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Characterization of Nitrogen Compounds in Coker Heavy Gas Oil and Its Subfractions by Liquid Chromatographic Separation Followed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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A coker heavy gas oil (CHGO) was separated into saturates, aromatics, resins, and asphaltenes (SARA) fractions. The resin fraction was separated into six subfractions by high-performance liquid chromatography (HPLC). The CHGO and its subfractions were characterized by electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The mass spectra showed that the mass range of basic and neutral nitrogen compounds was 200−450 and 160−400 Da, respectively. Five nitrogen class species, N_1, N_2, N_1O_1, N_1O_2, and N_1S_1, were assigned in the positive-ion spectrum. Six nitrogen class species, N_1, N_2, N_1O_1, N_1O_2, N_2O_1, and N_1S_1, were assigned in the negative-ion spectrum. Among the identified nitrogen compounds, the N_1 class species was dominant. The N_1 class species were enriched in the resin fraction. The N_2 class species are likely amphoteric molecules and were enriched in the asphaltene fraction. The composition of nitrogen compounds in the resin subfractions varied significantly in double-bond equivalence (DBE) and carbon number. As the polarity of the resin subfraction increased, the average molecular weights of the nitrogen compounds decreased, DBE values for each heteroatom class species increased, and the N_2 class species became the dominant nitrogen compounds at the expense of the N_1 class species.

Introduction

Nitrogen-containing compounds in petroleum are problematic in refinery processes, because they cause catalyst deactivation. They form nitrogen oxides (NO_x) in the combustion flue gas, which are environmentally regulated compounds. Among the refinery product streams, coker heavy gas oil (CHGO) is known to contain the most refractory nitrogen compounds. The analytical methods that are commonly used to characterize the nitrogen compounds in petroleum are gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC−MS).[1−3] Because of the low mass resolving power and selectivity for nitrogen compounds in traditional MS, the samples are prefractionated to either isolate or concentrate the nitrogen compounds prior to analysis.[2−5] In addition, GC−MS is not capable of analyzing samples that contain higher molecular-mass nitrogen compounds (greater than 300 Da) because of their low volatility.[6] Hence, nitrogen compounds identified by GC−MS account for a fraction of total nitrogen compounds present in petroleum.

Recently, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), which provides an ultrahigh mass resolution and mass accuracy, has been successfully used to analyze species in heavy petroleum fractions.[7] Electrospray ionization (ESI) can be used to selectively analyze polar compounds. It was first used in combination with low-resolution MS for a petroleum system.[8] Positive-ion ESI can selectively ionize heteroatom species, such as basic nitrogen compounds,[9−15] and negative-ion ESI can be used for acids and neutral nitrogen compounds.[9,11,13−20]

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Shi et al.[10] used positive-ion ESI coupled with FT-ICR MS to analyze basic nitrogen compounds in six coker gas oil (CGO) samples. These six CGO samples had similar mass spectra in the 200–500 Da mass range and composition of basic nitrogen compounds. However, the distributions of double-bond equivalence (DBE) versus carbon number for these six CGO samples were slightly different. Negative-ion ESI FT-ICR MS was used to determine the composition and distribution of neutral nitrogen compounds in Liaohe crude oil and its subfractions. Among the N_1, N_2, N_1O_1, N_1O_2, N_1O_3, N_1O_4, O_1, and O_2 class species identified in Liaohe crude oil, N_1 class species were dominant. The resin and asphaltene fractions of Liaohe crude oil contained highly aromatic and acidic species, which were enriched with oxygen- and nitrogen-containing compounds with lower molecular weights than those found in the aromatic fraction. The distribution patterns of N_1, N_1O_1, and O_1 class species in the resins and asphaltenes were similar.[16]

Most previous characterization studies for nitrogen compounds were with bulk oil samples using a method such as open-column chromatography. In this paper, the resin fraction, which was enriched in nitrogen compounds, was separated by

Table 1. Yield and Nitrogen Concentration of SARA Fractions

	saturates	aromatics	resins	asphaltenes	recovery
yield (wt %)	62.6	25.7	6.2	0.5	95
N (wt %)	< 0.0005	0.1	2.5	ND[a]	

[a] ND = not determined.

high-performance liquid chromatography (HPLC) into multiple subfractions. A detail characterization of basic and neutral nitrogen compounds in CHGO and its subfractions was then carried out by GC–MS and ESI FT-ICR MS.

Experimental Section

CHGO and Its Saturates, Aromatics, Resins, and Asphaltenes (SARA) Fractions. The CHGO sample was obtained from Petro-China Dushanzi refinery. It had a boiling range of 350–500 °C and contained 0.5 wt % total sulfur and 0.34 wt % total nitrogen. The SARA fractionation was carried out using the Chinese Petroleum Industrial Standard SY/T 5119-2008. A total of 30 mL of hexane was added to 50 mL of CHGO. The mixture sat for 12 h and then was filtered through a funnel covered with cotton wool. The hexane-insoluble matter on the cotton wool was washed with hexane until the filtrate was clear. The hexane-insoluble asphaltenes remaining on the cotton wool were dissolved and washed by dichloromethane.

The hexane-soluble matter collected was subjected to saturate, aromatic, and resin fractionation. A glass column (8 mm inner diameter×300 mm length) was packed with 3 g of silica gel (80–100 mesh, activated at 150 °C for 8 h) and 2 g of neutral alumina (100–200 mesh, activated at 400 °C for 4 h). Cotton wool was inserted at the bottom of the column. After the hexane-soluble matter was poured through the packed column, 25 mL of hexane was added to elute the saturate fraction. The aromatic fraction was obtained by eluting the column with a 15 mL mixture of hexane/dichloromethane (1:1, v/v). The resin fraction was obtained by eluting the column with 10 mL of ethanol, followed by 15 mL of chloroform. The SARA mass fractions and the concentration of nitrogen in SARA fractions are listed in Table 1. The amount of the asphaltene yield was low and insufficient for nitrogen analysis.

Resin Subfractions. The resin fraction obtained by SARA fractionation was separated into six subfractions using HPLC [Agilent 1200 HPLC, equipped with an refractive index detector (RID), an Agilent ZORBAX CN column (50 mm×4.6 mm inner diameter, 3.5 μm particle size), and an Agilent ZORBAX NH$_2$ column (250 mm × 4.6 mm inner diameter, 5 μm particle size) in series; the columns were eluted with HPLC-grade hexane/isopropanol (4:1, v/v) at a flow rate of 0.5 mL/min]. The resin fraction was dissolved in the mobile phase at a concentration of 5 mg/mL. A differential refractive index detector was used. The sample was passed through the columns, and six subfractions of resins were collected. The whole process was repeated 5 times and the eluants of subfractions were combined. The time intervals at which the subfractions were collected in sequence were 4–7.4, 7.4–10, 10–12, 12–14.1, 14.1–15, and 15–20 min. The retention time windows for sample collection were selected by the peak shape of the chromatogram. The polarity of the resin subfractions increased with the retention time.

Extraction of Basic Nitrogen Compounds. A total of 20 mL of dilute hydrochloric acid (HCl, 1 M) and 100 g of CHGO were mixed in a 250 mL beaker. The mixture was stirred at about 500 rpm for 10 min and then the aqueous phase was separated and collected. This process was repeated 3 times. The three extracted aqueous-phase samples had a total volume of 60 mL. The samples were mixed together, washed by hexane, and then basified with 5 wt % hydroxyl sodium (NaOH) solution to pH 10, followed by extraction with dichloromethane (CH_2Cl_2).

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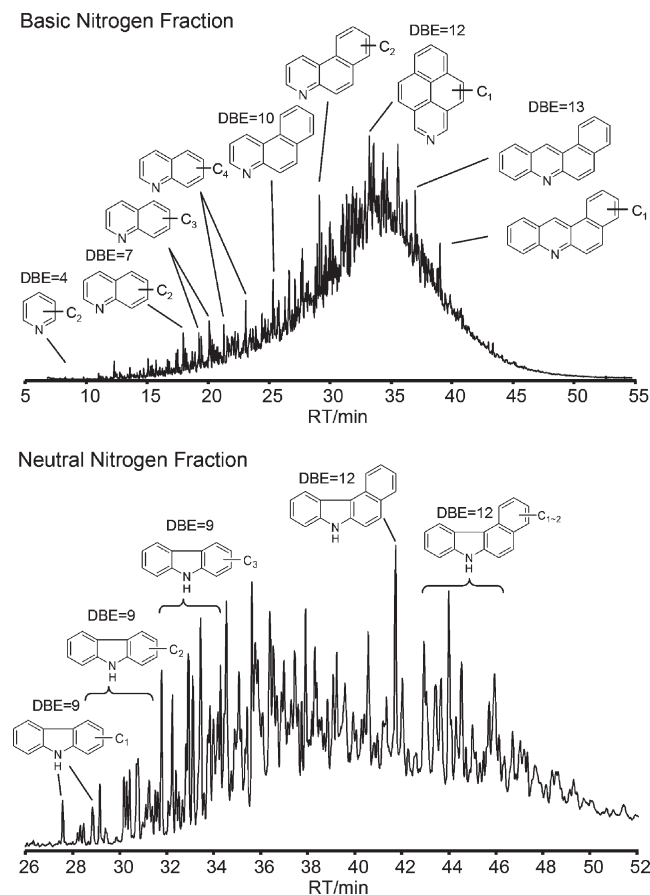
Figure 1. Gas chromatogram of basic and neutral nitrogen fractions of the CHGO. The basic nitrogen fraction of the CHGO was extracted with 0.1 M HCl. Large molecular species with 3−5 aromatic rings cannot be adequately identified by GC.

A highly viscous substance was obtained after CH_2Cl_2 was removed by vacuum evaporation.

Separation of Neutral Nitrogen Compounds. A total of 150 mg of CHGO was adsorbed onto 1 g of neutral alumina (not activated) and put on a chromatographic column. The column consisted of a 20 mm inner diameter column packed with 6 g of neutral alumina (100−200 mesh, activated at 400 °C for 4 h and added 1 wt % water). The packed column was eluted using 50 mL of *n*-hexane, 30 mL of toluene, and 70 mL of a chloroform/methanol mixture (98:2, v/v) in sequence to obtain the saturates, aromatics, and nitrogen-enriched fraction, respectively. The resins were further fractionated using a 10 mm inner diameter column packed with 2 g of silicic acid (100−200 mesh). The neutral nitrogen subfraction was obtained by eluting the column with 50 mL of *n*-hexane/toluene (1:1, v/v).

Sample Preparation and ESI FT-ICR MS Analysis. A total of 10 mg of oil sample was completely dissolved in 1 mL of toluene. A total of 20 mL of solution mixture was diluted with 1 mL of toluene/methanol (3:17, v/v) solution. Formic acid was added (5 μL to every 1 mL of sample solution) to ensure efficient ionization for positive-ion ESI analysis, and ammonium hydroxide was added (15 μL to every 1 mL of sample solution) for negative-ion ESI analysis. The toluene and methanol used were analytical-reagent-grade solvents that were distilled twice and kept in glass bottles with ground glass stoppers.

Samples were analyzed with a Bruker apex-ultra FT-ICR MS equipped with an actively shielded 9.4 T superconducting magnet. The sample solution was infused by a syringe pump via an Apollo II electrospray source at a flow rate of 180 μL/h. The conditions for positive-ion (or negative-ion) formation were −4 kV (or 3.5 kV) emitter voltage, −4.5 kV (or 4 kV) capillary
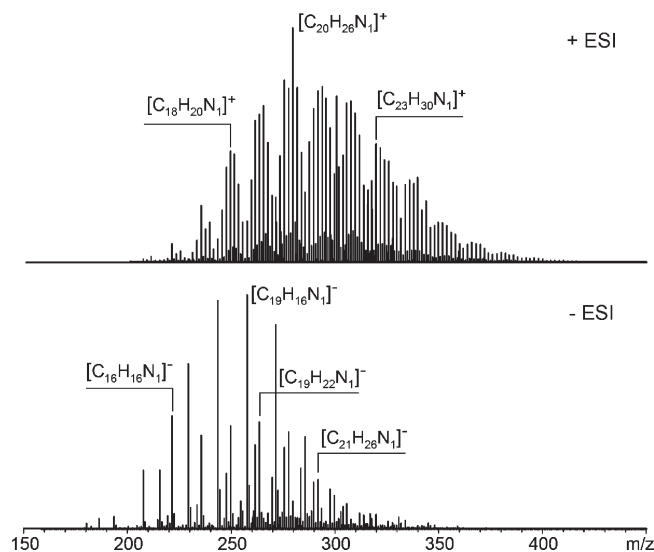

Figure 2. Mass spectra of the CHGO from positive- and negative-ion ESI FT-ICR MS.
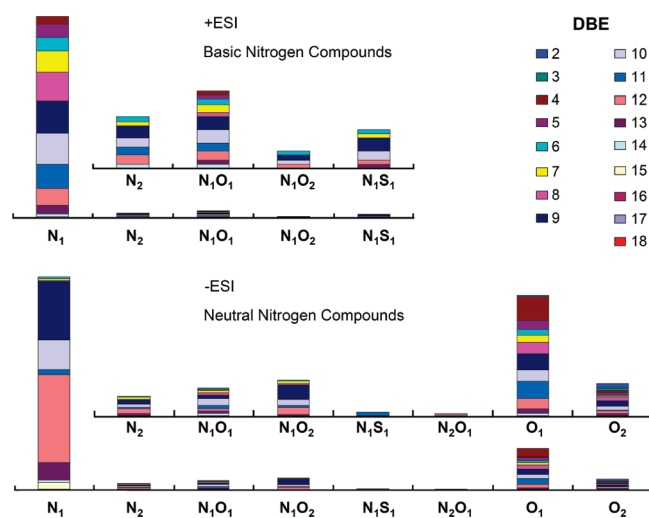

Figure 3. Relative abundance of basic and neutral nitrogen compounds in the spectra of the CHGO.

column front end voltage, and 320 V (or 320 V) capillary column end voltage. Ions accumulated for 0.1 s in a hexapole with 2.4 V (or −2.4 V) direct-current (DC) voltage and 200 V_{p-p} radiofrequency (RF) amplitude. The optimized mass for Q1 was 200 Da. Hexapoles of the Qh interface were operated at 5 MHz and 200 V_{p-p} RF amplitude, in which ions accumulated for 0.2 s (or 0.4 s). The delay was set to 0.8 ms to transfer the ions to an ICR cell by electrostatic focusing of transfer optics. The ICR was operated at 13 db (or 15 db) attenuation, 200−600 Da (or 160−600 Da) mass range, and 2 M acquired data size. The time domain data sets were co-added from 64 data acquisitions.

Mass Calibration and Data Analysis. The mass spectrometer was calibrated using sodium formate. The mass spectra obtained were calibrated internally according to a known and highly abundant homologous series of N-containing compounds. Peaks with a relative abundance greater than 5 times the standard deviation of the baseline noise were exported to a spreadsheet. Data analysis was performed using custom software that has been described elsewhere.[21] In general, the data

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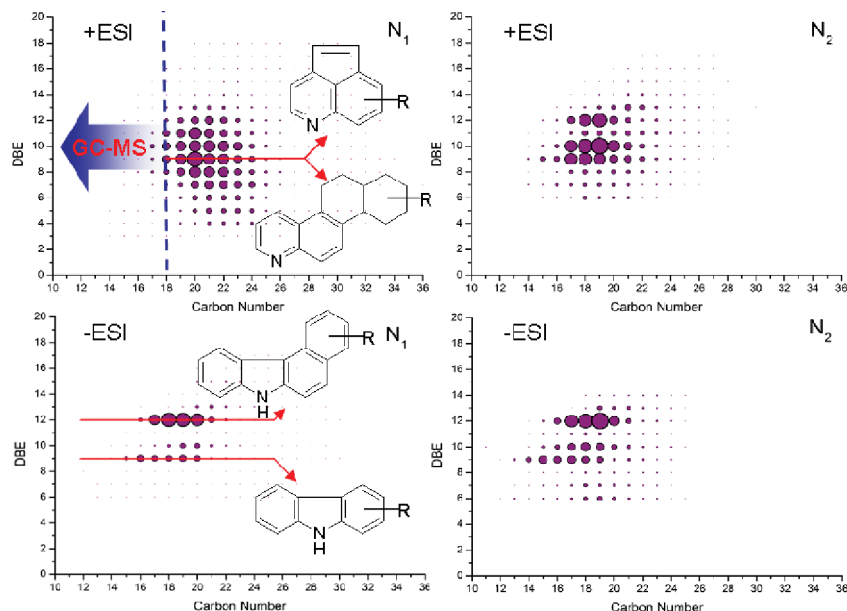
Figure 4. Plots of DBE as a function of the carbon number for heteroatom class species from positive- and negative-ion ESI FT-ICR mass spectra of the CHGO.

analysis was performed by selecting a two-mass scale-expanded segment in the middle of the spectrum, followed by detailed identification of each peak. The peak of at least one of each heteroatom class species was arbitrarily selected as the reference. Species with the same heteroatom class and its isotopes with different values by double-bond equivalence (DBE) and carbon number were searched within a set of ±0.001 Kendrick mass defect (KMD) tolerance.[22]

GC−MS Analysis. A Thermo-Finnigan Trace DSQ GC−MS coupled with a HP-5MS column (60 m×0.25 mm×0.25 μm) was used to analyze the composition of basic nitrogen compounds in the acid extract fraction and neutral nitrogen compounds obtained by open-column chromatography. The GC oven was maintained at 35 °C for 1 min, increased to 300 °C at 2 °C/min, then remained constant for 10 min. The sample was injected at 300 °C. The electron impact (EI) ionization source was operated under 70 eV of ionization energy. The mass range was set to 35−500 Da at a 1 s scanning period. The ion source temperature was 200 °C, and the ion current was 250 μA.

Results and Discussion

GC−MS Analysis for Basic and Neutral Nitrogen Fractions. Figure 1 shows the GC−MS spectra of the basic and neutral nitrogen fractions of CHGO. The results show that the spectrum peaks were overlapped greatly, indicating that the compositions of basic and neutral nitrogen fractions were highly complex. The separation for monomeric compounds cannot be adequately achieved by GC−MS, even though basic and neutral nitrogen compounds with 1−5 and 2−4 aromatic ring core structures were identified by mass spectra and GC retention indices.[16]

Also shown in Figure 1 are the molecular structures and DBE values of the nitrogen compounds. The basic nitrogen compounds were mainly pyridine-derived compounds, whereas the neutral nitrogen compounds were pyrrole-derived compounds. No multi-heteroatom nitrogen compounds, such as N_2 and N_1O_1, were identified by GC−MS.

This could be due to low volatility, low concentration of multi-heteroatom nitrogen compounds present in the samples, or the chromatographic peaks masked by an abundant N_1 class species. The results in Figure 1 show that low-concentration nitrogen compounds cannot be adequately characterized by GC−MS. The amount of low-volatile heavy hydrocarbon fractions that did not elute from the GC column was unknown. As a result, nitrogen compounds determined by GC−MS likely account for a fraction of total nitrogen compounds present in the heavy petroleum fractions.[16]

Heteroatom Class Distribution in the CHGO. Figure 2 shows the positive- and negative-ion ESI FT-ICR mass spectra of nitrogen compounds in the CHGO. The molecular weight of basic nitrogen compounds ranged from 200 to 450 Da, and the molecular weight of neutral nitrogen compounds ranged from 160 to 400 Da. The molecular-weight upper detection limit of ESI FT-ICR MS is higher than that for GC−MS (up to 300 Da). The even-mass peak nitrogen compounds were mostly N_1 class species, which were abundant. The difference between the positive- and negative-ion ESI FT-ICR mass spectra was the average molecular weight, of which those of the basic nitrogen species were higher than those of the neutral nitrogen species.

Figure 3 shows the relative abundance of the positive- and negative-ion heteroatom class species in the CHGO. Among the basic nitrogen compounds (N_1, N_2, N_1O_1, N_1O_2, and N_1S_1) identified by the positive-ion mass spectra and the neutral nitrogen compounds (N_1, N_2, N_1O_1, N_1O_2, N_1S_1, and N_2O_1) identified by the negative-ion mass spectra, the N_1 class species were the most abundant.

DBE versus Carbon Number for Nitrogen Class Species of the CHGO. The iso-abundance plot of DBE versus carbon number provides detailed compositional data of the species.[23] It also shows the hydrogen deficiency of a given species and is commonly used to analyze high-resolution

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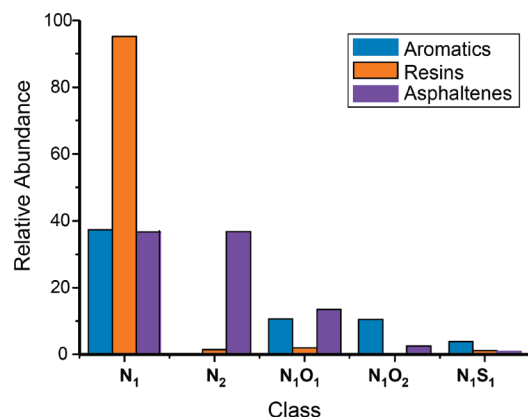
Figure 5. Relative abundance of basic nitrogen compounds in each spectrum of SARA fractions of the CHGO.
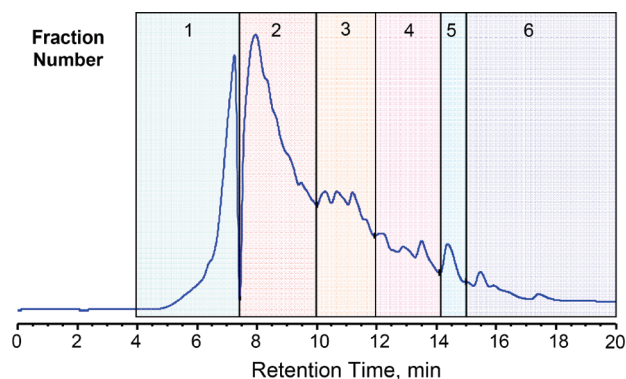

Figure 6. HPLC chromatogram of six CHGO resin subfractions obtained by a differential refractive index detector.

mass spectra of crude oils.[11,24,25] Figure 4 shows the plots of DBE versus carbon number for the N_1 and N_2 class species from the positive- and negative-ion ESI FT-ICR mass spectra of the CHGO. The basic N_1 class species had a DBE of 3−18 and carbon number of 14−34. However, nitrogen compounds with a carbon number greater than 18 cannot be adequately characterized according to the GC−MS results shown in Figure 1. The most abundant basic N_1 class species had a DBE of 9. The most likely compounds of these species are naphthenic (two-ring) quinolines. Compounds in this serial with a carbon number less than 18 should be azaacenphthylene. Aromatic compounds with these types of core structure widely present in the coal tar and aerosol range in fossil fuel combustion.[26] From the negative-ion ESI analysis, the most abundant neutral N_1 class species had DBE values of 9 and 12, which are carbazoles and benzocarbazoles, respectively. This was confirmed

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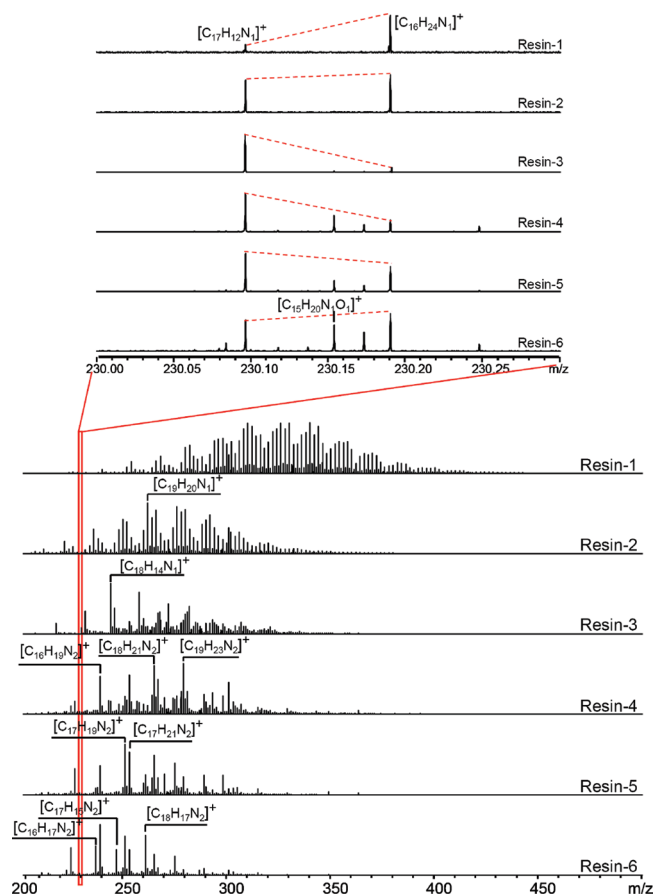

Figure 7. Positive-ion ESI FT-ICR mass spectra of resin subfractions. The inset shows the expanded mass scale at *m/z* 230.
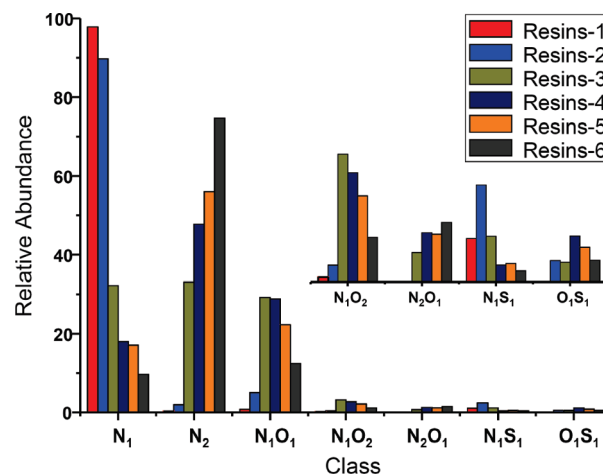

Figure 8. Relative abundance of basic nitrogen compounds in each spectrum of resin subfractions. The inset shows the expansion of the relative abundance of N_1O_2, N_2O_1, N_1S_1, and O_1S_1 class species.

by GC−MS analysis. Carbazoles are the most abundant neutral nitrogen compounds present in petroleum streams.[27,28]

In Figure 4, the abundant N_2 class species of basic and neutral nitrogen compounds had DBE values of 9, 10, and

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(28) Snyder, L. R.; Buell, B. E.; Howard, H. E. Nitrogen and oxygen compound types in petroleum. Total analysis of a 700−850 °F distillate from a California crude oil. *Anal. Chem.* **1968**, *40* (8), 1303–1317.
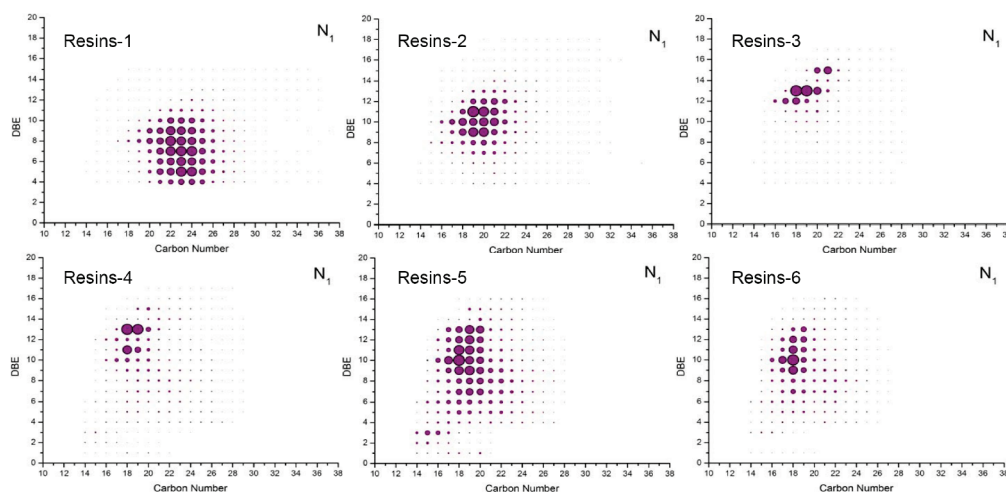
Figure 9. Plots of DBE as a function of the carbon number for N_1 class species from the positive-ion ESI FT-ICR mass spectra of resin subfractions.
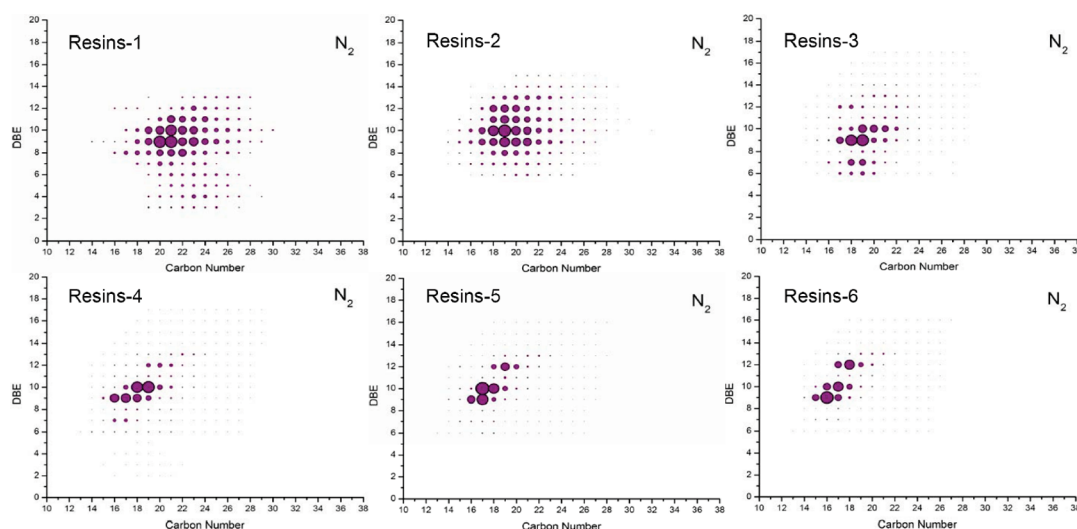

Figure 10. Plots of DBE as a function of the carbon number for N_2 class species from the positive-ion ESI FT-ICR mass spectra of resin subfractions.

12. These are likely amphoteric molecules with pyridine and pyrrole core structures. The N_2 class species are comprised of both basic and neutral nitrogen atoms, which can be detected by positive- and negative-ion ESI analyses. The core structure of nitrogen compounds with DBE of 12 was most likely the carbazole−pyridine or acridine−pyrrole.

Heteroatom Class Species Distribution in Resin Subfractions. The concentration of nitrogen in the SARA fractions is shown in Table 1. The weight percent of the nitrogen atom is for each fraction. The results indicated that nitrogen compounds were enriched in the resin fraction. Figure 5 shows the relative abundance of basic heteroatom class species in the SARA fractions. The N_1 class species in the resin fraction had the highest relative abundance compared to those in the aromatic and asphaltene fractions. The N_2 class species were not identified in the aromatics, but were enriched in the asphaltenes.

To achieve a detailed investigation of nitrogen compounds, the resin fraction was separated into six subfractions by HPLC and characterized by ESI FT-ICR MS. Figure 6 shows the LC chromatogram of the resins eluted by a solvent mixture [hexane/isopropanol (4:1, v/v)]. Six subfractions were collected according the retention time intervals, as shown in Figure 6. Figure 7 shows the positive-ion ESI FT-ICR MS broadband (m/z 200−500) spectrum of the resin subfractions. The average molecular weight of basic nitrogen compounds shifted to lower values when the polarity of the resin subfractions increased. The N_1 class species were the dominant nitrogen compounds in resin fractions 1−3, while the N_2 class species were dominant in resin fractions 4−6. The expanded MS spectrum at m/z 230, shown in the inset of Figure 7, indicated the difference in relative abundance of basic nitrogen in each resin subfraction. The relative abundance of N_1 class species with high DBE values increased from resin fractions 1−3 and then decreased from resin fractions 4−6. Resin fractions 4−6 had high relative abundances of N_2 and N_1O_1 class species.

Figure 8 shows the relative abundance of heteroatom species in the resin subfractions. The data in Figure 8 validated that shown in Figure 7. It indicated that, with increasing polarity of the resin subfraction, the relative abundances of N_1 class species decreased and those of N_2 class species increased.

DBE versus Carbon Number for N_1 and N_2 Class Species in Resin Subfractions. Plots of DBE versus carbon number for the basic N_1 and N_2 class species in the resin subfractions are shown in Figures 9 and 10, respectively. The N_1 class species in resin fraction 1 was distributed over a wide range of DBE values (4–15) and carbon numbers (14–36). The most abundant N_1 class species had DBE of 4–10. The DBE value of the abundant N_1 class species from resin fractions 1–3 gradually shifted to higher values with an increased carbon number. The DBE value of abundant species remained constant for fractions 3 and 4 and became spread for fractions 5 and 6. This suggests that nitrogen compounds in resin subfractions had different core structures. Fractions 1–3 are likely pyridinic compounds with various degrees of aromaticity, and fractions 4–6 are nitrogen compounds with different molecular structures from the first three fractions. Nitrogen compounds with DBE of 1–3 found in resin fractions 4 and 5 are likely amino compounds.

In comparison to the N_1 class species, the DBE and carbon number distribution of N_2 class species was discrete. The most abundant N_2 class species had DBE values of 9, 10, and 12. These are likely azacarbazole, naphthenic azacarbazole, and azabenzocarbazole, respectively. In resin fractions 1 and 2, the distribution of nitrogen compounds occurred over a wide range of DBE values. This indicates that nitrogen compounds had various degrees of condensed aromaticity. Even though the N_2 class species were not identified by GC–MS, they were detected by ESI FT-ICR analysis. This suggests that the N_2 class species were present in low concentrations or not eluted through the GC column because of their low volatility.

Conclusions

A CHGO was separated into SARA fractions. The resin fraction was separated into six subfractions by HPLC. The CHGO and its subfractions were characterized by ESI FT-ICR MS. The mass spectra showed that the mass range of basic nitrogen compounds in CHGO was 200–450 Da and the mass range of neutral nitrogen compounds in CHGO was 160–400 Da. Five nitrogen class species, N_1, N_2, N_1O_1, N_1O_2, and N_1S_1, were assigned in the positive-ion spectrum, and six nitrogen class species, N_1, N_2, N_1O_1, N_1O_2, N_2O_1, and N_1S_1, were assigned in the negative-ion spectrum. Among the nitrogen compounds identified in CHGO, the N_1 class species was dominant. The N_1 class species were enriched in the resin fraction. The N_2 class species, which are likely amphoteric molecules, were enriched in the asphaltene fraction. The composition of nitrogen compounds in the resin subfractions varied significantly in DBE and carbon number. As the polarity of the resin subfraction increased, the average molecular weights of nitrogen compounds decreased, DBE values for each heteroatom class species increased, and the N_2 class species became the dominant nitrogen compounds at the expense of the N_1 class species.