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Characterization of Basic Nitrogen Species in Coker Gas Oils by Positive-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Six coker gas oils (CGOs) and three basic fractions extracted from one of the CGOs by 0.1, 0.4, and 1 M HCl hydrochloric acid were characterized by positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) and compared to those analyzed by gas chromatography mass spectrometry (GC-MS). The ultra high mass resolving power and high mass accuracy of FT-ICR MS allow the assignment of a unique elemental composition to each peak in the mass spectrum. Basic nitrogen species were characterized by class, type, and carbon number. The mass spectra of the CGOs at the 200–500 Da mass range were similar, but the distribution of double bond equivalence (DBE) versus carbon number were different. Among the N, N₂, NO, and NS that were identified in CGOs, the N class nitrogen species were dominant. The results showed that hydrotreating reduced the relative abundance of all class species, except for the N class species. This suggests that some N class species are refractory to hydrotreating. The molecular weight of nitrogen species in the acid-extracted basic nitrogen fraction of CGO was lower than that of its parent CGO. The N₃, NO₂, and N₂O class species were clearly identified and concentrated in the basic nitrogen fraction, but were not detected in their parent CGO. The N class species with ring plus DBE value of 4–16 in the basic nitrogen fraction were also identified by GC-MS analysis.

Introduction

Coker gas oil (CGO), the vacuum distillate fraction of coking product, accounts for 20–30 wt % yield in thermal conversion of heavy feedstock.¹ CGO can be used either as blending stock for fuel oil or feedstock for catalytic cracking and hydrocracking.^{1,2} However, CGO contains high concentrations of basic nitrogen compounds,^{3–5} which cause rapid catalyst deactivation in downstream catalytic processes. Hence, more comprehensive and detailed characterization of the composition of basic nitrogen compounds present in CGO can be useful in the designing and developing of better catalysts for processing heavy feedstock.

Basic nitrogen compounds in petroleum feedstock are usually isolated by solvent extraction and/or liquid chromatography, followed by gas chromatography coupled with mass spectrometry (GC-MS) to separate and characterize.^{3,6–8} Although much research has been done on basic nitrogen compounds found in CGOs, crude oils, and their derived

products, most basic nitrogen compounds identified are those with molecular weight lower than 300 Da, due to their low volatility in GC-MS analysis.⁹ However, the results of elemental analysis of many crude oils show that the 90% nitrogen species present in vacuum residues,¹⁰ most of which cannot be identified by GC-MS. Hence, the nitrogen compounds identified by GC-MS represent only a fraction of total nitrogen species of those found in petroleum feedstock.

The Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has become a more frequently used method for probing the composition of complex mixtures.^{11–13} The advantages of conducting FT-ICR MS analysis for petroleum systems have been documented elsewhere.^{14–18}

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The FT-ICR MS offers the highest available broadband mass resolution, mass resolving power, and mass accuracy, which allows the assignment of a unique elemental composition to each peak in the mass spectrum.

The high selectivity of electrospray ionization (ESI) improves the analysis for identifying trace polar compounds found in petroleum systems.^{19,20} Zhan and Fenn²¹ first reported the use of an ESI coupled with low-resolution MS for a petroleum system. National High Magnetic Field Laboratory at Florida State University and ExxonMobil Research and Engineering Company implemented an in-depth studies on high-field FT-ICR applications to petroleum characterization.^{14,22–29} High-resolution ESI FT-ICR MS analysis on petroleum revealed the presence of more than 17 000 elemental compositions in crude oil.¹¹ Nonpolar sulfur molecules were also ionized by methylating them to methyl thiophenium salts^{30–32} and then characterized.

Positive ion ESI FT-ICR MS is now recognized as a powerful analytic technique for resolving and identifying basic heteroatom compounds found in crude oils;^{22,24,33} saturates, aromatic, resins, and asphaltines (SARA) fractions of crude oil;³⁴ diesel;³⁵ CGO;³⁶ bitumen;³⁷ straight run distillate fractions;^{38,39} light cycle oil (LCO), and refined chemical oil (RCO).⁴⁰ Heteroatoms identified by positive ESI include N, N₂, NO, NO₂, N₂O, NS, and NOS class species. The class species N and N₂ denote the compounds with one and two

Table 1. Elemental Composition of CGOs (wt %)

	C	H	S	N	BN ^a
SL	86.87	11.96	0.61	0.55	1830
LH	86.61	12.65	0.26	0.51	1374
DG	85.93	11.69	0.78	0.54	1600
YZ			1.41	0.46	
YZHT			0.22	0.27	

^a Basic Nitrogen, ppm.

nitrogen atoms in the molecule respectively, and the class NO denotes compounds with one nitrogen and one oxygen. Fu et al.³⁶ employed 10 eV electron ionization, field desorption ionization, and ESI FT-ICR MS for analysis of hydrocarbon and heteroatom species found in a narrow boiling point fraction (483–504 °C) of bitumen-derived CGO before and after hydrotreating. The compositional change of CGO as a function of the effectiveness of hydrotreating process was revealed at the molecular level. The majority of nitrogen-containing compound classes found in CGO were N, N₂, NS, NS₂, NO, and NOS. Molecules with N-class nitrogen are the dominant species and are more refractory to hydrotreatment than those containing additional sulfur, nitrogen, or oxygen heteroatoms.³⁶

In this paper, comprehensive compositional analyses using FT-ICR MS and GC-MS were performed for basic nitrogen compounds present in CGOs that were derived from conventional crude oils. Basic species were characterized by class (numbers of N, O, and S heteroatoms), type (rings plus double bond equivalence (DBE)), and carbon number. Furthermore, basic fractions were characterized by GC-MS analysis.

Experimental Section

Materials. Four conventional crude derived CGO samples (sample tags: DG, LH, SL, and YZ) and two hydrotreated CGO samples (sample tags: LHHT and YZHT) were obtained from Chinese refineries except LHHT CGO. The LHHT CGO was the hydrotreated product of LH CGO from a hydrotreater pilot operating at 480 °C, 6 MPa, with a NiW catalyst. Elemental composition of CGOs were listed in Table 1. Other properties of these types of CGOs have been reported elsewhere.^{1,2,4,5}

Extraction of Basic Nitrogen Compounds. Twenty milliliters of dilute hydrochloric acid (HCl) and 100 g of CGO were mixed in a 250 mL beaker. The mixture was stirred vigorously at 500 rpm for 10 min, and then the aqueous phase was separated and collected. This process was repeated three times. The three extracted aqueous phase samples with a total volume of 60 mL were mixed together and basified with a 5 wt % hydroxyl sodium (NaOH) solution to pH of 10, followed by extraction with dichloromethane (CH₂Cl₂). A “sticky” substance was obtained after CH₂Cl₂ was removed by vacuum evaporation. The concentration of HCl used in the extraction is 0.1, 0.4, and 1.0 M, respectively.

Sample Preparation for ESI FT-ICR MS Analysis. Ten milligrams of oil sample was mixed with 1 mL of toluene. Twenty microliters of the solution mixture was diluted with 1 mL of toluene/methanol (3:17) solution. The toluene and methanol used were analytical reagent grade solvents that were distilled twice and kept in glass bottles with ground glass stoppers. Glassware was used for solvent handling and transfer, except for the steel pistons of 10 µL Hamilton syringes.

FT-ICR MS Analysis. The CGO samples were analyzed using a Bruker apex-ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. The sample solution was infused via an Apollo II electrospray source at 150 µL/h by using a syringe pump. The conditions for positive ion formation were –2.5 kV emitter voltage, –3.0 kV capillary column front end voltage, and 320 V capillary column end voltage. Ions accumulated for 0.1 s in a hexapole with 2.4 V DC voltage and 300 Vp-p RF amplitude. Optimized mass for Q1 was 250 Da. Hexapoles of the

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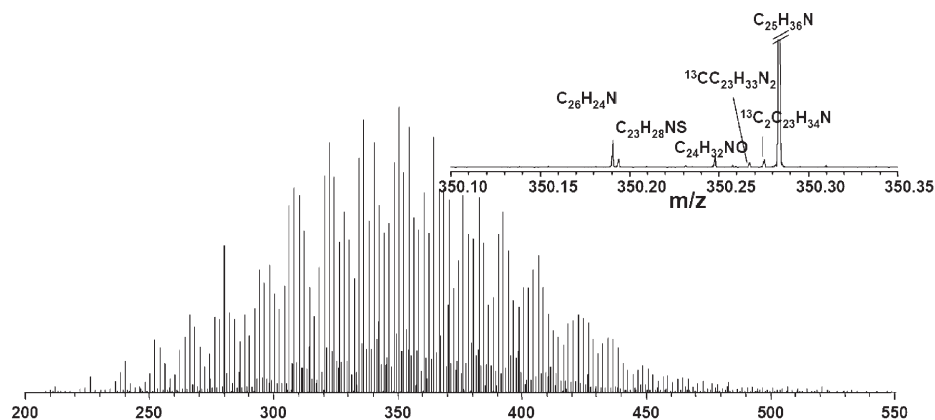


Figure 1. Positive-ion electrospray 9.4 T FT-ICR mass spectrum of DG CGO. The insert shows the expanded 350 mDa mass scale, indicating several of the mass splits commonly encountered in CGO.

Qh-Interface were operated at 5 MHz and 400 Vp-p RF amplitude, in which ions accumulated for 1 s. The delay was set to 1.3 ms to transfer the ions to an ICR cell by electrostatic focusing of transfer optics. ICR were operated at 11.75 db attenuation, 200–750 Da mass range, and 4 M acquired data size; and time-domain data sets were coadded 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 relative abundance greater than 5 times the standard deviation of the baseline noise were exported to a spreadsheet. Data analysis was performed using the software that was described elsewhere.⁴¹ In general, the data analysis 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.⁴²

GC-MS Analysis. A Thermo-Finnigan Trace DSQ GC-MS coupled with a HP-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used to analyze the composition of basic nitrogen compounds in the acid extract fraction. The GC oven was maintained at 35 °C for 1 min and increased to 300 at 2 °C/min, and then kept at 300 °C for 10 min. The sample was injected at 300 °C. The electron impact (EI) ionization source was operated under 12 and 70 eV ionization energy, respectively. Mass range was set to 35–500 Da at a 1 s scanning period. Ion source temperature was 200 °C, and ion current was 250 μA .

Results and Discussion

Heteroatom Class Distribution in CGOs. Figure 1 shows the positive ESI FT-ICR MS broadband (200–600 Da) spectrum (64 coadded time-domain acquisitions) of DG CGO. The abundant peaks with even masses in the 250–500 Da molecular weight range indicated that the dominant compounds are N-class species. Also shown in Figure 1 is the close-up view of expanded mass spectrum obtained under the resolving power of 554 000 ($m/\Delta m$ 50% at $m/z = 350$). The high-resolution distinct characteristics of abundant peaks allow the assignment of a unique elemental composition to each peak in the mass spectrum.

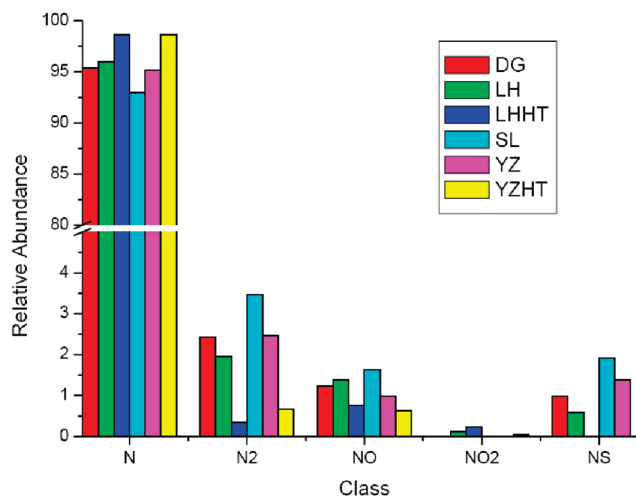


Figure 2. Relative abundances of basic heteroatom class species in various CGOs.

The relative abundances of positive ion heteroatom class species for four CGOs and two hydrotreated CGOs are shown in Figure 2. 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. Even if the relative abundance of a given class species is the same for two samples, the absolute abundance of that class species may not be the same as it depends on the abundances of other class species. Although the CGO samples were derived from crudes of different origins and processed at various refineries, the class compositions were similar between samples. Fewer types of heteroatom class species were identified in CGOs than in crude oils^{22,24,33} and their narrow boiling distillate fractions.³⁸ The N class nitrogen compounds are the dominant species with more than 93% abundance in the four CGOs. Other classes exhibit low abundances: 2–4% N₂, 1–2% NO, and 1–2% NS species. Negligible amounts of NO₂ class species were found, except for the LH CGO. The SL and YZ CGOs had more abundant NS class species than the LH and DG CGOs. The relative abundance of NS class species was not proportional to the total sulfur content of CGOs. No NS class species were detected in the two hydrotreated CGO samples.

To examine the molecular composition of various class species in CGO samples, iso-abundance dot-size coded plots

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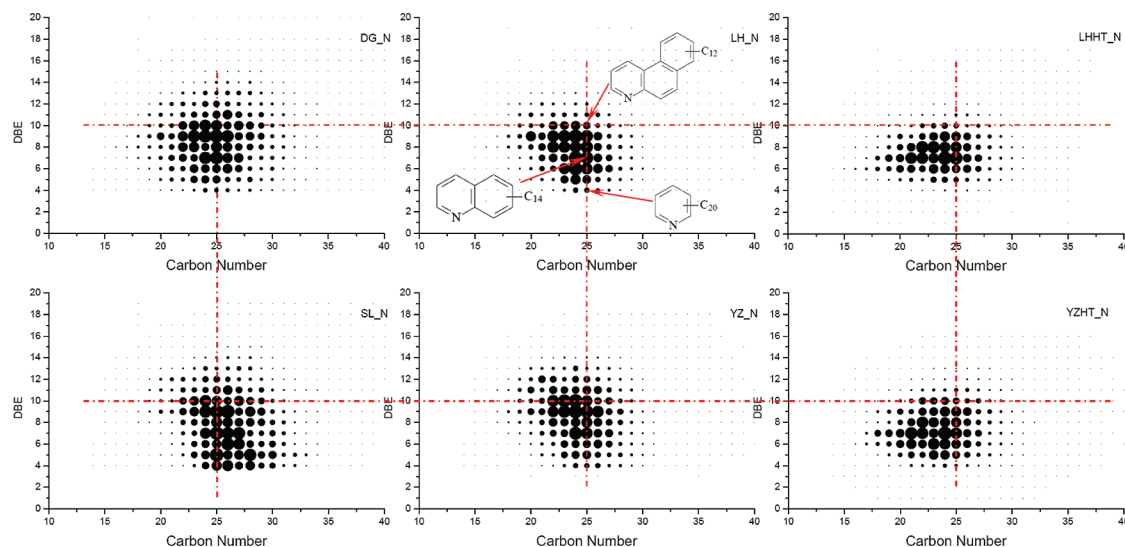


Figure 3. Plots of double bond equivalents (DBE) as a function of carbon number for N class species from the positive-ion ESI FT-ICR mass spectra of various CGOs. Three possible representative structures illustrate the pyridine compounds typically detected as positive ions.

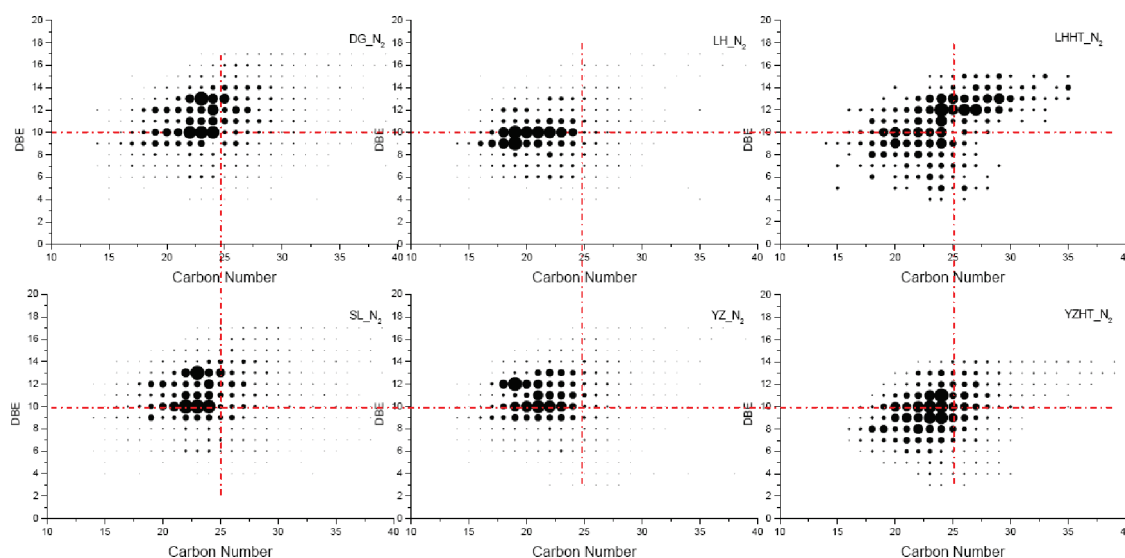


Figure 4. Plots of double bond equivalents (DBE) as a function of carbon number for N₂ species from the positive-ion ESI FT-ICR mass spectra of various CGOs.

are constructed by correlating DBE and carbon number distribution of species in the CGO samples.

DBE versus Carbon Number for N Class Species. Figure 3 shows the iso-abundance map of DBE versus carbon number for members of the N class species in various CGOs. The DG CGO has a DBE value of 4–15 and carbon number of 16–32. The highest relative abundance N class species is 9 DBE with 25 carbons. The possible core structure of this compound could be dinaphenicquinoline or azafluorene. The iso-abundance maps of N class species in LH and YZ CGO are similar to that of DG CGO, but with slightly lower DBE and carbon number values than those of DG CGO. The N class DBE of 4–15 and carbon number of 20–33 for SL CGO are different from those for other CGOs. The SL CGO has a high relative abundance of species with DBE of 4–10 and carbons number of 24–28, indicating a low molecular condensation in large carbon number molecules. Species with DBE of 4–5 correspond with the derivatives of pyridines and tetrhydroquinolines with long alky side chain.

DBE versus Carbon Number for N₂ Class Species. Figure 4 shows the iso-abundance map of DBE versus carbon number for members of the N₂ class species in various CGOs. The distribution of N₂ class species in DG and SL CGO were similar, even though the distributions of N class species in these two CGOs were different. The high relative abundance N₂ class species are 10 and 13 DBE with carbon number from 20–25. The N₂ class species has higher DBE and lower carbon number values compared to the N class species. This suggests that the N₂ class species has a high molecular condensation in small carbon number molecules. The high relative abundance N₂ class species in LH CGO had BDE of 9 and 10, while the YZ CGO were 10 and 12. The predominant N₂ class species with DBE value of 9 were azacarbazoles and those with DBE value of 10 were likely azabenzquinolines.⁴³

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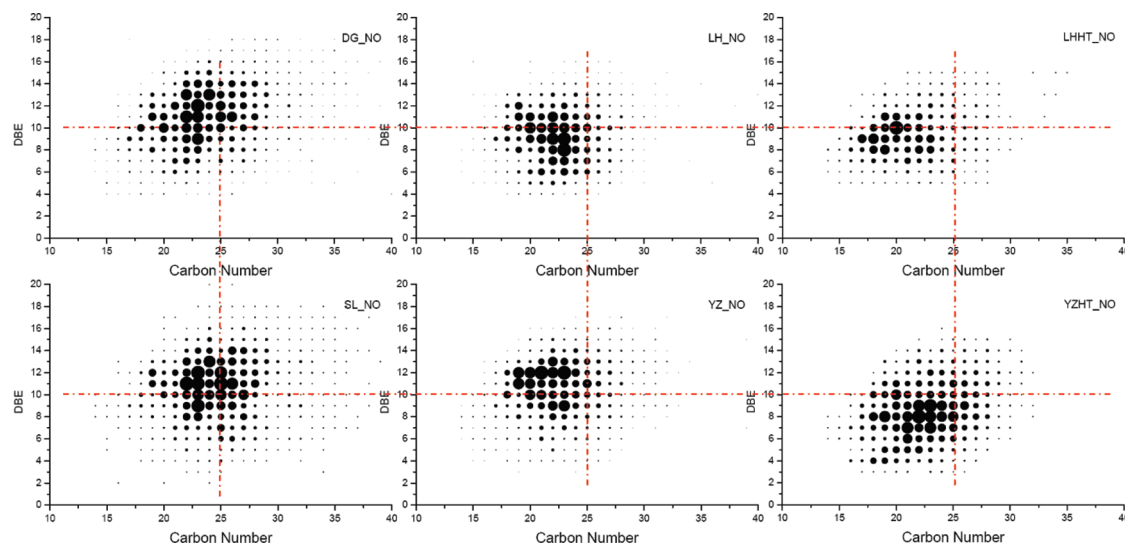


Figure 5. Plots of DBE as a function of carbon number for NO species from the positive-ion ESI FT-ICR mass spectra of various CGOs.

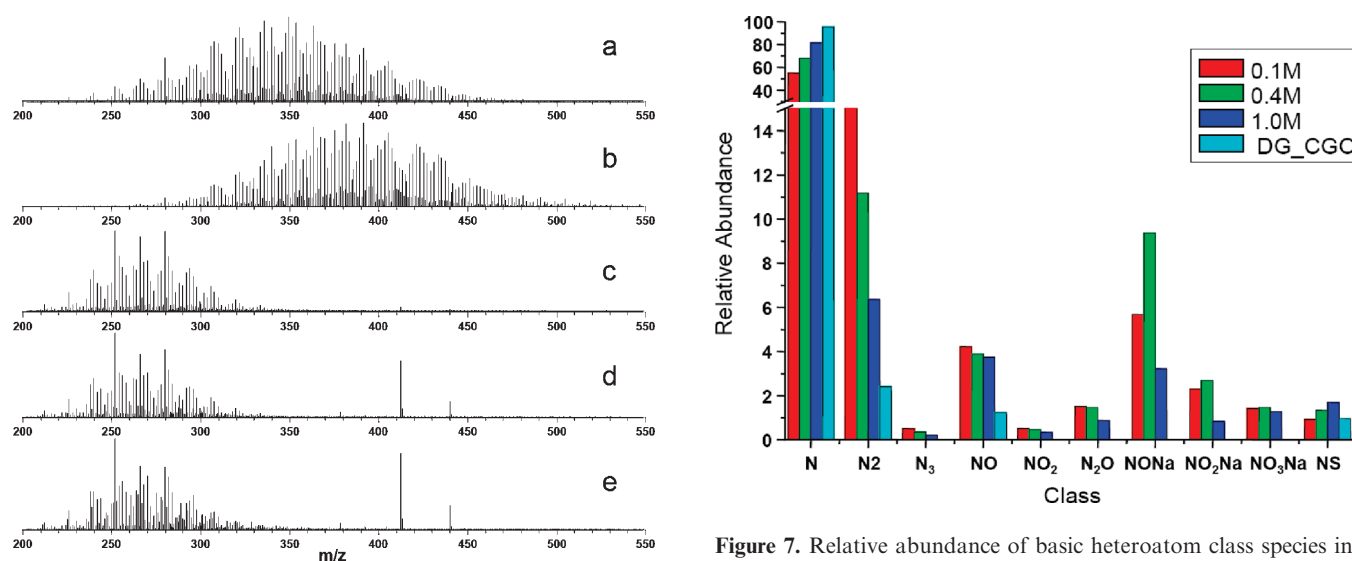


Figure 6. Broadband positive-ion electrospray 9.4 T FT-ICR mass spectra of DG CGO (a), acid-washed DG CGO (b), basic nitrogen fractions of DG CGO from acid extraction with various HCl solutions: 1 M (c), 0.4 M (d), and 0.1 M (e).

DBE versus Carbon Number for NO Class Species. Figure 5 shows the iso-abundance map of DBE versus carbon number for members of the NO class species in various CGOs. The distributions of NO class species were similar among the CGOs. The high relative abundance NO class species were DBE of 11 and 12 and carbon number from 18 to 28, except for the LH CGO that had a lower DBE of 8 and 9. The NO class species with high DBE and low carbon number results from combining pyridine (or higher benzologs) with a furan instead of hydroxy functionalities. This is because furan type core structures have at least three more DBEs than the hydroxyl type core structures. For the LH CGO that has a relative abundance of NO class species of 8 and 9 DBE and 23 carbon number, the O-atom in NO species were likely from the hydroxy functionalities that are abundant in LH crude.⁴⁴

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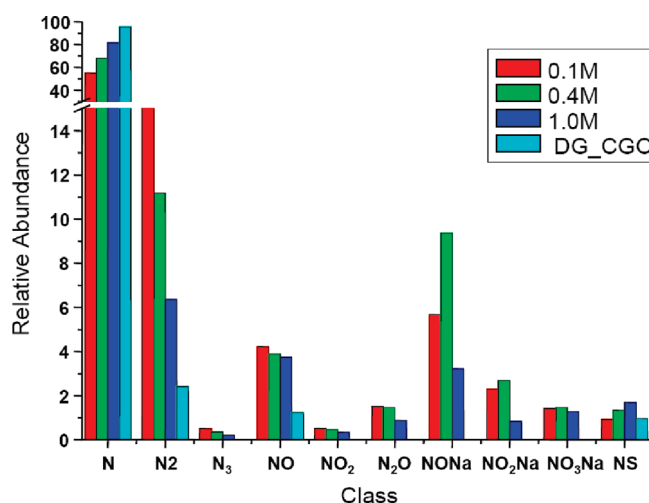


Figure 7. Relative abundance of basic heteroatom class species in DG CGO and its basic nitrogen fractions from acid extraction.

Heteroatom Class Distribution in CGO before and after Hydrotreating. Figure 2 shows the relative abundance for various class species in LH and YZ CGO before and after hydrotreating. The data show that hydrotreating reduced the relative abundance of all class species, except for the N class species. The predominant N class species that remained in hydrotreated CGO were consistent with earlier findings, indicating that N class species are refractory.^{35,36,38,40} The N class species are either in the parent CGO or generated from converting the multiheteroatom species during hydrotreating.³⁸ The data confirmed that hydrotreatment preferentially removes multiheteroatom species.

The plots of DBE versus the carbon number for N, N₂, and NO class species are shown in Figures 3–5, respectively, in LH and YZ CGO before and after hydrotreating. The DBE and carbon number of N and NO class species shift to lower values. This is likely due to the reduction of NS and NO class species to N class species during hydrotreating. The N class species in hydrotreated CGOs with DBE from 1 to 3 are more likely the amino compounds, which is the only basic nitrogen compounds class that has a DBE value less than 4. Previous studies have shown that polar nitrogen compounds such as

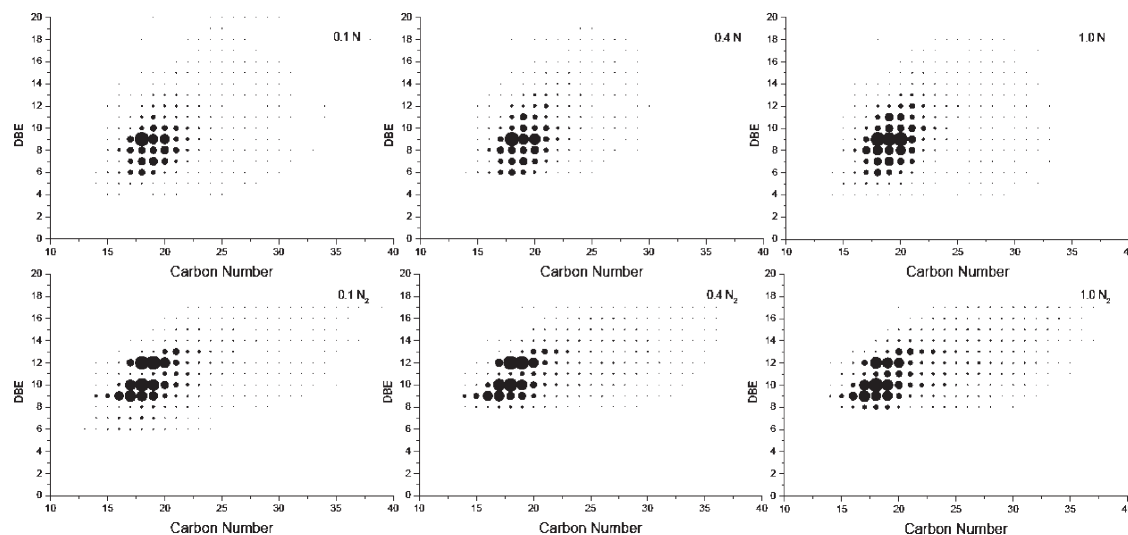


Figure 8. Plots of double bond equivalents (DBE) as a function of carbon number for N and N₂ species from the positive-ion ESI FT-ICR mass spectra of basic fractions of DG CGO from acid extraction.

pyridine and/or pyrrole type compounds convert to amino compounds in the hydrotreating process.⁴⁵ These findings are consistent with those reported by Klein.³⁸ The DBE and carbon number of N₂ compounds exhibit a slight shift to higher values after hydrotreating, which indicates that lower molecular N₂ species with lower DBE values were preferentially transformed in the hydrotreating processes. The data showed that at least one of the two N atoms was in pyridine form as detected by the positive ion spectrum; whereas the other N atom was in the form of either pyridine or pyrrole. The different trend of transformation of species in LH and YZ CGOs before and after hydrotreating could be partly due to the severity and the selectivity of hydrotreating processes, which determined the extent of transformation of second type N₂ nitrogen species.

Composition of Basic Nitrogen Compound Fractions. Figure 6 shows the broadband positive ESI FT-ICR mass spectra of DG CGO, acid-washed DG CGO, and basic nitrogen fractions of DG CGO from acid extraction with 1, 0.4, and 0.1 M HCl solutions. The mass distribution of basic species in DG CGO ranged from 220 to 500 Da, centered at 350 Da. The mass distribution of basic species in the acid-washed DG CGO shifted to a higher mass range (220 to 570, centered at 390 Da). Compared to the parent CGO, the species in basic nitrogen fractions exhibited a lower mass distribution (200–350 Da), which was independent of the concentration of HCl used in acid extraction. High molecular weight basic nitrogen compounds cannot be extracted from CGO, even with strong acids. This is similar to the principle of extracting naphthenic acid from crude oils.⁴⁶

Figure 7 shows the relative abundance of heteroatom class species in DG CGO and its basic nitrogen fractions from acid extraction. Species of N₃, NO, NO₂, and N₂O classes were not detected in the parent CGO, but are clearly identified in these basic fractions. Furthermore NO, NO₂, and NO₃ species have abundant sodium (Na) adduct ions, commonly present in the positive ESI mass spectra.³⁵ Sodium adduct ions

indicate that either carbonyl or carboxyl functional groups exist in the NO_x compound molecules.⁴⁷

The mononitrogen compounds are the most abundant class species in all of the samples, varying from 55 to 95% of the total assigned peaks in the samples (Figure 7). With increased acid concentration, relative abundances of N₂, N₃, NO, NO₂, and N₂O species decreased and the amount of N and NS species increased. Figure 8 shows the plots of DBE as a function of carbon number, indicating that the types of N and N₂ species in the basic nitrogen fractions were independent of acid concentration used in acid extraction.

GC-MS Analysis on Basic Nitrogen Fraction of DG CGO.

Figure 9 shows the GC-MS spectrum of the basic nitrogen fraction of DG CGO that was extracted with 0.1 M HCl solution. Also shown in Figure 9 are the molecular structures of key nitrogen species and their DBE values. The identified nitrogen species in Figure 9 are pyridine-derived compounds. No multiheteroatom nitrogen compounds were identified. By contrast, other classes of nitrogen species, such as N₂ and NO, were identified by the ESI mass spectrum and are present in relatively high abundances. It is likely that the multiheteroatom compounds have difficulty passing through the GC capillary column due to their low volatility. In some cases, these compounds are highly isomerized so the amount is not high enough to be identifiable by GC-MS. The nitrogen compounds with 1–3 aromatic rings such as alkylpyridine, quinoline, and benzoquinoline can be easily identified using MS and GC retention characteristics, as reported elsewhere.³ However, large molecular species with 4–5 aromatic rings cannot be adequately identified. The molecular structures of these high molecular species can be estimated by extrapolating data from the low-resolution MS by assuming similar type species are present in the lighter fractions flanked by benzo groups.

Figure 10 shows the cumulative total mass spectrum of the chromatogram shown in Figure 9. The mass spectra of GC-MS in Figure 10 are significantly different from those of FT-ICR MS in Figure 6. This is likely because the GC capillary column allows only the low molecular weight compounds to pass through and reach the ion source. However, when the

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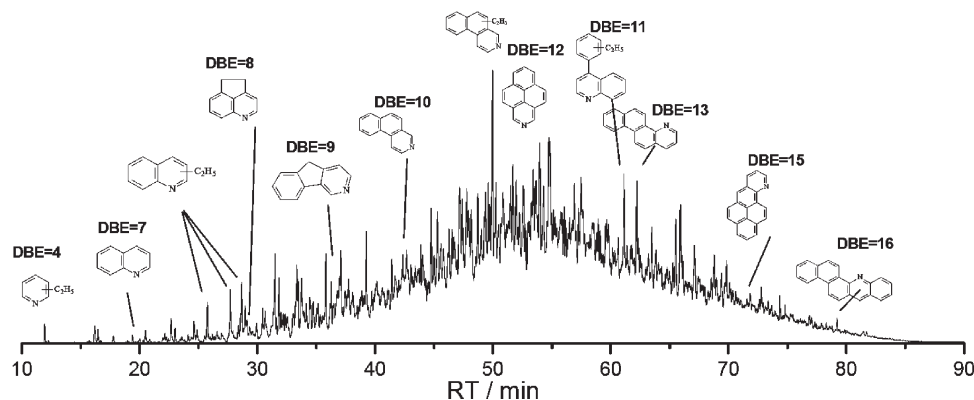


Figure 9. Gas chromatogram of the basic fraction of DG CGO extracted with 0.1 M HCl solution.

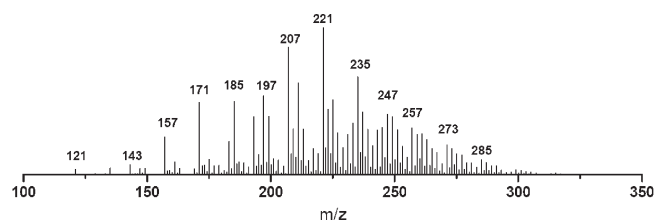


Figure 10. Co-added 12 eV electron impact mass spectra of DG CGO extracted with 0.1 M HCl solution (added 4756 scans at 35–400 Da with retention time from 11 to 89 min).

same sample was analyzed using the FT-ICR MS, the results show that the relative abundance of various nitrogen compound types varied in the same mass range. Figure 10 shows that a high relative abundance of the mass series of m/z $143 + 14n$ and m/z $193 + 14n$ ($n = 0, 1, 2, \dots$) corresponding to a DBE value of 7 (alkyl quinolines) and 10 (alkyl benzoquinolines). The relative abundance of $143 + 14n$ mass series in Figure 10 was much lower than that in Figure 6, indicating that nitrogen compounds with different DBE values exhibit different ionization efficiencies in electron impact (EI) and ESI. Furthermore, the operating conditions of FT-ICR MS used in this work caused a large mass discrimination at the

lower mass ranges (less than 200 Da). This is likely a result of limitations of ion transfer system of FT-ICR MS.

Conclusions

A detailed characterization of basic nitrogen compounds in CGOs before and after hydrotreating was performed by positive ESI FT-ICR MS and compared to characterization performed by GC-MS. Molecular classes such as N, N₂, NO, and NS were identified in CGOs, however the N class nitrogen species were dominant. The results showed that hydrotreating reduced the relative abundance of all class species except for the N class species. This suggests that N class species are refractory to hydrotreating. The molecular weight of nitrogen species in the acid extracted basic nitrogen fraction of CGO was relatively lower than that of its parent CGO. The ionization efficiency of nitrogen compounds with varied DBE values was significantly different between low energy EI and ESI.

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