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Characterization of Acidic Compounds in Heavy Petroleum Resid by Fractionation and Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Analysis

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Supporting Information

ABSTRACT: Negative-ion electrospray ionization (ESI) enabled the direct mass spectrographic analysis of phenols, naphthenic acids, and neutral nitrogen compounds in petroleum fractions without prefractionation; however, ESI results provide few quantitative and structural information about the analytes: the composition of acidic compounds in heavy oil, such as distillate resid, is still unclear. In this study, extrography was used to fractionate oilsands bitumen-derived vacuum-topped bitumen (VTB) and its maltene and asphaltene fractions into multiple subfractions. The molecular compositions of acidic functional compounds in the VTB and its subfractions were analyzed by negative-ion ESI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Extrographic separation was a necessary step to isolate acidic compounds of various acidities and/or polarities in vacuum resid fractions to achieve a systematic analysis. The results showed that the O₂ class species in VTB were highly condensed phenols and carboxylic acids. The maltene fraction contained most of the less condensed naphthenic acids, whereas the asphaltene fraction contained highly condensed carboxylic acids and phenolic compounds with a double-bond equivalent (DBE) higher than 6. The presence of acids had no significant impact on the yield of asphaltenes in *n*-C₇ solvent precipitation. Acid-free asphaltene fractions, which account for more than 90 wt % of the asphaltenes, cannot be ionized by negative-ion ESI.

■ INTRODUCTION

Oxygen-containing compounds in petroleum include alcohols, phenols, furans, carboxylic acids, ketones, quinones, esters, and compounds with multiple functional groups.^{1–4} Phenols and carboxylic acids in petroleum are commonly known as petroleum acids.^{5–7} Among them, naphthenic acids are the dominant petroleum acids,⁶ which have a detrimental effect on the quality and property of crude oil, causing a lot of operational and handling problems, such as corrosion and low thermal stability during oil exploitation, transportation, and production.^{5,8} Naphthenic acids are also commonly used as chemicals for emulsifying/demulsifying agents, timber anti-septics, and paint-dyeing reagents.⁹

Research studies on petroleum acids started in 1925,¹⁰ devoting efforts on isolating and analyzing acid compounds in crude oil. Distillation,¹¹ liquid–liquid extraction,^{12–15} ion-exchange chromatography,^{4,16} chromatographic adsorption,^{17,18} and extraction chromatography (extrography)^{19–21} have been used to isolate acid fractions from crude-oil-derived streams. The efficiencies of isolating acid compounds by various sample preparation methods were determined.^{13,22,23} It was concluded that the selection of the sample preparation method was dependent upon the characteristics of acid compounds in the sample. Solvent extraction was effective in isolating low-molecular-weight acid compounds.¹³ The ion-exchange resin separation method was used to separate acids from the vacuum gas oil (VGO) fraction of Athabasca bitumen. Aminopropyl silica was used to isolate acids from a South American crude

oil.²⁴ The extrography method developed by Ramljak et al.²⁰ was highly effective and reproducible in separating the acid fraction from crude oils with high total acid numbers (TANs).¹⁹

Acids have high polarity and are usually converted to corresponding esters by derivatization to facilitate analysis by gas chromatography/liquid chromatography mass spectrometry (GC/LC MS).^{25,26} Hsu et al. evaluated chemical ionization (CI), fast ion bombardment mass spectrometry (FIB–MS), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI) in positive- and negative-ion modes for characterization of acids in crude oil without derivatization.²⁷ ESI is a “soft” ionization technique, capable of ionizing crude acids with high selectivity. The coupling of ESI with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used directly to characterize acidic compounds in conventional crude oils, oilsands bitumen, and their derived light fractions and asphaltenes. The crude acids and asphaltenes were dominated by multi-oxygen-containing compounds.^{24,28–42} It was found that 50–75% of oxygen-containing compounds in Athabasca bitumen-derived asphaltenes contained hydroxyl groups.^{2,20,43} The effects of asphaltene acidic fractions on the stability of oil/water emulsions were reported.^{29,44–46} The molecular aggregation of asphaltenes

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has been investigated.^{16,47–51} It was proposed that the π – π stacking^{52,53} and hydrogen bonding^{16,54,55} were the two main contributors, leading to asphaltene aggregation. However, the molecular association of acids is by hydrogen bonding.^{16,56} Therefore, it is not known if the presence of petroleum acids would impact the yield of asphaltenes in the solvent precipitation process.

In this paper, extrography was used to fractionate oilsands bitumen-derived vacuum-topped bitumen (VTB) and its maltene and asphaltene fractions into multiple subfractions. All subfractions were characterized by negative-ion ESI FT-ICR MS analyses to determine the acidic functional groups. The impact of acidic compounds in vacuum resid on the yield of precipitated asphaltenes will be discussed.

EXPERIMENTAL SECTION

Materials. VTB was obtained from a Syncrude commercial oilsands plant. Normal heptane (n -C₇), toluene, isopropanol, chloroform (CHCl₃), formic acid (HCOOH), and potassium hydroxide (KOH) were commercial products. Prior to usage, the solvents were purified by distillation. The 100–200-mesh silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. (Shandong, China) was purified by Soxhlet extraction with CHCl₃ for 24 h and activated by heating at 120 °C for 2 h.

Preparation of VTB Fractions. Figure 1 shows the separation scheme for preparing VTB fractions. The asphaltene precipitation was

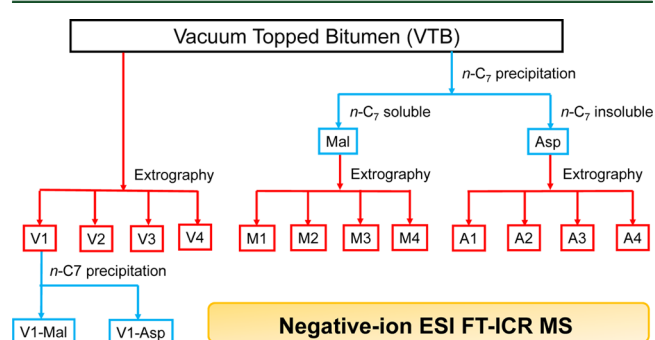


Figure 1. Fractionation scheme of VTB.

conducted in a 250 mL flask equipped with a heating jacket, an extractor, and a condenser (see Figure S-1 of the Supporting Information). A total of 1 g of VTB and 70 mL of n -C₇ were added to the flask and heated to reflux for 2 h. The mixture was cooled to ambient temperature and kept standing for at least 2 h until the insoluble matters settled down. The precipitate was obtained by filtration with a 1–3 μ m filter paper. The filtrate was subjected to vacuum rotary evaporation to remove the n -C₇ solvent and yield the maltenes (Mal, n -C₇-soluble matters of VTB). The filter paper covered with n -C₇-insoluble matters was transferred into the extractor and extracted with 60 mL of reflux toluene for 6 h. The toluene solution was subjected to vacuum rotary evaporation to remove the toluene solvent and yield the asphaltenes (Asp, the organic n -C₇-insoluble matters of VTB).

The extrographic separation was performed in a modified Soxhlet extractor equipped with a chromatographic column, as described in the literature.^{19,20} Alkali-treated silica gel was prepared by dissolving 3 g of KOH in 60 mL of isopropanol and mixing the resulting solution with 30 g of silica gel and 100 mL of CHCl₃. After standing for 5 min, the slurry mixture was introduced into the chromatographic column. The alkali-treated silica gel was rinsed with 50 mL of recirculating CHCl₃ for 30 min, and the spent CHCl₃ was discarded. A solution mixture containing 1 g of VTB and 2 mL of CHCl₃ was introduced onto the top of the alkali-treated silica gel in the chromatographic column, which was capped with 2 g of silica gel (without alkali treatment). The VTB was separated into four fractions using the solvent systems in sequence: (1) 100 mL of CHCl₃ refluxing for 2 h, (2) 100 mL of CHCl₃ refluxing for 4 h, (3) 50 mL of CHCl₃/HCOOH (5:3, v/v) refluxing for 1 h, and (4) 120 mL of CHCl₃/HCOOH (5:3, v/v) refluxing for 6 h. The V1–V4 fractions were obtained from the solutions after removing the solvent by vacuum rotary evaporation at 120 °C. Similar extrography was performed on maltenes (Mal) and asphaltenes (Asp), and the extrographic subfractions were M1–M4 and A1–A4, respectively.

From the mixture of KOH–isopropanol solution and silica gel, potassium silicate was presumably formed by an ion-exchange reaction and retained on silica. In the separation process, neutral, basic, and weak acidic materials would be eluted off by CHCl₃ extraction, while acidic materials and/or strongly polar substances would be eluted off by the mixture of CHCl₃ and HCOOH.²⁰ When the elution time was set, acid-free or acidic fractions were separated into two parts with different polarity.

The ASTM D664 method was used to determine the TAN of VTB and its subfractions. TAN is defined as milligrams of KOH required to neutralize all acid compounds in 1 g of oil sample. Elemental analyses of VTB and its subfractions were performed using the Flash EA 1112

Table 1. Yields and Properties of VTB and Its Subfractions

	yields (wt %)	TAN (mg of KOH/g)	elemental content (wt %)					atomic ratio			
			C	H	N	S	O	H/C	N/C	S/C	O/C
VTB	100.00	3.33	78.42	9.42	0.68	6.84	2.57	1.441	0.007	0.033	0.025
V1	87.70	0.07	78.64	9.63	0.68	6.58	2.48	1.470	0.007	0.031	0.024
V2	0.56	ND ^a	78.07	7.72	0.93	7.44	2.84	1.187	0.010	0.036	0.027
V3	0.28	ND ^a	75.65	7.25	0.66	7.43	3.79	1.150	0.007	0.037	0.038
V4	4.56	16.88	75.40	9.75	0.29	5.45	4.60	1.552	0.003	0.027	0.046
Mal	81.63	ND ^a	78.90	9.94	0.61	5.99	2.56	1.512	0.007	0.028	0.024
M1	90.79 ^b	ND ^a	78.79	9.96	0.61	6.16	2.74	1.516	0.007	0.029	0.026
M2	0.16 ^b	ND ^a	77.89	8.36	1.17	7.63	3.30	1.288	0.013	0.037	0.032
M3	0.04 ^b	ND ^a	75.64	8.24	0.76	8.37	3.54	1.307	0.009	0.041	0.035
M4	2.87 ^b	ND ^a	76.34	8.96	0.78	7.77	3.63	1.408	0.009	0.038	0.036
Asp	16.74	ND ^a	77.69	7.69	1.20	8.22	2.93	1.188	0.013	0.040	0.028
A1	84.94 ^b	ND ^a	76.74	7.54	1.22	8.57	2.13	1.178	0.014	0.042	0.021
A2	0.97 ^b	ND ^a	77.27	6.71	1.29	10.25	2.39	1.042	0.014	0.050	0.023
A3	0.58 ^b	ND ^a	76.22	7.20	1.00	10.77	2.44	1.133	0.011	0.053	0.024
A4	5.71 ^b	ND ^a	75.73	8.22	0.93	8.49	2.65	1.303	0.011	0.042	0.026

^aND = not determined. ^bYields of M1–M4 and A1–A4 were based on maltenes (Mal) and asphaltenes (Asp).

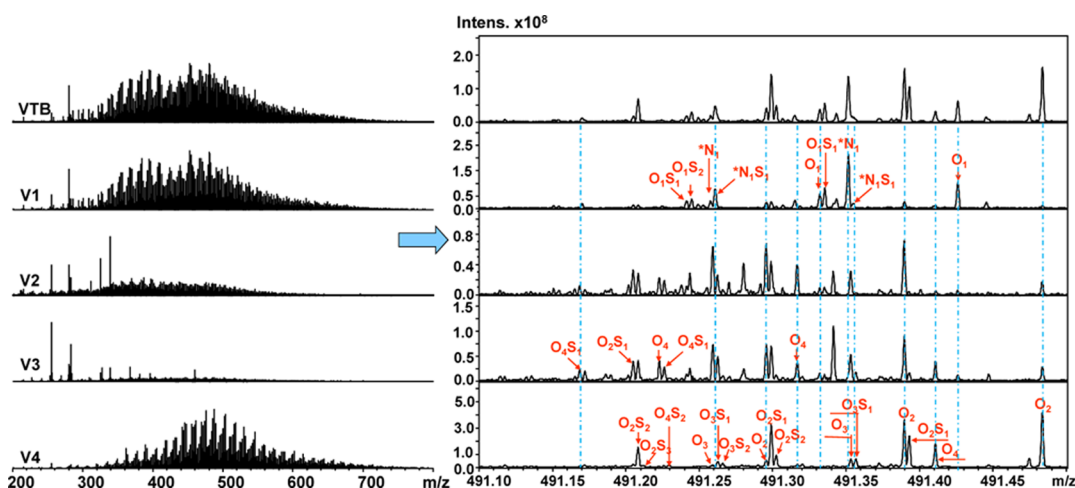


Figure 2. (Left) Broadband negative-ion ESI FT-ICR MS mass spectra of VTB and its extrographic subfractions V1–V4 and (right) their expanded mass spectra at m/z 491.

elemental analyzer (Thermo Electron Co.) according to the GB/T 19143-2003 method.^{57,58}

ESI FT-ICR MS Analysis. Bruker Apex Ultra FT-ICR MS equipped with a 9.4 T superconducting magnet and ESI in negative-ion mode was used to analyze the molecular composition of VTB and its fractions. The sample preparation for negative-ion ESI FT-ICR analysis and the equipment operating conditions have been described elsewhere.⁵⁹ The sample concentration is 0.2 mg/mL in toluene/methanol (1:3, v/v).

Data processing of FT-ICR MS has also been described elsewhere.^{60,61} In brief, the mass spectra were internally calibrated by one or two abundant class homologous series using the commercial software by Bruker Daltonics data analysis. For example, the V1 and V4 were internally calibrated by N_1 and O_2 species (see Figures S-2 and S-3 in Supporting Information). Mass spectra peaks with relative abundance 4 times greater than the standard deviation of baseline noise were included in calculation. The composition assignment of each peak was performed within 0.0010 Kendrick mass defect (KMD) tolerances.

RESULTS AND DISCUSSION

Yields and Elemental Composition of Separated Fractions. Table 1 shows the yields, elemental contents, and atomic ratios of VTB and its subfractions: Mal, M1–M4, Asp, and A1–A4. Asphaltene precipitation from VTB has good material balance, with 81.6 wt % Mal and 16.7 wt % Asp. However, the total yields of extrographic subfractions of VTB, Mal, and Asp are 93.1, 93.9, and 92.2 wt %, respectively. The material loss is likely due to residuals absorbed onto the alkali-treated silica gel in the chromatographic column and could not be eluted off.

The V1 is dominant and accounts for 88 wt % of VTB; however, it is a relatively weak acidic fraction, with a TAN value of 0.07. The V4 accounts for 4.5 wt % of VTB and is a highly acidic fraction, with a TAN value of 16.88. The TAN values of V2 and V3 were not determined because of insufficient sample amount.

Table 1 also shows that the atomic ratios (H/C, N/C, S/C, and O/C) of VTB are similar to those of V1. Subfractions V2 and V3 have low H/C atomic ratios, indicating that these components have a highly condensed molecular structure. Subfraction V4 should be acidic components, which are more likely naphthenic acids; high H/C and O/C atomic ratios indicate that these species are highly saturated in nature.⁶²

The yields of M1 and A1 are 91 and 85 wt %, respectively. The elemental composition of M1 is similar to that of Mal. The A1–A3 subfractions have similar elemental composition with Asp. The yields of M4 and A4 are about 2.9 and 5.7 wt %, respectively. The H/C atomic ratio of M4 is larger than that of A4, indicating less condensed acids in M4.

The total yields of second and third fractions are very low, about 0.8 wt % in VTB, only 0.2 wt % in maltene, and 1.5 wt % in asphaltene. Results suggest that the extrography partitioned the VTB, Mal, and Asp into two fractions by molecular acidity.

Petroleum Acids in VTB. Figure 2 shows (left) broadband negative-ion ESI FT-ICR MS mass spectra of VTB and subfractions V1–V4 and (right) their expanded mass spectra at m/z 491 to elucidate the variation of class species in various samples. The N_1 - and O_1 -containing compounds are mainly detected in V1. The abundant N_1 peaks in the full mass ranges of V1 produced similar mass distribution profiles with VTB. The O_2 - and multi-oxygen-containing compounds are detected in V2–V4. High double-bond equivalent (DBE) oxygen-containing compounds (located at low-molecular-weight regions of the spectra) have relatively high abundance in V2 and V3. However, V2 and V3 show very low peak intensities at full-range mass spectra. The mass spectra of V4 shifts to higher values, indicating a larger average molecular weight of the acidic fraction.

Figure 3 shows the relative abundances of the dominant class species in VTB and its subfractions V1–V4. The high relative

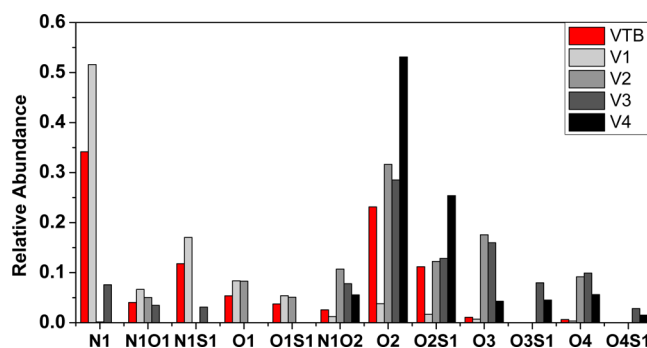


Figure 3. Relative abundances of the dominant class species in VTB and extrographic subfractions V1–V4.

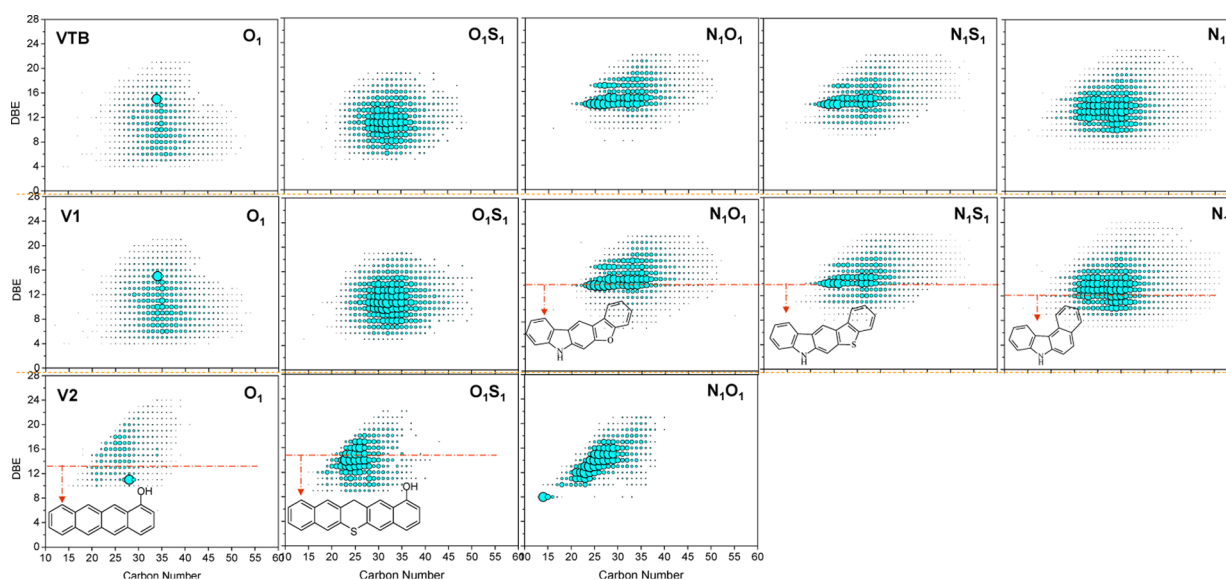


Figure 4. Isoabundance maps of DBE as a function of the carbon number for O_1 , O_1S_1 , N_1O_1 , N_1S_1 , and N_1 class species in VTB, V1, and V2.

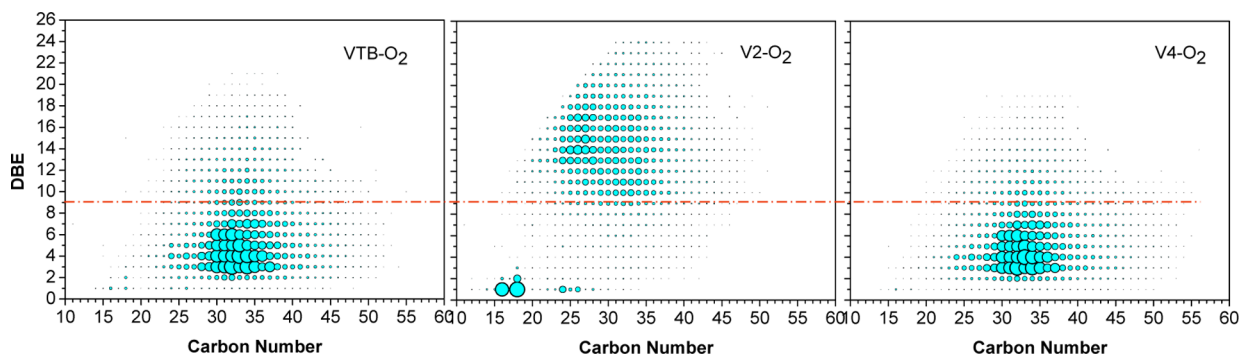


Figure 5. Isoabundance maps of DBE as a function of the carbon number of O_2 species in VTB, V2, and V4.

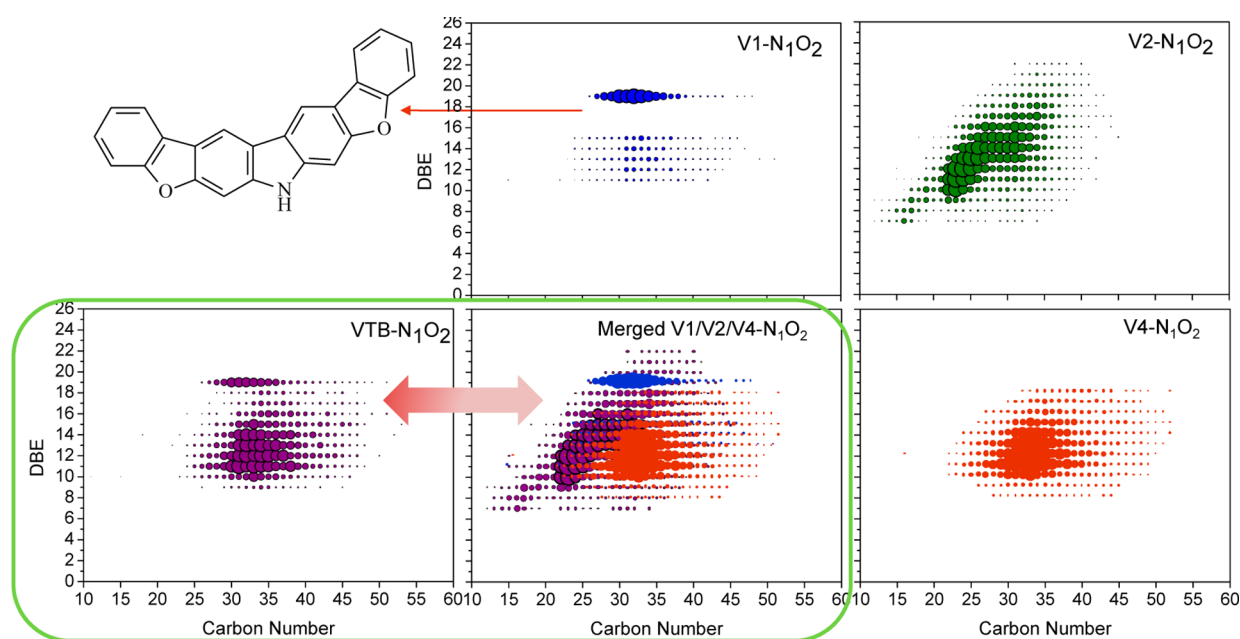


Figure 6. Isoabundance maps of DBE as a function of the carbon number of N_1O_2 species in VTB, V1, V2, and V4.

abundant class species in V1 are O_1 , O_1S_1 , N_1S_1 , N_1O_1 , and N_1 species, whereas those in subfraction V2 are O_1 , O_1S_1 , and

N_1O_1 species. Subfraction V4 should be acidic compounds, which have abundant O_2 , O_3 , and O_4 class species with or

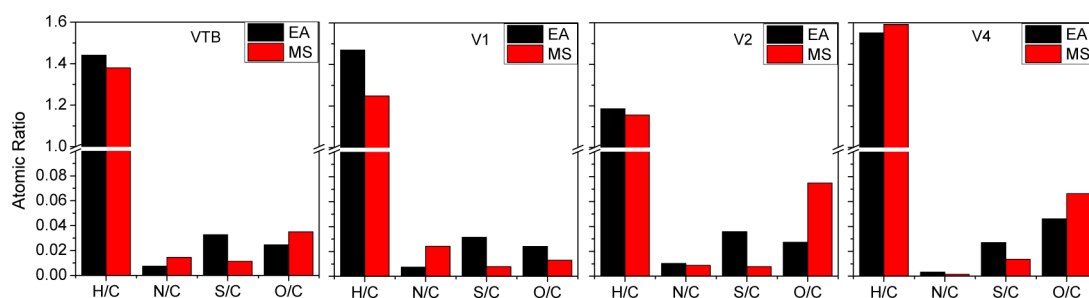


Figure 7. Atomic ratios of VTB and its extrographic fractions calculated from elemental analysis (EA) and ESI FT-ICR MS analysis (MS).

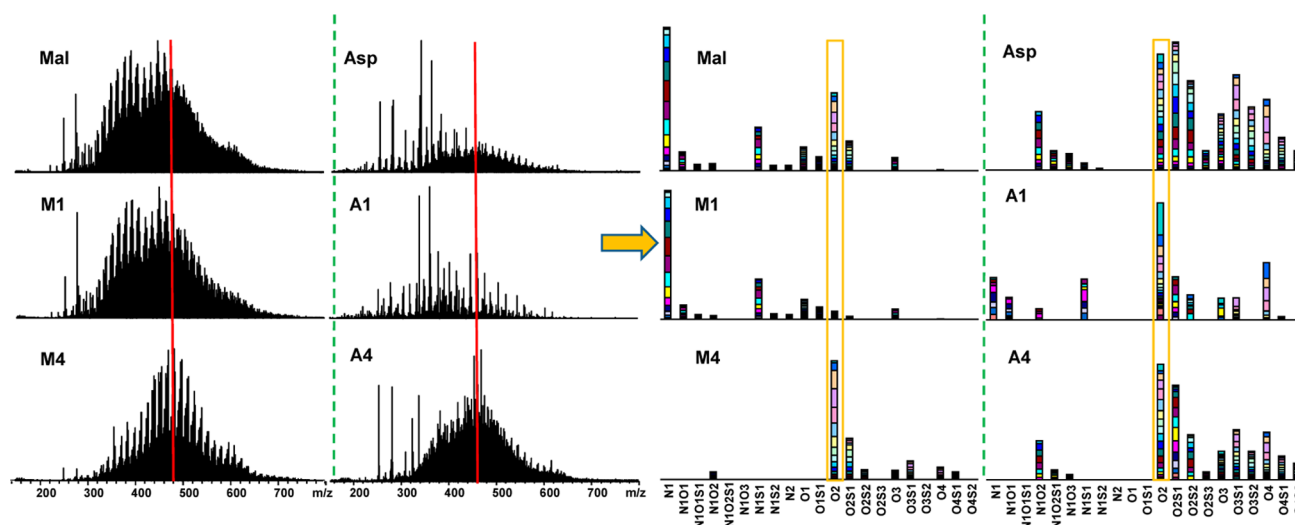


Figure 8. Broadband negative-ion ESI FT-ICR MS mass spectra and abundances of various heteroatom class species in Mal, Asp, and their first and fourth subfractions.

without sulfur atoms. High abundances of O_xS class species and their similar relative abundance distribution with O_x class species indicate that these sulfur-containing compounds have a similar acidic function group with O_x class species. The N_1 and O_1 class species identified by negative-ion ESI FT-ICR MS are pyrroles and phenols.^{19,24,28,62} Multi-heteroatom-containing compounds, such as N_1O_1 , N_1O_2 , and O_1S_1 species, possess multi-functional groups and may present different compound distribution patterns in various subfractions.

Figure 4 shows the isoabundance maps of DBE as a function of the carbon number for O_1 , O_1S_1 , N_1O_1 , N_1S_1 , and N_1 class species in VTB and its subfractions V1–V2. The DBE values and carbon numbers for these five species in V1 are the same as those in subfraction VTB. An increment of 2 of the DBE distribution center from N_1 species (DBE = 12) to N_1O_1/N_1S_1 species (DBE = 14) indicates that oxygen and sulfur atoms are likely in furanic and thiophenic rings, respectively, as shown in the insets of Figure 4.

The O_1 , O_1S_1 , and N_1O_1 class species in subfraction V2 have a higher DBE and lower carbon number distribution center than that in V1, suggesting more condensed molecular structures of compounds in V2. These species should be sulfur- and nitrogen-containing phenolic compounds. Therefore, by extrographic separation, molecular composition of highly condensed phenols, which was separated into subfraction V2, is obtained.

Figure 5 shows the isoabundance maps of DBE as a function of the carbon number for O_2 class species in VTB and subfractions V2 and V4. The O_2 class species in VTB and V4

are similar, which should be carboxylic acids, including naphthenic acids with 3–6 DBE (2–5 naphthenic rings) and aromatic acids with at least 5 DBE. Carboxylic acids are the most abundant acidic compounds in petroleum and can be easily ionized by ESI.^{7,63} However, the O_2 class species in subfraction V2 have higher DBE values and lower carbon numbers than those in VTB or V4. The O_2 and O_1 class species in subfraction V2 had similar DBE values and carbon numbers (shown in Figure S-4 of the Supporting Information). The O_2 class species, which have a condensed molecular structure, eluted out of the column first and then the acidic components with a low DBE value in V4, indicating that they are phenolic compounds instead of naphthenic acids.

Figure 6 shows the isoabundance maps of DBE as a function of the carbon number for N_1O_2 class species in VTB and subfractions V1, V2, and V4. The abundant N_1O_2 class species in VTB are with 11–14 and 19 DBE, which correspond to those in subfractions V4 and V1. The N_1O_2 class species with 11–14 DBE in V4 were postulated as nitrogen-containing carboxylic acids. The N_1O_2 class species with 19 DBE in subfraction V1 was suspected of having a core structure of benzocarbazole/naphthocarbazole moiety fused with two furan rings, as shown in the inset of Figure 6. In subfraction V2, the DBE values and carbon numbers of N_1O_2 class species in subfraction V2 are similar to those of N_1O_1 class species (see Figure S-4 of the Supporting Information), suggesting that the difference between these two classes is an hydroxyl, which has no impact on the DBE value. By extrographic separation, the trace amounts and/or low-polarity phenolic O_1 and O_2 class

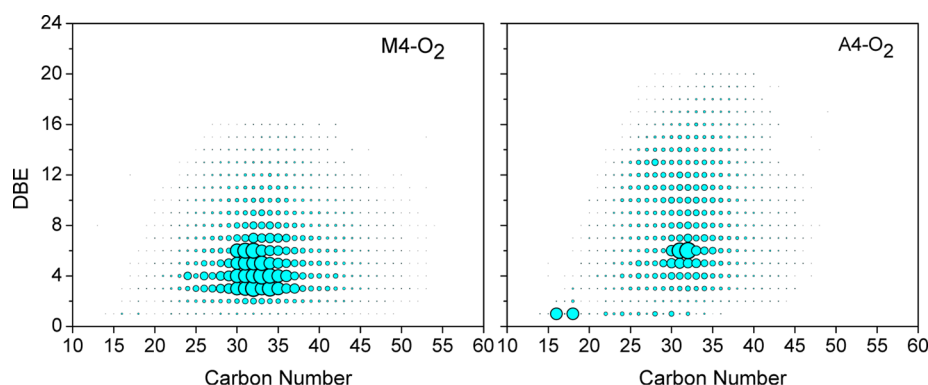


Figure 9. Isoabundance maps of DBE as a function of the carbon number for O_2 class species in M4 and A4.

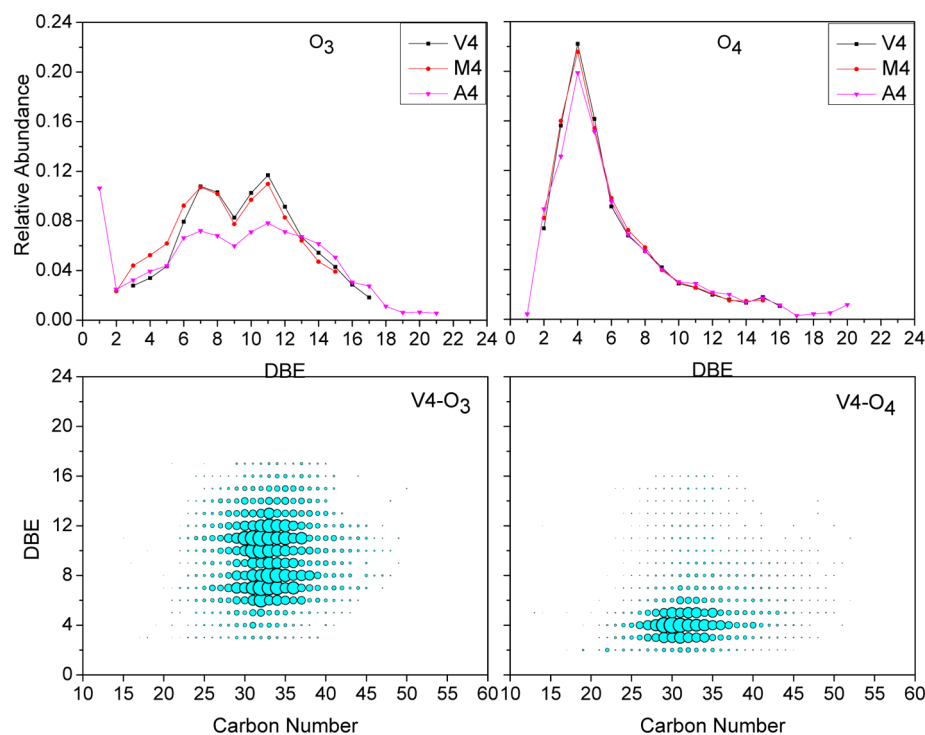


Figure 10. (Top) Relative abundance of O_3 and O_4 class species as a function of DBE in V4, M4, and A4 and (bottom) isoabundance maps of DBE as a function of the carbon number of O_3 and O_4 species in V4.

species with highly condensed structures can be isolated from carboxylic acids and analyzed.

Considering ESI is a selective ionization method for polar compounds, the atomic ratios (H/C, N/C, S/C, and O/C) of VTB, V1, V2, and V4 calculated from elemental analysis (EA) were compared to those obtained from ESI FT-ICR MS (MS), as shown in Figure 7. For VTB, MS exhibits lower H/C and S/C but higher N/C and O/C ratios than EA. That is because of the selective ionization of N- and O-containing compounds in the ESI source. This phenomenon is more noticeable in V1 because of its enrichment of hydrocarbons and sulfur-containing compounds, which are nonpolar and cannot be ionized in the ESI source. In comparison to EA results, V2 by MS has lower H/C and N/C and higher O/C ratios, whereas V4 by MS has higher H/C and O/C ratios. This is in accordance with analysis results mentioned above that high condensed phenols and carboxylic acids are enriched in subfractions V2 and V4, respectively. The H/C and O/C atomic ratios calculated from MS are a little higher than those

of EA because ESI source has high ionization selectivity and efficiency to carboxylic acids. These results indicate that molecular composition of compounds identified by ESI FT-ICR MS could reflect the compositional character of acidic polar fractions.

Petroleum Acids in *n*-C₇ Maltenes and Asphaltenes of VTB. Figure 8 shows the broadband negative-ion ESI FT-ICR MS mass spectra and abundances of various heteroatom class species in Mal, Asp, and their first and fourth fractions. Mal and VTB have similar mass spectra and heteroatom class species. Asp is enriched with multi-oxygen-atom-containing compounds, including O_3 , O_3S_x , O_4 , and O_4S_x class species ($x = 1$ or 2). The analysis of maltene- and asphaltene-derived extrographic subfractions will provide some insight on the characteristics of acidic compound distributions in maltenes and asphaltenes. Subfraction M1 has similar mass spectra as Mal, whereas M4 has a higher average molecular weight than Mal and M1. The N_1 - and O_1 -containing species and O_x -containing species ($x \geq 2$) in Mal are partitioned into

subfractions M1 and M4, respectively. Subfraction A4 has similar abundant classes as asphaltenes, indicating that compounds that could be ionized in the ESI source are enriched in subfraction A4.

The O₂-containing compounds are the most abundant compounds in M4 and A4, and the abundant O₂ peaks in the full mass ranges produced a larger average molecular weight of M4 than A4 (see Figure 8). It suggests that the acids in M4 and A4 may have different structures. Figure 9 shows the isoabundance maps of DBE as a function of the carbon number for O₂ class species in subfractions M4 and A4. In subfraction M4, the abundant O₂ class species are naphthenic acids with 3–6 DBE. In subfraction A4, the DBE distribution of abundant O₂ class species centers at about 6 and 11 DBE. The O₂ class species with 6 DBE are likely multi-ring naphthenic acids and/or aromatic acids. The O₂ class species of 11 DBE are likely highly condensed aromatic acids and/or phenols. Because the acid compounds with DBE around 6 are present in subfractions M4 and A4, it suggested that part of these acids can dissolve in the *n*-C₇ solvent.

Figure 10 shows that the relative abundance of O₃ and O₄ class species as a function of DBE in subfractions V4, M4, and A4; the relative abundance was normalized for each fraction. The O₃ and O₄ class species in various fractions seem to have similar structures. Also shown in Figure 10 is the DBE versus carbon number of O₃ and O₄ class species in V4. A previous study showed that the monomers of O₂ class species formed O₄ molecular aggregates with double DBE values and carbon numbers if the concentration of the oil sample was too high and/or the separation conditions of ESI FT-ICR MS analysis were not optimized.¹⁶ The carbon number distribution range reveals that the O₄ class species were monomers; the minimum DBE value of O₄ class species is 2, indicating that these compounds more likely dicarboxylic acids. Because O₂ and O₄ class species were suspected to be carboxylic compounds, it is reasonable to assign O₃ class species as mainly carboxylic compounds with an additional oxygen group. Most of the additional oxygen atoms should have an aromatic group based on the fact that O₃ class species have a higher DBE value than O₂ and O₄ class species.

Heteroatom Compounds in the Acid-Free Fraction of VTB. When subfraction V1 was subjected to *n*-C₇ precipitation, the maltene (V1-Mal) and asphaltene (V1-Asp) yields are 82.8 and 16.6 wt %, respectively. The V1-Mal and V1-Asp subfractions were analyzed by negative-ion ESI FT-ICR MS. Figure 11 shows the broadband negative-ion ESI FT-ICR MS mass spectra and abundances of various heteroatom class species in subfractions V1, V1-Mal, and V1-Asp. The results show that subfractions V1 and V1-Mal had similar mass spectra and heteroatom class species, indicating that compounds that could be ionized in an ESI source were extracted into V1-Mal. However, only contaminant peaks presented in the spectrum of V1-Asp. It implies that more than 90 wt % component of Asp (yield_{V1-Asp} × yield_{V1}/yield_{Asp}) cannot be analyzed by negative-ion ESI. Hence, other ionization techniques, such as FI/FD^{64,65} and atmospheric pressure photoionization (APPI),⁶⁶ would be needed for further study on this part of acid-free Asp.

The ratio of V1-Mal/V1-Asp is 5:1, similar to the ratio of Mal/Asp, which is separated directly from VTB (see Table 1). The ratios of maltenes/asphaltenes before (in VTB) and after (in V1) acidic fraction removal are constant, indicating that the existence of the acidic fraction that could be analyzed by ESI

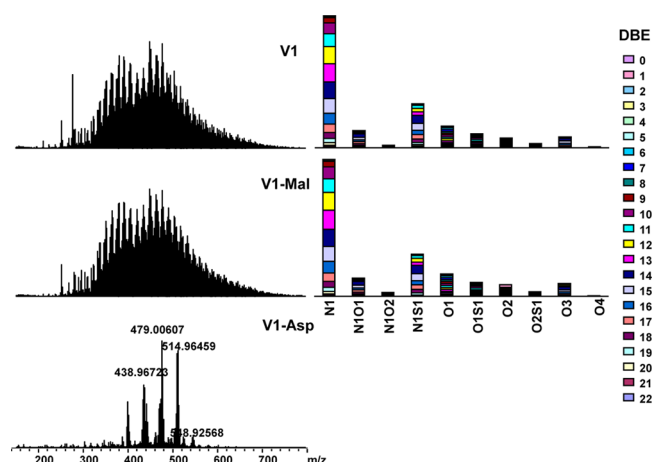


Figure 11. Broadband negative-ion ESI FT-ICR MS mass spectra and relative abundances of heteroatom class species in subfractions V1, V1-Mal, and V1-Asp.

FT-ICR MS has no obvious impact on the amount of precipitated asphaltenes.

CONCLUSION

VTB was fractionated into 16 subfractions by combining extrographic and deasphalting separation and subsequently analyzed by ESI FT-ICR MS. Acidic components in heavy oil were successfully separated from a vacuum residue by extrography. From the separation, some acidic components and neutral nitrogen compounds in trace amounts or with lower ionization efficiency could be characterized by ESI MS. The O₂ species in VTB were separated into highly condensed phenols and carboxylic acids. Naphthenic acids are mainly enriched in maltenes, whereas highly condensed carboxylic acids and phenolic compounds with DBE higher than 6 are enriched in asphaltenes. The existence of acids has no obvious impact on the amount of precipitated asphaltenes. Although more than 90.0 wt % component of asphaltenes separated from VTB cannot be ionized in the ESI source, results from ESI FT-ICR MS provided important clues for the structural investigation of asphaltenes.

ASSOCIATED CONTENT

Supporting Information

Asphaltene separation device and the extractor size (Figure S-1), mass error of N₁ species in the V1 fraction after internal calibration (Figure S-2), mass error of O₂ species in the V4 fraction after internal calibration (Figure S-3), and isoabundance maps of DBE as a function of the carbon number for O₁, O₂, N₁O₁, and N₁O₂ class species in subfraction V2 (Figure S-4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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