Nonpolar Compositional Analysis of Vacuum Gas Oil Distillation Fractions by Electron Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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We analyzed three vacuum gas oil distillation fractions, 295–319 °C, 319–456 °C, and 456–543 °C, with a home-built external electron ionization (EI) 7 T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. EI at 10 eV allows soft ionization of aromatic compounds in the vacuum gas oil range. Unambiguous elemental composition assignment provides insight into compositional variations at the molecular level; for example, ultrahigh resolving power ($m/\Delta m_{50\%} \approx 300\,000$ at m/z 300) and mass accuracy (<0.4 ppm) readily resolve C_3/SH_4 doublets (3.4 mDa mass difference) across the full m/z range of interest. To our knowledge, this is the first time that hydrocarbons and sulfur-containing hydrocarbons have been completely mass-resolved across the full VGO range. Aromatic hydrocarbons are the major detected components in all three samples. In addition, many sulfur-, nitrogen-, and oxygen-containing compounds were directly observed. The concentrations of the heteroatomic species increase with boiling point. Detailed data analysis revealed compound types (rings plus double bonds) and their carbon number distributions for hydrocarbon and heteroatomic compounds in the distillation fractions and increasing average molecular weight (or carbon number distribution) and aromaticity with increasing boiling temperature of the petroleum fractions. The present analysis requires only micrograms of sample, is fast (single time-domain data set acquired in a few seconds), and highly reproducible.

Introduction

Transportation fuels are produced from light distillates (nominal boiling point less than 300 °C) of petroleum crude oil or distillation of cracked petroleum products. Vacuum gas oils (VGO), usually distilled under reduced pressure, are higher distillation cuts (atmospheric boiling point range ~300–540 °C) of crude oil.[1] They can be refined to produce high-value lubricating base oils. At a much higher volume, VGO is used to generate lower-boiling gasoline and diesel fuels via catalytic cracking and hydrotreating refining processes.[2–4] The yield and quality of products depend on the process conditions, as well as feedstock composition.[5–8] Chemical composition profiling of petroleum feedstocks and products is important in optimizing refining processes and product utilization. Polyaromatic hydrocarbons can inhibit catalysis by competitive adsorption on the active catalytic surface. Sulfur- and nitrogen-containing compounds, even at low levels, can strongly inhibit an expensive catalyst and/or cause air pollution upon combustion by release of NO_x or SO_x gases.[9] However, molecular compositions of vacuum gas oils, particularly the large polyaromatics (four aromatic rings and higher) and heteroatomic species, are not yet completely defined.

VGO distillation cuts are too compositionally complex for analysis by conventional gas chromatography/mass spectrometry (GC/MS) due to limited chromatographic and mass resolution.[10]

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Although gas chromatography (GC) is currently the most common analytical technique in the petroleum industry, it does not even resolve hydrocarbons beyond the gasoline range.[11] Comprehensive two-dimensional gas chromatography (GC × GC), with higher resolution and sensitivity, has been applied for analysis of compounds in light and middle distillates.[12,13] However, identification of resolved components remains problematic due to a lack of chemical standards. Selective detectors (flame photometry, atomic emission, or chemiluminescence) are often used to monitor a specific compound class.[14−17]

By far, detailed characterization of vacuum gas oils involves extensive use of high-performance liquid chromatography (HPLC) followed by soft ionization mass spectrometry.[10] With online HPLC-MS, Hsu et al.[18] analyzed a heavy petroleum distillate (340−510 °C) and were able to differentiate aromatic hydrocarbons and thiophenes with different aromatic ring numbers at relatively low mass resolving power, because the two compounds were present in different LC fractions. However, some ambiguities still existed for distinguishing aromatic hydrocarbons and thiophenes with same aromatic ring numbers and a mass difference of 0.0034 Da (C_3 versus SH_4).[18,19] A mass resolving power greater than 100 000 is required to resolve them at a mass-to-charge ratio (m/z) of 340. Only Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) can achieve such high resolving power.

Ultrahigh mass resolving power and mass accuracy afforded by FT-ICR MS[20] allows for elemental composition assignment of all resolved species and is especially suited to analyze unknown complex mixtures.[21,22] Various ionization methods, including electron ionization (EI),[23−25] chemical ionization (CI),[26] field desorption (FD) ionization,[27,28] atmospheric pressure photoionization (APPI),[29] matrix-assisted laser desorption ion-

ization (MALDI),[30,31] and electrospray ionization (ESI)[32−35] have been interfaced with FT-ICR MS for analysis of complex mixtures. Recently, Schaub et al. introduced continuous-flow FD FT-ICR MS[36] and applied it to the detailed chemical speciation of aromatic compounds in several vacuum gas oils from different origins.[37] Although elemental composition assignment does not differentiate isomers with the same mass, FT-ICR MS results can nevertheless provide a valuable basis for structure elucidation.[38]

In conventional EI, 70 eV electron beam energy typically generates extensive fragmentation, which is undesirable for separation and identification of components of mixtures. Low-voltage (10−18 eV) electron ionization coupled with low and medium resolution mass spectrometers[18,39,40] has been applied

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to analysis of aromatic compounds in petroleum-derived materials ranging from gasoline to heavy crude oil since its first introduction by Field and Hastings[41] in 1956. Hsu et al.[23] and Guan et al.[24] first applied internal low-voltage EI FT-ICR MS to accurate mass measurement of a heavy petroleum distillate (atmospheric pressure boiling range of 343−566 °C). Ion formation inside the ICR cell has disadvantages of chamber contamination, elevated pressure, and self-chemical ionization. Also, C_3/SH_4 doublets were not resolved across the entire mass range. External formation and accumulation of ions before transfer to the ICR ion trap in the center of the magnet reduces the duration of the experiment and increases the signal-to-noise ratio and resolving power relative to internal ionization.[42] Recently, we interfaced an external EI source to a 7 T FT-ICR mass spectrometer and demonstrated its advantages for volatile complex mixture analysis.[43] A single 200-nL sample injection produced a stable signal for more than 2 h. Such stability enables averaging of a large number of ICR spectra for an improved signal-to-noise ratio at relatively low ion number in the ion trap, for higher mass resolution and mass accuracy.

Here we characterize nonpolar volatile constituents in the low-, middle-, and high-boiling fractions from a VGO sample, by use of low-voltage (10 eV) external EI high-resolution and high-mass accuracy 7 T FT-ICR MS. Low-voltage EI eliminates some structural ambiguities (e.g., alkyl benzenes versus alkyl tetranaphthenes) by selective ionization of aromatic hydrocarbons. FT-ICR MS resolves and identifies hundreds of compositions in three samples, including hydrocarbons and S-, N-, and O-containing compounds, without prior fractionation. This analysis provides the first detailed qualitative picture of distillation temperature-dependent changes in heteroatom class, type (hydrogen deficiency; rings plus double bonds), and carbon number (extent of alkylation) by FT-ICR MS.

Experimental Methods

Samples. Three distillation fractions from a VGO sample were obtained from the ExxonMobil Research and Engineering Company at Annandale, NJ: low-boiling fraction (LBC, 295−319 °C), light yellow and transparent; middle-boiling fraction (MBC, 319−456 °C), brown and cloudy; and high-boiling fraction (HBC, 456−543 °C), dark and viscous. The low- and middle-boiling samples were used as received. The high-boiling sample was completely dissolved in methylene chloride (HPLC grade, Fisher Scientific, Pittsburgh, PA) at ∼200 mg/mL.

Mass Analysis. Mass analyses were performed with an in-house designed 7 T FT-ICR mass spectrometer with an external EI source (Agilent Technologies, Palo Alto, CA).[43] A quantity of 200−500 nL of oil sample or oil solution was injected into an inert expansion unit preheated to 200 °C, with the EI source at 240 °C. Sample flow from the expansion unit to the EI source was controlled by a fused silica capillary tube (180-μm ID, 50-cm long) heated together with the expansion unit. The electron energy was set to 10 eV to minimize ion fragmentation. The RF ion guides were operated at

2.4 MHz, 190 $V_{(p-p)}$ for ion accumulation, and 2.4 MHz, 130 $V_{(p-p)}$ for ion transfer. All three samples were measured at a 0.7-ms transfer interval and 1.6-s data acquisition period to monitor compositional changes in the VGO samples as a function of increased distillation temperature. The ion accumulation period was 0.5 s for low- and middle-boiling fractions and 2 s for high-boiling fraction due to its low volatility.

The ICR cell end cap (trapping) electrodes were gated to −1 V (source end) and 2 V (analyzer end) during ion transfer, after which both electrodes were set to 1 V and ions were allowed to relax for 0.1 s. The trapping voltage was then lowered to 0.5 V prior to broadband chirp excitation (160 kHz−1.6 MHz @ 300 Hz/μs, 200 V_{p-p}) followed by direct-mode image current detection to yield 4 M word time-domain data. The time-domain data were Hanning-apodized and zero-filled once prior to fast Fourier transformation and generation of the magnitude-mode frequency domain spectrum. Frequency was converted to mass-to-charge ratio (m/z) by the quadrupolar electric trapping potential approximation.[44,45]

Elemental Composition Assignment. Mass spectra were externally calibrated with respect to perfluorotributylamine (PFTBA) and then internally recalibrated with respect to the identified alkylbenzenes in each sample to yield a mass error of <0.4 ppm across the entire mass range, 100−500 Da. At a threshold of S/N > 3, the mass values were peak-picked and homologous series were sorted according to Kendrick mass defect values.[46,47] Elemental formulas were assigned by use of a molecular formula calculator in the in-house FT-ICR analysis software. The peak assignment was limited to a maximum of 50 ^{12}C atoms, 100 ^1H, 5 ^{14}N, 5 ^{16}O, 5 ^{32}S, 2 ^{13}C, and 1 ^{34}S with a mass error tolerance of ±1 ppm. If two or more elemental compositions were found within the mass tolerance, either the composition containing heavy isotope(s) could be confirmed or eliminated unequivocally by the presence or absence of the corresponding monoisotopic peak, or the composition containing the least number of heteroatoms was selected. Because members of a homologous series differ only by integer multiples of CH_2, an elemental composition was assigned to the lowest m/z value at each Kendrick mass defect value, and higher mass peaks in the homologous series were assigned by adding integer multiples of CH_2 to the designated elemental formula. The routinely attainable mass resolving power ($m/\Delta m_{50\%} \approx 300\,000$ at m/z 300, in which $\Delta m_{50\%}$ is peak full width at half-maximum peak height) and sub-ppm mass accuracy allowed for unique elemental composition assignment of >97% of mass spectral peaks. Tentative structures may be assigned to major hydrocarbons and sulfur compounds based on prior literature.[48−51] All structures in the text are for illustrative purposes only, and there are many possible assignments.

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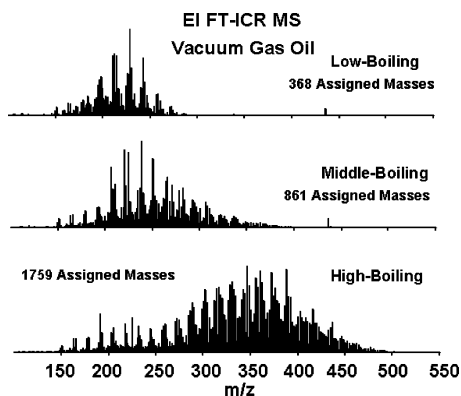
Figure 1. FT-ICR broadband mass spectra (100 scans) of VGO distillation fractions under identical experimental conditions. (Top) Low-boiling, (center) middle-boiling, and (bottom) high-boiling fractions.
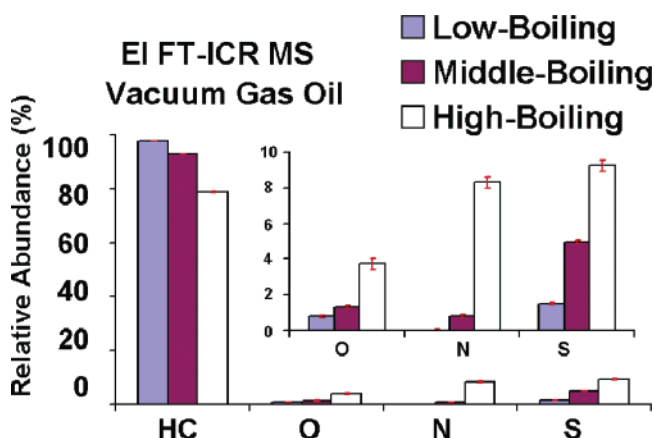

Figure 2. Relative abundances of compound classes in the three VGO fractions. The error bars display relative abundance variation from three separate runs for each sample.

Table 1. Number of Elemental Compositions Identified in Each of the Three VGO Fractions (Only the Monoisotopic Molecular Ions Are Counted)

	low-boiling	middle-boiling	high-boiling
hydrocarbons	92	217	318
sulfur compounds	18	78	140
nitrogen compounds	0	28	121
oxygen compounds	4	27	137

Results and Discussion

Compositional Complexity. Figure 1 shows 10 eV EI FT-ICR broadband (100−500 Da) mass spectra (from 100 summed time-domain acquisitions) for VGO low-, middle-, and high-boiling fractions. All ions are singly charged, based on unit m/z separation between the monoisotopic ($^{12}C_c$) and $^{13}C^{12}C_{c-1}$ species of the same elemental composition. The molecular weight distribution shifts to higher mass with increasing distillation temperature: number-average molecular weight, ~216 Da (low-boiling), ~256 Da (middle-boiling), and ~336 Da (high-boiling), respectively. The number of assigned masses (including both monoisotopic and heavy-isotope-containing species), and thus increase in compositional complexity, increases with boiling point: 364, 859, and 1757 for low-, middle-, and high-boiling fractions. Table 1 lists the number of assigned elemental compositions (counting only monoisotopic molecular ions). The number of heteroatom-containing compounds increases more than the number of hydrocarbon compounds in proceeding from the low-boiling to the high-boiling fraction.

Heteroatom Class Distribution. Figure 2 shows relative abundances for several compound classes (defined by their
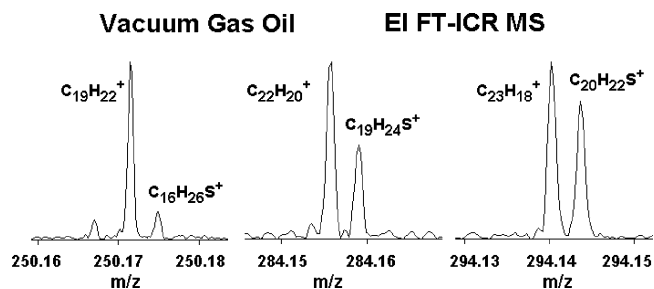

Figure 3. Mass scale expanded segments from the FT-ICR mass spectra in Figure 1, demonstrating baseline resolution of C_3/SH_4 doublets (3.4 mDa mass difference). (Left) Low-boiling, (center) middle-boiling, and (right) high-boiling fractions.

heteroatom content) in the three VGO fractions, demonstrating a gradual increase in the relative abundance of heteroatomic compound classes (i.e., N-, O-, and S-containing compounds) proceeding from the low-boiling to high-boiling fractions. Uniform response factors were assumed for this article, although low-voltage electron ionization efficiency of various compound classes has been extensively studied.[52] Relative abundance was calculated by summing the peak magnitudes for ions of each class and scaling them relative to the summed peak magnitudes for all assigned masses. The variation of calculated relative abundance from multiple analyses is ±1% for hydrocarbons (high abundance) and ±15% for heteroatomic compounds (low abundance). Note that the relative abundances of ions in the mass spectrum do not necessarily reflect the relative abundances for their parent neutrals in original mixture, due to variation in ionization efficiency and volatility (particularly between compounds from different heteroatom classes). Moreover, mass measurement generally cannot by itself distinguish isomers. The relative ionization efficiencies for individual compounds are largely unknown because most standard compounds are not commercially available. At electron ionization energy of 10 eV, the ionization efficiencies of aromatic compounds are much higher than those for saturated compounds (such as *n*-paraffins and cycloparaffins) whose ionization potentials are usually greater than 10 eV. Thus, the present analysis focuses on aromatic components. In general, the higher the molecular weight or the more aromatic the compound, the lower its volatility. Thus, any analysis based on boiling point necessarily discriminates against the less volatile compounds of a given molecular weight. Despite these limitations, the present results represent the most complete compositional analysis to date by a single technique for vacuum gas oil.

Mass Doublets. The ultrahigh resolving power ($m/\Delta m_{50\%} = 300\,000$ at m/z 300) and mass accuracy (<0.4 ppm) provided by the present FT-ICR instrument are sufficient to resolve the critical 3.4 mDa mass difference (C_3/SH_4 doublet) across the full m/z range of interest. Mass scale expanded segments in Figure 3 demonstrate baseline resolution of C_3/SH_4 doublets in all three VGO fractions, up to at least 300 Da in mass. Note that the relative abundance of the sulfur-containing species relative to aromatic hydrocarbon increases with increasing distillation temperature. We shall now show how an unambiguous elemental composition assignment provides previously unavailable insight into the change in composition as a function of distillation temperature.

Hydrocarbons. Figure 4 shows relative isoabundance contours as a function of double bond equivalents (DBE) and carbon number for hydrocarbon compounds, revealing increasing

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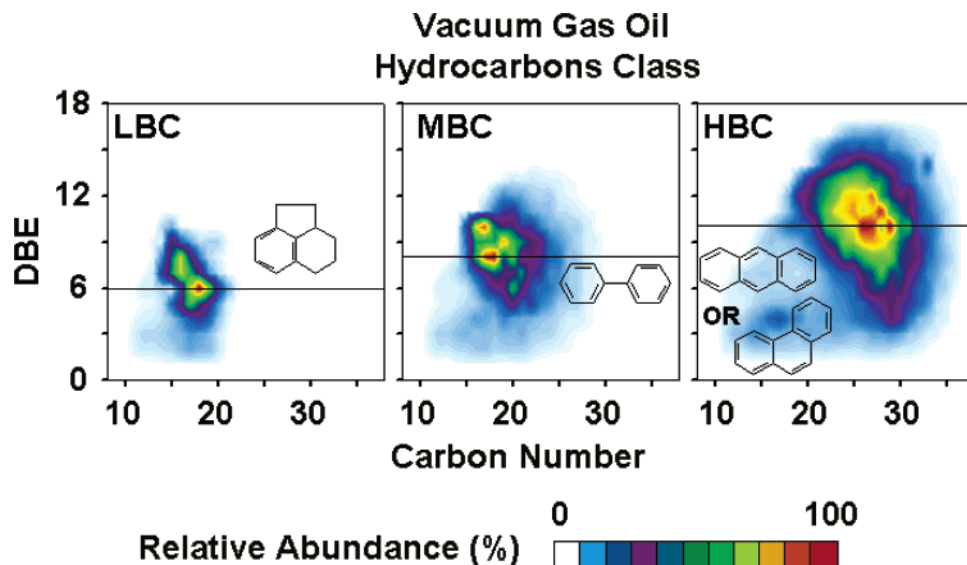
Figure 4. Relative isoabundance contours as a function of double bond equivalents and carbon number for hydrocarbons from each of the three fractions. Abundance is scaled relative to the highest magnitude peak in each spectrum. Possible core structures are shown for benchmark hydrocarbon types of DBE = 6, 8, and 10.
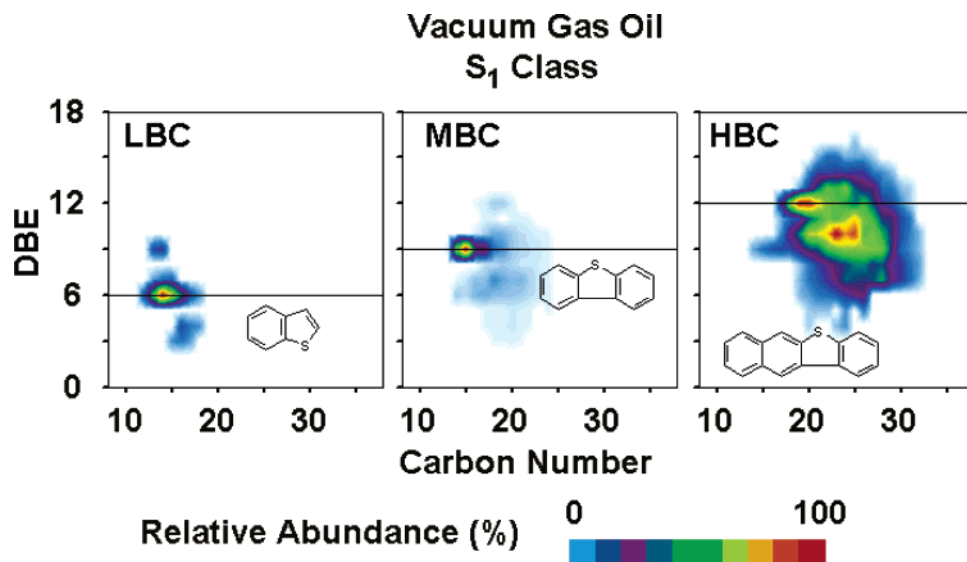

Figure 5. Relative isoabundance contours as in Figure 4, but for monosulfur compounds in each of the three fractions. Possible core structures are shown for benchmark S-compound types of DBE = 6, 9, and 12.

aromaticity and extent of alkylation proceeding from the low-boiling to high-boiling fraction. The low-boiling fraction exhibits mainly DBE = 5−9 with carbon number range from 14 to 20. The DBE distribution for the middle-boiling fraction moves up to 6−11 with carbon number range from 15 to 22, and the dominant hydrocarbons in the high-boiling fraction range over DBE = 7−15 with carbon numbers of 20−32. As benchmarks, DBE values are 4 for alkyl benzenes, 7 for alkyl naphthalenes, 10 for alkyl phenanthrenes, 13 for alkyl chrysenes, and 15 for alkyl benzopyrenes. Interestingly, the DBE = 10 series for the high-boiling hydrocarbons is bimodal, suggesting the presence of homologous series with two different core structures; for example, anthracenes/phenanthrenes (starting at a carbon number of 14) or tricyclonaphthalenes (starting at a carbon number of 19). In all three fractions, we observed a shift to lower carbon number with increasing aromaticity, consistent with the widely accepted argument[53] that higher aromaticity is associated with lower molecular weight at a given boiling point.

Sulfur-Containing Compounds. The relative isoabundance contours for monosulfur compounds as a function of DBE and carbon number are shown in Figure 5. As for the hydrocarbons, the aromaticity and extent of alkylation of monosulfur compounds increase with increasing distillation temperature. The low-boiling fraction contains mainly diaromatic sulfur compounds (DBE = 6); for example, benzothiophenes, with carbon numbers of 12−18 (4−10 additional methylene groups, CH_2). The middle-boiling fraction contains mainly triaromatic sulfur compounds (DBE = 9); for example, dibenzothiophenes (DBTs), with carbon numbers of 13−24 (1−12 additional methylene groups). The DBE distribution maximum of sulfur compounds in the high-boiling fraction shifts upward to 10 and 12. The dominant carbon numbers range from 22 to 25 at DBE = 10 to 19−21 at DBE = 12 in the high-boiling fraction. The DBE = 10 series may be either naphtheno DBTs or phenyl-benzothiophenes. The sulfur-containing compounds with DBE = 12 are most likely benzo DBT homologues (addition of one aromatic ring to dibenzothiophene). The more condensed

(53) Speight, J. G. *Handbook of Petroleum Analysis*; Wiley & Sons: New York, 2001; Vol. 158, Chapter 12.
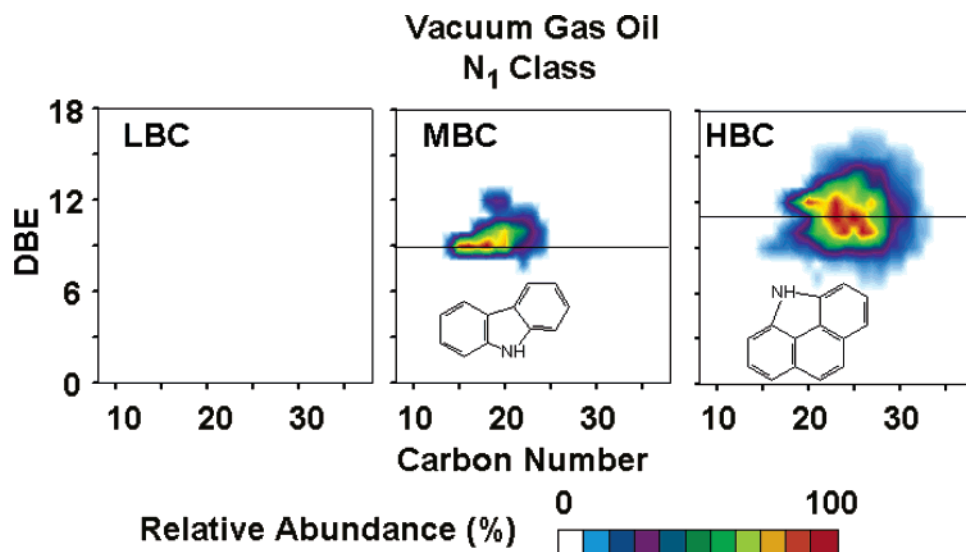
Figure 6. Relative isoabundance contours as in Figure 4, but for mononitrogen compounds in each of the three fractions. Possible core structures are shown for benchmark N-compound types of DBE = 9 and 11.
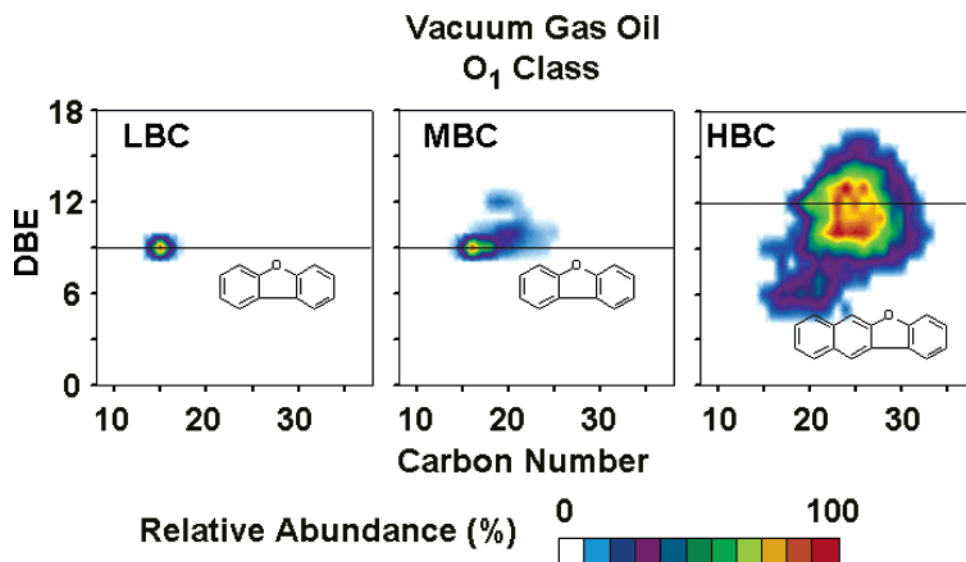

Figure 7. Relative isoabundance contours as in Figure 4, but for monooxygen compounds in each of the three fractions. Possible core structures are shown for benchmark O-compound types of DBE = 9 and 12.

aromatic sulfur-containing compounds in the middle- and high-boiling fractions may account for the difficulty of deep hydrodesulfurization of oil fractions distilling above 340 °C.[54] The different sulfur-containing compound types predominant in the three VGO fractions may imply that different hydrotreating conditions should be applied to remove sulfur compounds from the different fractions.[55]

Nitrogen-Containing Compounds. Figure 6 shows the distribution of mononitrogen compounds as a function of DBE and carbon number. No nitrogen-containing compounds were detected in the low-boiling fraction, in agreement with negative electrospray ionization (ESI) 9.4 T FT-ICR MS results[56] and

prior observations that nitrogen compounds are present mainly in distillation fractions above 345 °C.[53] We also observed an[58] increase in compositional complexity, molecular weight distribution, and aromaticity with increasing distillation temperature for nitrogen-containing compounds. The middle-boiling fraction contains mainly triaromatic nitrogen compounds (DBE = 9); for example, carbazoles, with carbon numbers of 14−24 (i.e., 2−12 additional methylene groups). DBE values for nitrogen compounds in the high-boiling fraction range from 10 to 12, with dominant carbon numbers from 20 to 28 for DBE = 10−12. The nitrogen-containing compounds with DBE = 10 are likely benzoquinoline homologues (i.e., addition of one aromatic ring to quinoline) or acridines with 4−20 additional methylene groups. Benzoquinolines are basic nitrogen compounds considered to be the strongest inhibitors during hydrotreatment.[57]

(54) Stratiev, D.; Ivanov, A.; Jelyaskova, M. Effect of feedstock end boiling point on product sulphur during ultra deep diesel hydrodesulphurization. *Oil Gas Eur. Mag.* **2004**, *30*, 188−192.

(55) Ancheyta, J.; Morales, P.; Betancourt, G.; Centeno, G.; Marroquin, G.; Munoz, J. A. D. Individual Hydrotreating of FCC Feed Components. *Energy Fuels* **2004**, *18*, 1001−1004.

(56) Stanford, L. A.; Kim, S.; Rodgers, R. P.; Marshall, A. G.; Qian, K. Characterization of Compositional Changes in Vacuum Gas Oil Distillation Cuts by Negative Ion ESI FT-ICR Mass Spectrometry. *Energy Fuels*, manuscript in preparation.

(57) Girgis, M. J.; Gates, B. C. Reatvities, Reaction Networks, and Kinetics in High-Pressure Catalytic Hydroprocessing. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021−2058.

(58) Shiraishi, Y.; Yamada, A.; Hirai, T. Desulfurization and Denitrogenation of Light Oils by Methyl Viologen-Modified Aluminosilicate Adsorbent. *Energy Fuels* **2004**, *18*, 1400−1404.

The DBE = 11 series for the high-boiling fraction is most likely benzo[def]carbazole with 4−19 additional methylene groups. The nitrogen-containing compounds with DBE = 12 are most likely benzocarbazole homologues (addition of one aromatic ring to carbazole) with 1−16 additional methylene groups. The higher level of nitrogen compounds in the high-boiling fraction could poison the catalyst during hydrotreatment. It has been suggested that removal of nitrogen-containing compounds prior to hydrotreatment should be considered.[58]

Oxygen-Containing Compounds. Due to their low volatility and thermal instability, crude acids (mostly naphthenic acids) were not detected by EI FT-ICR MS; they are better analyzed by negative-ion ESI FT-ICR MS. Figure 7 shows the distribution of monooxygen compounds as a function of DBE and carbon number. The low-boiling fraction exhibits solely a DBE = 9 series with carbon numbers ranging from 14 to 17, most likely dibenzofurans with 2−5 additional methylene groups. The DBE distribution maximum for O_1 compounds in the middle-boiling fraction remains at 9, with carbon numbers increasing to 15−21. Low abundance species with DBE = 12, most likely benzonaphthofurans, are also observed for the middle-boiling fraction. The DBE distribution of O_1 compounds in the high-boiling fraction broadens to 5−16. The monooxygen compounds with DBE = 5−8 might be polycyclic phenols. However, the most abundant O_1 species in the high-boiling fraction have DBE = 10−13, with carbon numbers of 20−29. Synder[51] previously observed the same DBE distribution for polyaromatic oxygen compounds in a 454−538 °C distillate from a California crude oil and assigned the compounds as dibenzofurans and benzonaphthofurans.

Conclusion

We have applied low-voltage (10 eV) electron ionization combined with 7 T FT-ICR MS for detailed compositional analysis of VGO distillation cuts. The present analytical data are consistent with our knowledge of VGO composition and their distillation cuts. We also show for the first time that the full VGO range of aromatic hydrocarbons can be resolved from sulfur-containing molecules by ultrahigh-resolution mass spectrometry, a goal previously accomplished by coupling chromatography and mass spectrometry. In addition, nitrogen (mostly carbazoles and acridines) and oxygen (mostly dibenzofurans) containing species may be determined togather with their hydrocarbon counterparts. Thus, the technique has significant implications for quantification of VGO hydrocarbon compositions and possibly process applications.