

Characterization of Acidic Species in Athabasca Bitumen and Bitumen Heavy Vacuum Gas Oil by Negative-Ion ESI FT–ICR MS with and without Acid–Ion Exchange Resin Prefractionation

Donald F. Smith,[†] Tanner M. Schaub,[†] Sunghwan Kim,^{†,‡} Ryan P. Rodgers,^{*,†,§}
Parviz Rahimi,^{||} Alem Teclemariam,^{||} and Alan G. Marshall^{*,†,§}

National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive,
Tallahassee, Florida 32310-4005, Department of Chemistry and Biochemistry, Florida State University,
Tallahassee, Florida 32306-4390, and National Centre for Upgrading Technology (NCUT), 1 Oil Patch
Drive, Devon, Alberta, AB T9G 1A8, Canada

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Because acids in petroleum materials are known to corrode processing equipment, highly acidic oils are sold at a discount [on the basis of their total acid number (TAN)]. Here, we identify the acidic species in raw Canadian bitumen (Athabasca oil sands) and its distilled heavy vacuum gas oil (HVGO) as well as acid-only and acid-free fractions isolated by use of an ion-exchange resin (acid–IER) and negative-ion electrospray ionization Fourier transform ion cyclotron resonance (ESI FT–ICR MS) mass spectrometry. The ultrahigh mass resolving power ($m/\Delta m_{50\%} > 400\,000$) and high mass accuracy (better than 500 ppb) of FT–ICR MS, along with Kendrick mass sorting, enable the assignment of a unique elemental composition to each peak in the mass spectrum. Acidic species are characterized by class ($N_nO_oS_s$ heteroatom content), type [number of rings plus double bonds to carbon or double-bond equivalent (DBE)], and carbon number distribution. We conclude that the analytical capability of FT–ICR MS and the selectivity of the ESI process eliminate the need for acid fractionation to characterize naphthenic acids in bitumen. However, because the acid-free fraction (not retained on the acid–IER) contains S_xO_y heteroatomic classes not observed in the parent bitumen, acid–IER fractionation does help to identify such low-abundance species. Further, we observe that a subset of the acids identified in the parent bitumen distill into the HVGO fraction. Variations in the carbon number and aromaticity of the classes are discussed in detail.

Introduction

Oil sands bitumen deposits in Alberta, Canada represent a substantial reserve of recoverable crude oil: an estimated 175 billion barrels, second only to Saudi Arabia with ~260 billion barrels of recoverable crude oil.¹ These deposits are either extracted from sand after conventional mining or brought to the surface by *in situ* techniques, such as steam-assisted gravity drainage (SAGD). Mined and SAGD bitumen are highly viscous (<100 000 cP), have low American Petroleum Institute (API) gravity values (7–15°), and cannot be transported by pipeline. Diluents, such as natural gas condensate or synthetic diluents, are added to bitumen to reduce viscosity (350 cSt) and density (0.94 g/cm³) for pipeline transportation.

Solid contaminants and minor organic components of bitumen and heavy oils play a major role in the refinery processing of these feedstocks. Organic acids known as “naphthenic acids”

constitute a small portion of the total bitumen. However, those components are known to be corrosive in refinery operations.² A crude oil is typically deemed safe for refining according to its total acid number (TAN). TAN is defined as the quantity of base (in milligrams of KOH) required to neutralize all acidic species in 1 g of sample. Many refineries refuse to process crude oils with TAN greater than 0.5 mg of KOH/g of oil and streams with TAN greater than 1.5 mg of KOH/g of oil, because of their refinery metallurgy. Athabasca bitumen has a TAN of ~3.2–5.5 mg of KOH/g of oil (i.e., well above the accepted limit). Accurate TAN determination by ASTM 664³ is difficult because of the high viscosity of Athabasca bitumen. It is not clear how much (if any) of this increased TAN contributes to refinery corrosion. Reports and data on refinery corrosion because of naphthenic acids in oil sands processing is limited and a matter of controversy. In any case, Athabasca crude is penalized in market price because of its high TAN number. Naphthenic acids may not be the sole cause of high TAN and/or high corrosivity, because some sulfur compounds have been shown to affect corrosivity and TAN values.^{4,5}

* To whom correspondence should be addressed: Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310-4005. Telephone: +1-850-644-0529 (A.G.M.); +1-850-644-2398 (R.P.R.). Fax: +1-850-644-1366 (A.G.M. and R.P.R.). E-mail: marshall@magnet.fsu.edu (A.G.M.); rogers@magnet.fsu.edu (R.P.R.).

[†] National High Magnetic Field Laboratory, Florida State University.

[‡] Current Address: FT–ICR Program, Korea Basic Science Institute, 52 Yeosu-Dong, Yusung-gu, Daejeon 305-333, Korea.

[§] Department of Chemistry and Biochemistry, Florida State University.

^{||} National Centre for Upgrading Technology (NCUT).

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Techniques used to characterize petroleum acids include Fourier transform infrared spectroscopy,^{6–8} ¹³C nuclear magnetic resonance,^{7,8} two-dimensional gas chromatography,⁹ hyphenated mass spectrometric techniques, such as GC-MS,^{10–12} LC-MS,¹³ and liquid-secondary ion mass spectrometry.¹⁴ Ionization techniques for mass spectrometry have included fast atom bombardment (FAB),^{15–17} chemical ionization,¹⁴ atmospheric pressure chemical ionization (APCI),^{7,14} electrospray ionization (ESI),^{7,14,18,19} field desorption ionization,²⁰ and atmospheric pressure photoionization.²¹

The advantages of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)²² for the analysis of complex petroleum mixtures are well-documented.^{18,19,21,23–41} Briefly, such measurements make possible the correlation (and ultimately prediction) of the properties and behavior of petroleum and its products: a field now known as petroleomics.^{34,42,43} Here, we exploit the selectivity of negative-ion electrospray ionization to provide heteroatom class ($N_nO_oS_s$), type [double-bond

equivalents (DBE = number of rings plus double bonds involving carbon)], and carbon number analysis for the organic acids in raw Athabasca bitumen, its distilled heavy vacuum gas oil (HVGO) fraction, and acid-only and acid-free fractions of the HVGO isolated by use of an ion-exchange resin (IER). We

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discuss the advantages of IER isolation of naphthenic acids as well as common features of the various acid distributions.

Materials and Methods

Sample Description and Bulk Property Measurements. Athabasca bitumen was obtained from the oil sands mining operation in Fort McMurray, Alberta, Canada. The heavy gas oil fraction (HVGO) of approximately 30 wt % (boiling range of 350–525 °C) was obtained by American Society for Testing and Materials (ASTM) D1160 distillation.³ TAN was measured by the ASTM D-664 method,³ and molecular weights were determined by vapor pressure osmometry at 120 °C in *o*-dichlorobenzene.⁴⁴ Naphthenic acids were separated from the heavy vacuum gas oil fraction by the acid–IER method.⁴⁵ Calculated TAN for the acid-only and acid-free fractions was determined by (weight % recovery × (measured TAN)/100). For example, the calculated TAN for the HVGO acid-only fraction is its weight percent (2.96 wt %) multiplied by its measured TAN (135.7); $(2.96 \times 135.7)/100 = 4.017$.

Sample Preparation for ESI FT–ICR MS. Sample solutions were prepared to ~1 mg/mL in 50:50 toluene/methanol. A total of 10 µL of ammonium hydroxide was added to each 1 mL of sample solution to ensure efficient deprotonation for negative-ion electrospray analysis. All solvents were high-performance liquid chromatography (HPLC)-grade (Thermo Fisher Scientific, Pittsburgh, PA).

Instrumentation. Bitumen samples were analyzed with a custom-built FT–ICR mass spectrometer^{46,47} equipped with a 9.4 T horizontal 220 mm bore diameter superconducting solenoid magnet (Oxford Corp., Oxney Mead, U.K.). Sample solutions were infused via a microelectrospray source⁴⁸ (50 µm i.d. fused silica emitter) at 400 nL/min by a syringe pump. Typical conditions for negative ion formation were emitter voltage, –2.0 kV; tube lens,

–350 V; and heated metal capillary current, 4 A. Electrosprayed negative ions were accumulated in an external linear octopole ion trap⁴⁹ for 5–30 s and transferred by rf-only octopoles to a 10 cm diameter, 30 cm long open cylindrical Penning ion trap. Octopoles were operated at 1.8 MHz and 120 V_{p-p} rf amplitude. Broadband frequency sweep (chirp) dipolar excitation (70–641 kHz at 150 Hz/µs sweep rate and 190 V_{p-p} amplitude) was followed by direct-mode image current detection to yield 4 Mword time-domain data sets. Time-domain data sets were co-added (100 acquisitions), Hanning apodized, and zero-filled once before fast Fourier transformation and magnitude calculation. Frequency was converted to the mass-to-charge ratio by means of the quadrupole electric trapping potential approximation to generate mass spectra.^{50,51} A modular ICR data station (MIDAS) facilitated instrument control, data acquisition, and data analysis.^{52,53} FT–ICR *m/z* range coverage was verified by a comparison to low-resolution mass spectra, acquired with a linear quadrupole ion-trap mass spectrometer (LTQ, Thermo Fisher Scientific, San Jose, CA) under negative-ion electrospray conditions analogous to those described above for FT–ICR MS.

Mass Calibration and Data Analysis. FT–ICR mass spectra were internally calibrated with respect to a high-abundance homologous alkylation series of ions each containing two oxygen atoms, as previously described.¹⁸ The *m/z* values (for singly charged ions) of 300–900 Da with relative abundance greater than 6 times the standard deviation of the baseline noise were exported to a spreadsheet. Measured masses were converted from the International Union of Pure and Applied Chemistry (IUPAC) mass scale to the Kendrick mass scale⁵⁴ and sorted according to Kendrick mass defect values to facilitate identification of homologous alkylation series. Peak assignments were performed by Kendrick mass defect analysis as described previously.⁵⁵

Results and Discussion

Feedstock Bulk Properties. Table 1 summarizes the bulk properties of the samples analyzed by FT–ICR MS. The bitumen and its HVGO fraction exhibit relatively high sulfur and low oxygen content, whereas the oxygen content of the acid-only fraction is very high. The IER-separated acid from the HVGO accounts for approximately 3 wt % and is assumed to contain entirely naphthenic acids. Because HVGO is about 30 wt % of bitumen, the naphthenic acid content is about 1 wt % of total bitumen. The good agreement between the

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Table 1. Feedstock Bulk Properties

| feedstock | H/C | N (wt %) | S (wt %) | O (wt %) | wt % | measured TAN (mg of KOH/g of oil) | calculated TAN (mg of KOH/g of oil) | MW (g/mol) |
|-------------------|------|----------|----------|----------|-------|--------------------------------------|--|------------|
| Athabasca bitumen | 1.41 | 0.41 | 4.90 | 1.28 | | 5.58 | | 557 |
| HVGO | 1.47 | 0.14 | 3.48 | 0.83 | | 4.32 | | 345 |
| HVGO acid-only | 1.75 | 0.12 | 1.28 | 9.12 | 2.96 | 135.7 | 4.02 | 541 |
| HVGO acid-free | | | | | 97.04 | 0.31 | 0.3 | 357 |

measured HVGO and calculated TAN for the acid-only fraction suggests that most acidic species in the HVGO are naphthenic in nature. Although the molecular weights of all of the components shown in Table 1 were measured in a polar solvent and at high temperature to prevent aggregation (hydrogen bonding), the acid fraction showed higher molecular weight than the HVGO because of the removal of lower molecular-weight hydrocarbons in the non-acidic fraction by the IER extraction.

Mass Spectrometric Analysis. Naphthenic Acids in Bitumen versus HVGO and Ion-Exchange Fractions. Figure 1 shows broadband negative-ion electrospray FT-ICR mass spectra of the four samples. More than 4000 raw bitumen species were resolved and identified, compared to >1000 for the HVGO and HVGO acid-only fraction and >2000 for the HVGO acid-free fraction. All observed ions are singly charged, as evidenced by the observed unit m/z difference between $^{12}\text{C}_x$ and $^{13}\text{C}_1^{12}\text{C}_{x-1}$ signals for each elemental composition.⁵⁶ The average mass resolving power ($m/\Delta m_{50\%}$) was greater than 400 000 in all cases, namely, sufficient to resolve the 3.4 mDa mass doublet for species whose elemental compositions differ by SH_4 versus C_3 across the entire observed mass range. The molecular-weight range is largest for the raw bitumen. The HVGO, HVGO acid-only fraction, and HVGO acid-free fraction do not contain the higher molecular-weight species (700–900 Da) present in the raw bitumen. The

HVGO and IER fraction exhibit narrower molecular-weight distributions because their speciation is limited by the distillation cut temperature. The insets in Figure 1 show low-resolution linear quadrupole ion-trap mass spectra that provide independent verification of the molecular-weight distributions obtained by FT-ICR MS.

Molecular formulas could be assigned to 95% of all observed species. From the molecular formula assignments, complete class ($\text{N}_n\text{O}_o\text{S}_s$, heteroatom content), type [the number of rings and double bonds: double bond equivalent (DBE)], and carbon number analyses are straightforward. Figure 2 shows the class distribution for raw bitumen, HVGO, and the IER-isolated acid-only and acid-free fractions. The O_2 class presumably contains carboxylic acids, which predominate in all but the HVGO acid-free fraction. The similarity in class distribution between the raw bitumen, HVGO, and HVGO acid fraction suggests that carboxylic acid molecular composition may be determined from the FT-ICR MS analysis of the raw bitumen alone, so that further fractionation and/or purification is unnecessary.

Furthermore, a subset of the O_2 and S_1O_2 acids distill from the bitumen to the HVGO fraction. Acid-IER fractionation enables identification of S_1O_4 and S_2O_4 multi-heteroatom classes (in the HVGO acid-free fraction) that were not observed in the HVGO, because of the removal of high relative abundance O_2 species. In addition, the HVGO acid-free fraction also contained low abundance S_1O_5 – S_1O_8 series (data not shown). Interestingly, the $\text{S}_{1+x}\text{O}_{2+y}$ classes in the acid-free fraction start at much lower DBE (as low as DBE = 0), suggesting noncarboxylic (or sulfonic) acid functionalities. Their preferential enrichment in the acid-free fraction implies that sulfur-based acids are not retained on the acid-IER resin as strongly as carboxylic acids. We are currently trying to identify the S_xO_y functionalities and will confirm their retention behavior on the acid-IER resin through the use of standards. Low-abundance, noncarboxylic acid-containing classes, such as N_1O_1 , N_1S_1 , and S_1O_1 , distill

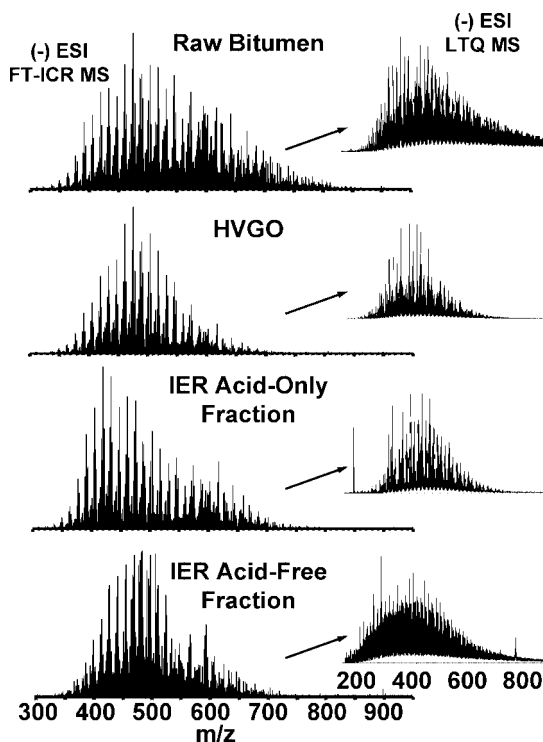


Figure 1. Broadband negative-ion electrospray 9.4 T FT-ICR mass spectra of Athabasca Canadian bitumen, distillation-isolated HVGO, IER-isolated HVGO acid fraction, and IER-isolated HVGO acid-free fraction. Insets on the right show low-resolution linear ion-trap mass spectra that validate the molecular-weight distributions observed by FT-ICR MS.

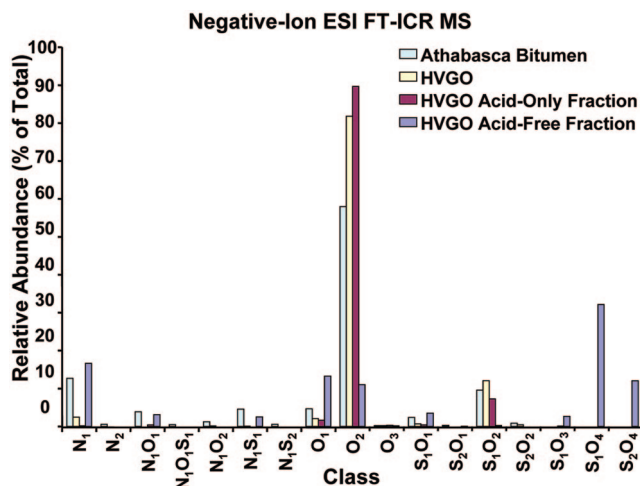


Figure 2. Heteroatom class analysis for Athabasca Canadian bitumen, HVGO, IER-isolated HVGO acid fraction, and IER-isolated HVGO acid-free fraction, derived from the high-resolution ESI FT-ICR mass spectra of Figure 1.

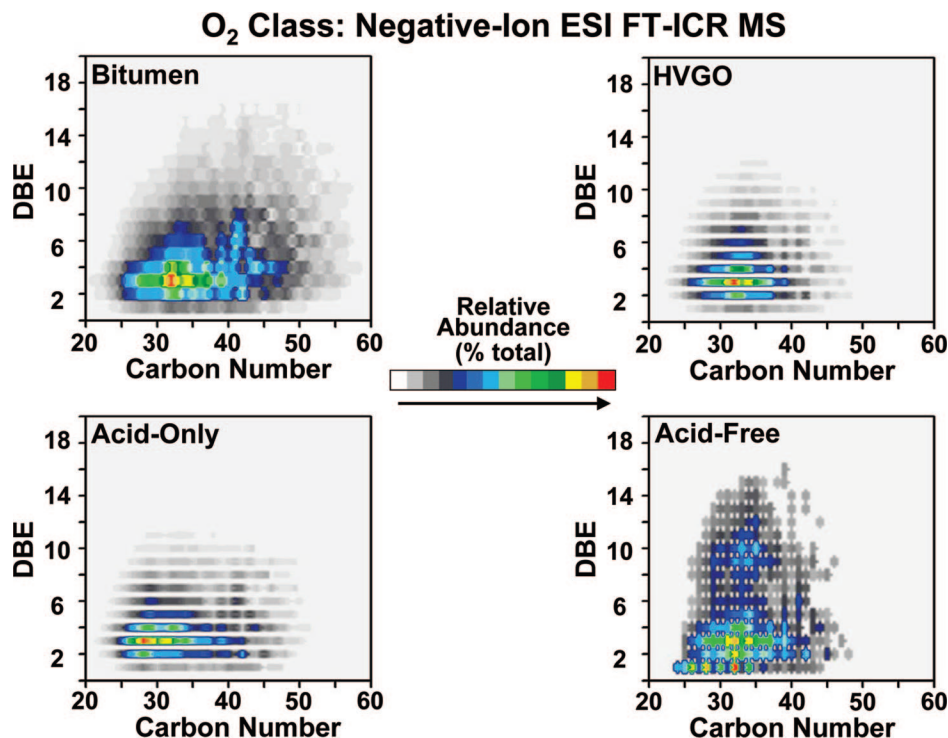


Figure 3. Color-coded isoabundance contours for plots of DBE versus carbon number for the O_2 class for Athabasca Canadian bitumen, HVGO, IER-isolated HVGO acid fraction, and IER-isolated HVGO acid-free fraction.

into the HVGO and are subsequently identified in the HVGO acid-free fraction. To provide a more detailed look at acid molecular composition, the data in Figure 2 were used to construct isoabundance color-coded plots to investigate the differences in DBE and carbon number distribution of the samples.

DBE versus the Carbon Number for O_2 Class Species. Figure 3 shows color-coded isoabundance contours for DBE versus the carbon number for members of the O_2 class. Raw bitumen mainly contains acids from DBE = 1–10 with ~25–46 carbons. The highest relative abundance acids are non-aromatic (DBE = 2–4, consistent with a structure of two cyclic alkane rings and a carboxylic acid), with 25–40 carbons, centered at ~32 carbons. Acids from HVGO display narrower DBE (2–7) and carbon number ranges (26–40) than raw bitumen, suggesting that the higher molecular-weight and/or more aromatic acids do not distill into the HVGO fraction. The HVGO acid-only fraction O_2 species extend to a slightly higher carbon number than those from HVGO and a lower carbon number than for raw bitumen and HVGO, suggesting that shorter alkyl chain, less sterically hindered naphthenic acids may preferentially bind to the acid–IER. A few “acids” are not retained by IER and elute in the acid-free fraction. In contrast, the HVGO acid-free fraction exhibits more extensive aromatic O_2 species (DBE = 7–11) that are not visible from raw bitumen. The high DBE species could arise from low-acidity phenols (a phenyl ring with an ionizable hydroxyl group) or a phenol combined with a furan (oxygen contained in a five-membered ring) that are thought to exist in the parent bitumen.

DBE versus the Carbon Number for S_1O_2 Class Species. Figure 4 shows isoabundance contours for DBE versus the carbon number for the S_1O_2 class. Raw bitumen contains S_1O_2 species with DBE = 4–11 and carbon number = 27–46. The two regions of higher relative abundance (DBE = 4–7 and carbon numbers of 28–34; DBE = 7–11 and carbon numbers of 37–42) indicate two stable core structures,

consistent with thiophenic and benzothiophenic acids. As for the O_2 class, only a subset of the S_1O_2 class identified in the raw bitumen distills into the HVGO fraction, corresponding to S_1O_2 species of DBE = 3–8 and carbon numbers of 25–35. The species of high relative abundance are similar to those for bitumen but with less aromatic cores. As for the O_2 class, the HVGO acid-only fraction S_1O_2 species have DBE values similar to those for HVGO but with somewhat larger carbon numbers. The S_1O_2 species are presumed to contain acid functionalities, because they are less abundant in the acid-free fraction.

DBE versus the Carbon Number for N_1 Class Species. Figure 5 shows plots of N_1 class DBE versus the carbon number. The N_1 species [pyrrolic (“neutral”) nitrogen] in raw bitumen are highly aromatic, with DBE values from 10–18 and carbon numbers of 32–46. The most abundant species exhibit DBE = 13 (consistent with a core structure of 5*H*-benzo[*b*]carbazole with an additional cyclic alkane ring). The DBE and carbon number distributions for the HVGO are narrower than for raw bitumen: the most abundant N_1 species (DBE = 12–13) do not contain the high carbon number species found in the raw bitumen. Few nitrogen species are extracted into the HVGO acid-only fraction, indicating that the fractionation is not selective for neutral nitrogen compounds, as expected. N_1 species in the acid-free fraction have slightly higher DBE values and carbon numbers than the HVGO. These species are in the HVGO fraction but are masked by the O_2 carboxylic acids that are ionized more efficiently than pyrrolic nitrogen.⁵⁷ However,

(56) Senko, M. W.; Beu, S. C.; McLafferty, F. W. Automated assignment of charge states from resolved isotopic peaks for multiply charged ions. *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 52–56.

(57) Hughey, C. A.; Rodgers, R. P.; Marshall, A. G.; Qian, K.; Robbins, W. K. Identification of acidic NSO compounds in crude oils of different geochemical origins by negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Org. Geochem.* **2002**, *33* (7), 743–759.

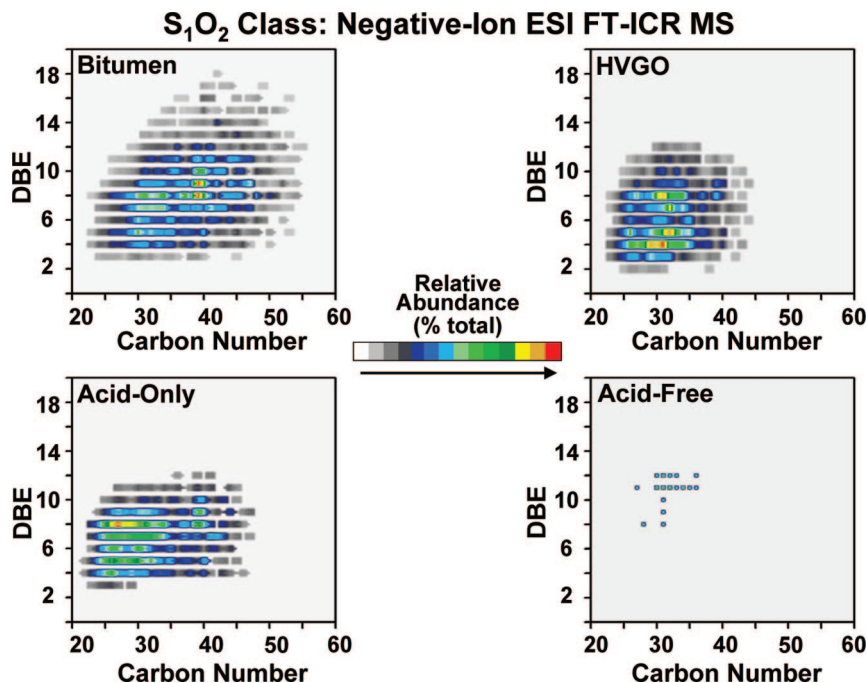


Figure 4. Color-coded isoabundance contours for plots of DBE versus carbon number for the S₁O₂ class for Athabasca Canadian bitumen, HVGO, IER-isolated HVGO acid fraction, and IER-isolated HVGO acid-free fraction.

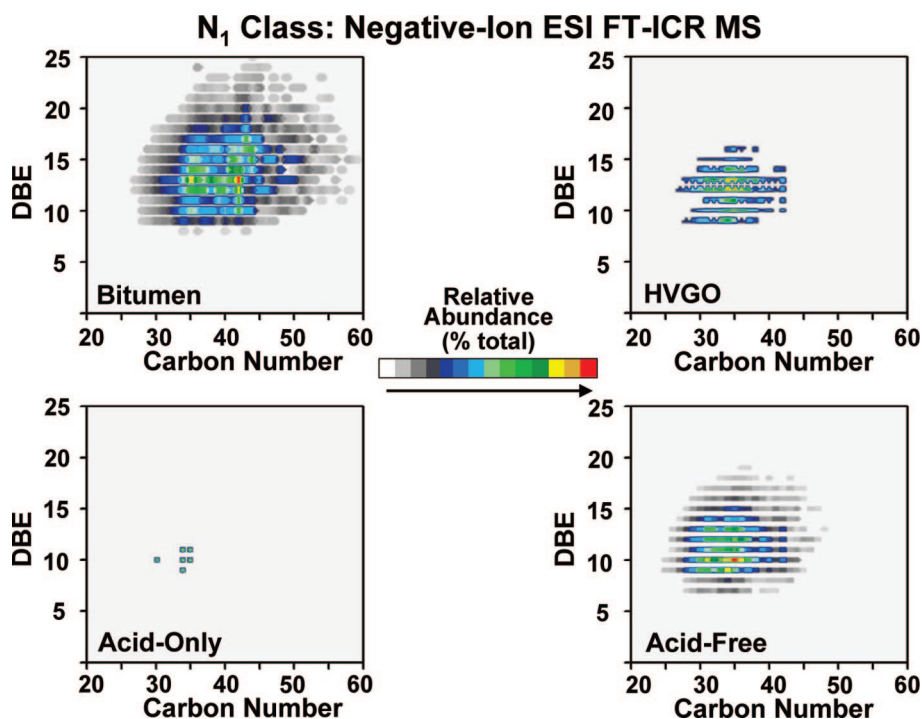


Figure 5. Color-coded isoabundance contours for plots of DBE versus carbon number for the N₁ class for Athabasca Canadian bitumen, HVGO, IER-isolated HVGO acid fraction, and IER-isolated HVGO acid-free fraction.

removal of the O₂ species by acid–IER fractionation does enable identification of species in low relative abundance in the original bitumen.

In summary, negative-ion electrospray FT–ICR MS allows for selective ionization of polar acidic species of Athabasca Canadian bitumen and its IER-isolated HVGO acid-only and acid-free fractions. The ultrahigh resolution and mass accuracy of FT–ICR MS, combined with Kendrick mass sorting, enable the assignment of unique elemental compositions to all above-threshold mass spectral peaks. Naphthenic acids (O₂ and S₁O₂ classes) in the raw bitumen distill into

the HVGO but with truncated DBE and carbon number distributions because of the boiling point constraints of the HVGO fraction.

Comparison of the class, type, and carbon number distributions of the raw bitumen, HVGO, and HVGO acid-only fraction indicates that carboxylic acid (O₂ class) molecular composition can be determined from the raw bitumen alone, so that IER fractionation does not yield new information about the acid molecular composition. However, the acid–IER fractionation increases the relative abundance of species in the acid-free fraction, because of the removal of O₂ components, and thus

improves N_1 speciation. In addition, IER may preferentially concentrate short-chain naphthenic acids. The elution of S_1O_2 species in the acid-only fraction suggests they are most likely thiophene-based carboxylic acids. The presence of higher S_xO_y classes in the acid-free fraction (not observed in the raw bitumen or HVGO) suggests that they are a non-naphthenic acid in character.

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