{45}O_1S_1$ | 393.3187 | 393.3186 | −0.4 | 60 | 480 324 |
| 4 | $S_1O_2$ | $C_{24}H_{41}O_2S_1$ | 393.2823 | 393.2822 | −0.4 | 240 | 432 335 |
| 5 | $S_1$ | $C_{27}H_{37}S_1$ | 393.2612 | 393.2610 | −0.4 | 168 | 443 844 |
| 6 | $S_1O_3$ | $C_{23}H_{37}O_3S_1$ | 393.2459 | 393.2458 | −0.4 | 82 | 474 341 |
| 7 | $S_2O_1$ | $C_{23}H_{37}O_1S_2$ | 393.2282 | 393.2280 | −0.3 | 17 | 472 098 |
| 8 | $S_1O_1$ | $C_{26}H_{33}O_1S_1$ | 393.2248 | 393.2247 | −0.4 | 50 | 445 493 |
| 9 | $S_1O_4$ | $C_{22}H_{33}O_4S_1$ | 393.2096 | 393.2094 | −0.6 | 123 | 460 042 |
| 10 | $S_1O_2$ | $C_{25}H_{29}O_2S_1$ | 393.1884 | 393.1883 | −0.4 | 225 | 447 411 |
| 11 | $S_2$ | $C_{25}H_{29}S_2$ | 393.1707 | 393.1705 | −0.6 | 45 | 471 034 |
| 12 | $S_1$ | $C_{28}H_{25}S_1$ | 393.1673 | 393.1671 | −0.4 | 89 | 458 047 |
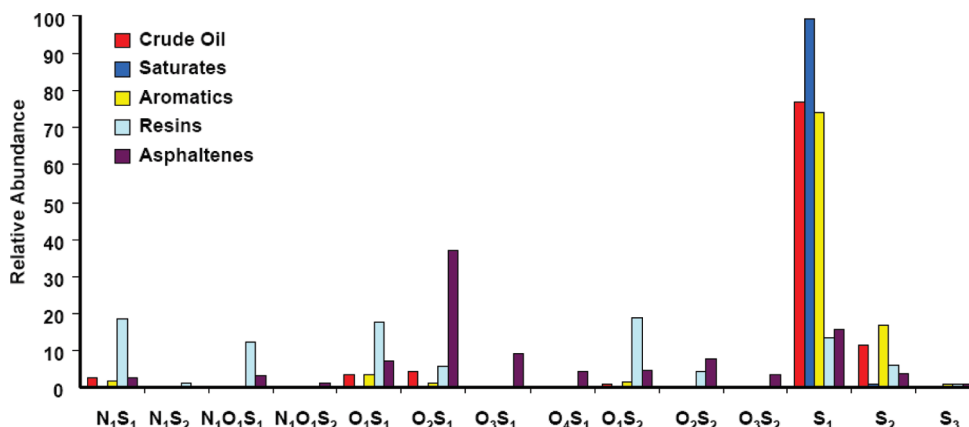


**Figure 3.** Relative abundance of heteroatom classes for the methylated Venezuela crude oil and its SARA fractions derived from the positive-ion ESI FT-ICR mass spectrum. Only those classes with >1% relative abundance are shown. Relative abundance is defined as the magnitude of each peak divided by the sum of magnitudes of all identified peaks (excluding the isotopic peaks) in the mass spectrum.

$S_1O_1$, $S_1O_2$, and $S_2O_1$ class species. Only $S_1$ and $S_2$ class species with low DBE values were identified in the saturates fraction. Of these, the $S_1$ class species were predominant and accounted for more than 99% of the total relative abundance of sulfur species. The distribution of heteroatoms in the aromatics fraction was similar to that of the crude oil, except the $S_1$ class species had low DBE values. The resins fraction had the most complex heteroatom composition of the SARA fractions. The resins fraction had high relative abundances of $N_1S_1$, $N_1O_1S_1$, $S_1O_1$, $S_2O_1$, $S_1$, $S_2$, and $S_3$ classes species and low relative abundances of other multiheteroatom class species. The asphaltenes fraction had the highest relative abundance of $S_1O_2$ species among the SARA fractions and also had high relative abundances of other $S_xO_y$ and $N_1O_xS_y$ even mass class species.

Detailed molecular composition analyses of the class species in the crude oil and its SARA fractions were carried out by plotting the relative abundance maps of DBE as a function of carbon number.

**Molecular Compositional of Crude Oil and Its Fractions.** *$S_1$ Class Species.* Figure 4 shows the relative abundance maps of DBE as a function of the carbon number for the $S_1$ class species in the methylated Venezuela crude oil and its SARA fractions. The carbon numbers shown on the *x* axis of Figure 4 include all carbon atoms in the derivatization groups in the methylated oil sample, which had one additional carbon atom compared to the molecules in the original oil sample.

The DBE distribution of $S_1$ class species in Venezuela crude oil is similar to that of Canadian oilsands bitumen.[38]

In general, the $S_1$ class species in Venezuela crude oil had DBE values of 1−19 and carbon numbers of 11−55. The abundant $S_1$ class species had 2−12 and 20−35 carbon numbers. The most abundant $S_1$ class species had 6 DBE, indicating a benzothiophenic core with alkyl side chains and benzo-homologues of two cyclic-ring sulfides.[38] Despite the high abundance of $S_1$ class species in all SARA fractions, the patterns of DBE versus carbon number plots of $S_1$ class species in the individual fractions are significantly different. The $S_1$ class species in the saturates fraction had lower DBE values than those in the parent crude oil. The abundant $S_1$ class species in the saturates fraction had 2−6 DBE and 20−35 carbon atoms, indicating low aromaticity $S_1$ class species such as cyclic-ring sulfides[40] with higher relative abundance than that in parent crude oil. The most abundant $S_1$ class species in the aromatics fraction had DBE > 5, indicating that the aromatics fraction was enriched with thiophenic sulfur compounds. The plot of DBE vs carbon number of the $S_1$ class species in the resins fraction shows a bimodal distribution. An abundant group of $S_1$ class species was centered at 14 < DBE < 22 with 22−38 carbon numbers. This indicates that high aromaticity sulfur compounds were eluted into the resins fraction. Another abundant group of $S_1$ class species was found at 2 < DBE < 12. These compounds are sulfides and thiophenes. However, on the basis of the solubility and polarity of sulfides and thiophenes, it was expected that these compounds would be found in the saturates and aromatics fractions. It is likely that these compounds were carryovers from the SARA fractionation. Also, $S_1$ class species with 20−22 DBE were not observed in the
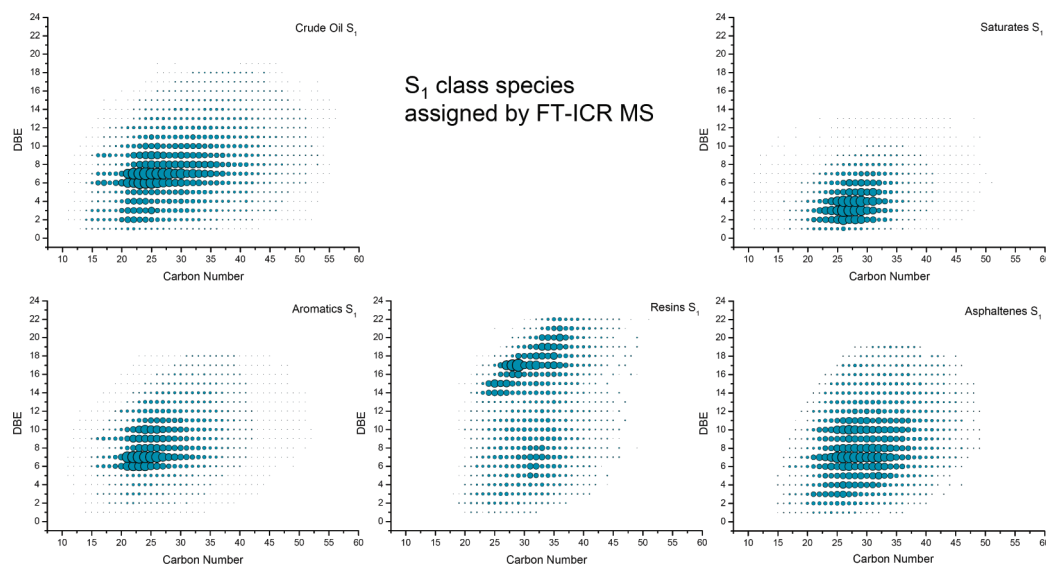
**Figure 4.** Plots of DBE versus the carbon number for $S_1$ class species in methylated Venezuela crude oil and its SARA fractions from the positive-ion ESI FT-ICR MS. The largest dot corresponds to the most abundant monosulfur species in the sample.
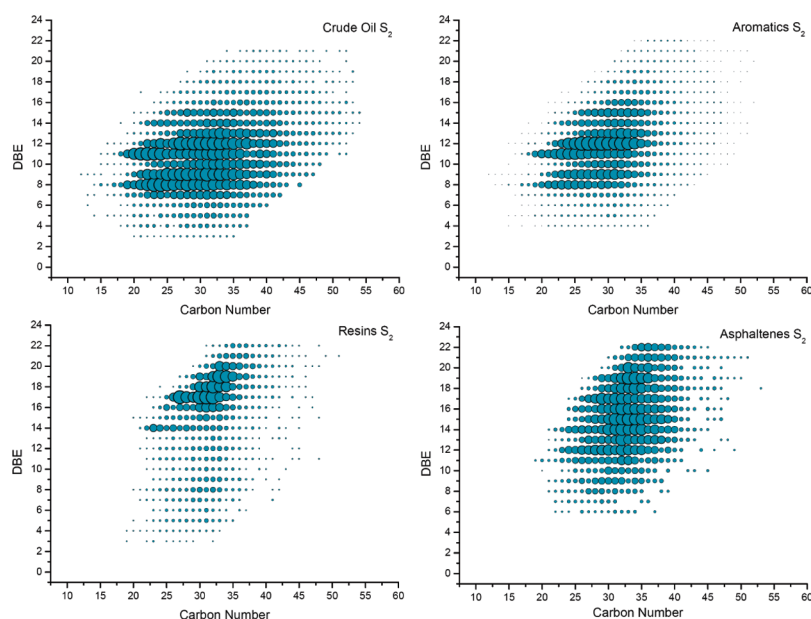


**Figure 5.** Plots of DBE versus the carbon number for the $S_2$ class species in methylated Venezuela crude oil and its SARA fractions from the positive-ion ESI FT-ICR MS. The relative abundance of $S_2$ class species in the saturates fraction is very low.

parent crude oil. This shows that SARA fractionation isolated the highly aromatic $S_1$ class species in the resin fraction, which were not detected in the parent crude oil due to low concentrations. With increasing polarity of the solvent used in elution, the DBE distribution of $S_1$ class species in the SARA subfractions shifts to higher values, except for the asphaltenes. The $S_1$ class species in the asphaltenes fraction had a similar distribution of DBE versus carbon number to the parent crude oil. Since the $S_1$ class species accounted for a small fraction of total abundance of sulfur compounds in asphaltenes fraction (cf. Figures 2 and 3), it is likely that some maltenes coprecipitated in the asphaltenes fraction.

*$S_2$ Class Species.* Figure 5 shows the relative abundance maps of DBE as a function of the carbon number for the $S_2$ class species in methylated Venezuela crude oil and its SARA

fractions. In theory, both sulfur atoms in the $S_2$ class species are methylated, and the resulting species should contain two additional methylene groups. However, no double-charged ions were observed in the spectra. The $S_2$ class species in Venezuela crude oil had 3−21 DBE values and 13−52 carbon numbers. The abundant $S_2$ class species had DBE values of 8, which are likely benzodithiophenes with a type I and II core structures. The 9 DBE species are likely benzodithiophenes with a fused cyclo-alkane ring. The 10 DBE species are likely a dihydrothiophene flanked on a dibenzothiophene with type III core structure. The species with DBE values of 11, 12, and 13 are likely benzo-homologues derived from 8, 9, and 10 DBE species.

The $S_2$ class species in the aromatics fraction had a similar distribution of DBE versus carbon number to that of the parent crude oil, with a lower and upper limit of the DBE
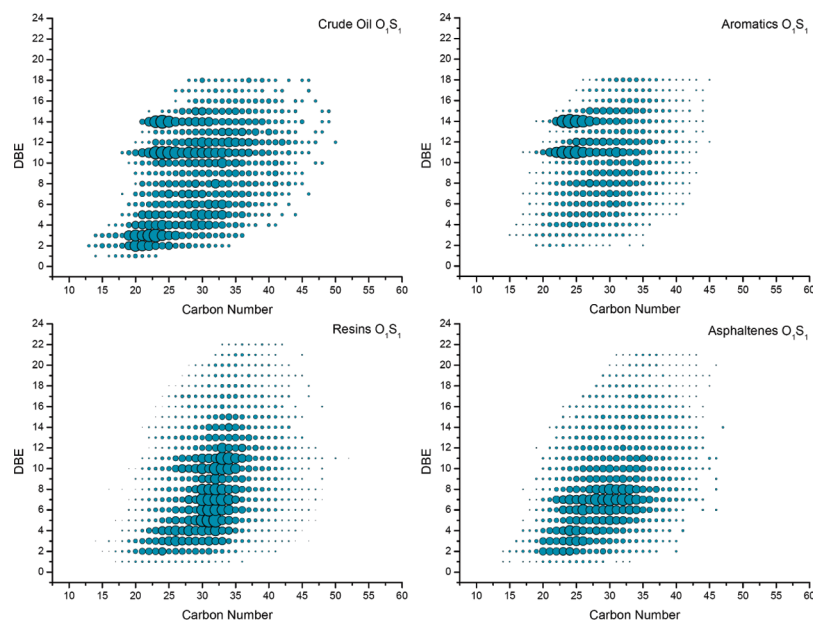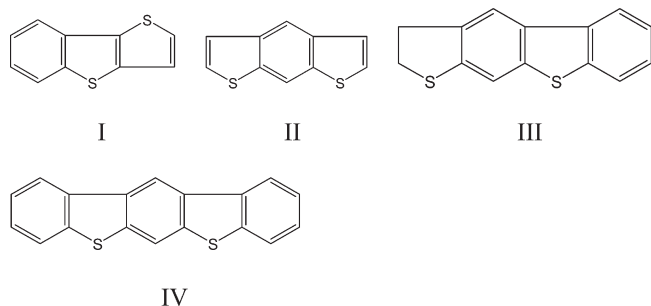
**Figure 6.** Plots of DBE versus the carbon number for the $O_1S_1$ class species in methylated Venezuela crude oil and its SARA fractions from the positive-ion ESI FT-ICR MS. The saturates fraction did not contain $O_1S_1$ species.

value of 4 and 22, respectively. The abundant $S_2$ class species had $8 < DBE < 13$ and 19−36 carbon numbers. The $S_2$ class species in the resins fraction had a wider range of DBE values (3−22) and a narrower range of carbon number (20−45) distribution than the parent crude oil. The resins fraction also had a high relative abundance of $S_2$ class species that were highly aromatic with $14 < DBE < 22$ and 21−38 carbon numbers. The $S_2$ class species with a 14 DBE value are consistent with a benzothiophene flanked on a dibenzothiophene with type IV core structure. The $S_2$ class species in the asphaltenes fraction had 6−22 DBE values and 20−50 carbon numbers. The most abundant $S_2$ class species in the asphaltenes fraction had 11−22 DBE values.



*$O_1S_1$ Class Species*. Figure 6 shows the relative abundance maps of DBE as a function of the carbon number for the $O_1S_1$ class species in the methylated Venezuela crude oil and its aromatics, resins, and asphaltenes fractions. Unlike other sulfur species, $S_1O_1$ class species can be easily ionized to the sulfoxide form. Therefore, the oxygen-containing molecules are likely sulfoxide, hydroxyl, carbonyl, and ether groups.

The $O_1S_1$ class species in the parent crude oil had $1 < DBE < 18$ and 13−50 carbon numbers. The abundant $O_1S_1$ class species had DBE values of 11 and 14. These two series of $O_1S_1$ class species were enriched in the aromatics fraction. The $O_1S_1$ class species with 11 DBE are likely a dibenzofuran

flanked to a thiophene. The $O_1S_1$ class species with 14 DBE are likely benzo-homologues with 11 DBE.[38] The $O_1S_1$ class species in the resins and asphaltenes fractions had a wider range of DBE values than that of the parent crude oil, indicating that SARA fractionation allows for identification of highly aromatic sulfur species.

The oxygen atoms in the $O_1S_1$ class species in the resins and asphaltenes fractions were likely hydroxy and sulfoxide groups. There are two reasons for this. The $O_1S_1$ class species have been identified in the resins and asphaltenes fractions of an Arabian Medium crude oil using the positive ESI FT-ICR mass spectrum.[42] This suggests that the $O_1S_1$ class species in the resins and asphaltenes fractions are derived from sulfoxides. In addition, the $O_1$ class species, which were hydroxyl-containing compounds, were eluted into resins and precipitated in the asphaltenes fraction. These species have been identified in the resins and asphaltenes fractions of a Liaohe crude oil by negative-ion ESI FT-ICR mass spectrum analysis.[7]

*$O_2S_1$ Class Species*. Figure 7 shows the relative abundance maps of DBE as a function of the carbon number for the $O_2S_1$ class species in the methylated Venezuela crude oil and its resins and asphaltenes fractions. The $O_2S_1$ class species in the parent crude oil had 2−15 DBE and 13−50 carbon numbers. The highest relative abundance of $O_2S_1$ class species had DBE values of 7 and 8. The $O_2S_1$ class species in the resins and asphaltenes fractions had a wider range of DBE values. The oxygen atoms in the $O_2S_1$ class species were likely from a carboxylic acid group. This was determined because, first, Figure 3 showed that $O_2S_1$ class species were abundant in the resins and asphaltenes fractions (especially in the asphaltenes fraction). The relative abundance of $O_2S_1$ class species in the aromatics fraction was very low. No $O_2S_1$ class species were found in the saturates fraction. This is in good agreement with a previous study,[7] indicating that the acidic compounds ($O_2$ class species) were mostly eluted

(42) Smith, D. F. *Petroleomics applications of Fourier transform ion cyclotron resonance mass spectrometry: Crude oil and bitumen analysis.* The Florida State University: Tallahassee, FL, 2007.
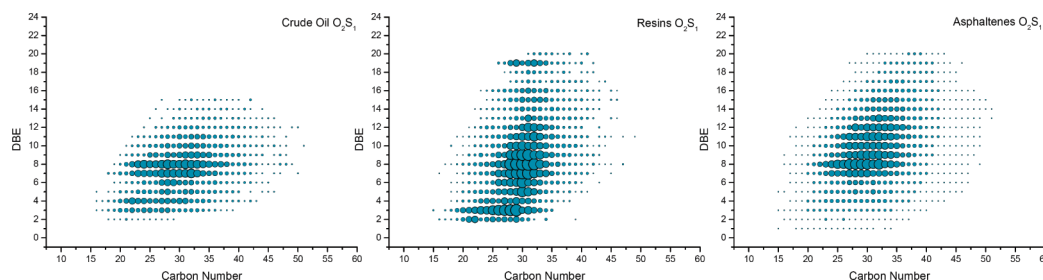
**Figure 7.** Plots of DBE versus the carbon number for the $O_2S_1$ class species in methylated Venezuela crude oil and its SARA fractions from the positive-ion ESI FT-ICR MS. The saturates fraction did not contain $O_2S_1$ species, and the relative abundance of $O_2S_1$ species in the aromatics fraction is very low.

in resins and precipitate in the asphaltenes fraction during SARA fractionation. Second, the DBE distribution of $O_2S_1$ class species resembles that obtained from negative-ion ESI of bitumen distillation fractions.[43] This suggests that these compounds are acidic and the oxygen atom is in the form of a carboxyl.[38] Third, the most abundant $O_2S_1$ class species in the parent crude oil had DBE values of 7 and 8, consistent with the addition of a carboxylic acid group (an unity DBE value increment) to the aromatic core of the $S_1$ class species with DBE values of 6 and 7 (see Figure 4).

The $O_2S_1$ class species in the asphaltenes fraction with a DBE value of 1 are likely the fatty sulfides with a carboxyl group. Thiophene and benzothiophene cores attached with a carboxylic acid group ($O_2S_1$ class species) are consistent with DBE values of 4 and 7.[21] The $O_2S_1$ class species with DBE values of 2 and 3 are likely one- and two-ring cyclic sulfides with a carboxyl group.

(43) Smith, D. F.; Rahimi, P.; Teclemariam, A.; Rodgers, R. P.; Marshall, A. G. Characterization of Athabasca bitumen heavy vacuum gas oil distillation cuts by negative/positive electrospray ionization and automated liquid injection field desorption ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2008,** *22* (5), 3118–3125.

**Conclusions**

The detailed composition of sulfur species in the Venezuela crude oil and its SARA fractions were determined by methylation, followed by ESI FT-ICR MS analysis. The results showed that sulfur compounds are present in all the SARA subfractions; however, the molecular composition and mass distribution of sulfur compounds in these subfractions are significantly different. The saturates fraction had the least amount of sulfur species among the SARA fractions. The $S_1$ class species are likely cyclic-ring sulfides. Thiophenic sulfur compounds were mostly present in the aromatics fraction. The resins and asphaltenes fractions contained high amounts of multiheteroatom ($N_1S_y$, $O_xS_y$, $N_1O_yS_z$) class species.

The relative abundance plots of DBE versus carbon number of $S_1$, $S_2$, $O_1S_1$, and $O_2S_1$ class species were presented and discussed. With increasing molecular polarity of the solvent used in elution, the DBE of the abundant $S_x$ class species shifts to a higher DBE value. SARA fractionation allows for the identification of highly aromatic sulfur species in the resins and asphaltenes fractions, which were not observed in the parent crude oil.