THE CONTINUUM OF PETROLEUM COMPOSITION AND ITS IMPLICATION FOR ASPHALTENE COMPOSITION EXAMINED BY FT-ICR MASS SPECTROMETRY

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Introduction

The immense compositional complexity of crude oil prohibits direct detailed characterization by routine analytical techniques. Ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) allows detailed characterization of complex petroleum samples at the molecular level. Species present in crude oil range from saturated hydrocarbons to highly aromatic structures with varying degrees of alkylation and heteroatom content (nitrogen, oxygen, sulfur and metals such as nickel and vanadium). The Boduszynski model, proposed over 20 years ago, describes the progression of petroleum composition as a function of atmospheric equivalent boiling point [1]. Based on his model, Boduszynski concluded that most crude oil components do not exceed a molecular weight of 2 kDa. He acknowledged the controversial nature of his results, *"These findings are significant because of the existing controversy over whether there is an appreciable concentration of molecules in petroleum having molecular weights greater than 2000 Da. Data show there is not."* However, a definitive proof of the Boduszynski model requires direct, complete compositional characterization of complex distillate cuts--unavailable at that time. If substantiated, the Boduszynski model would impose strict limits on molecular weight distributions for both distillable and nondistillable petroleum fractions in direct contradiction to many previously published assertions about petroleum molecular weight and composition.

FT-ICR MS allows detailed characterization of complex petroleum samples at the level of elemental composition assignment. Ultrahigh resolving power (450,000-650,000 at m/z 500) enables identification of isobaric species that differ in mass by 3 milliDalton or less, and high mass accuracy (better than 300 ppb mass error) allows for unambiguous molecular formula assignment to each of more than ten to thirty thousand peaks in each mass spectrum. Thus, it is now possible to identify, sort and monitor simultaneously thousands of elemental compositions as a function of boiling point as well as provide a comprehensive analysis of nondistillable species. Column chromatography and subsequent characterization with FT-ICR mass spectrometry provides enhanced speciation of the chemical functionalities present in crude oil and further subdivides maltenes into nonpolar and polar fractions based on aromaticity, polarity and molecular weight. Here, we present our cumulative efforts in heavy oil characterization by (+/-) electrospray and Atmospheric Pressure PhotoIonization (APPI) FT-ICR mass spectrometry and summarize class, type and molecular weight trends for distillable and nondistillable petroleum species and compare results to proposed asphaltene structural models.

Experimental

Asphaltene Separation. Asphaltene and maltene fractions were isolated per IP 143/90 from four different crudes.

Column chromatography Separation. Deasphaltened crude oils were first adsorbed onto a 60 g silicic acid chromatographic column. Components of the crude oils were selectively eluted by solvents of increasing polarity (*i.e.,* solvent strength). The most polar components are adsorbed on the active sites of the adsorbent. Four fractions were collected in the following elution order: hydrocarbons, neutral nitrogen, basic nitrogen, and polars.

Sample Preparation. Stock solutions of crude oil fractions were prepared by dissolving ~5 mg of material in 5 mL of toluene. A 2 mL aliquot was further diluted with 6 mL of toluene to yield 8 mL of stock solution (250 µg/mL) for APPI FT-ICR analysis. Electrospray samples were diluted to a final concentration of 250 µg/mL in 1:1 (v/v) toluene/methanol. Solutions for electrospray were further modified with 1% (by volume) of NH_4OH or tetramethylammonium hydroxide (TMAH) to aid in deprotonation for negative ions, or formic acid for positive ions.

Mass Analysis. The crude oils were analyzed at the National High Magnetic Field Laboratory (NHMFL) with a custom 9.4 tesla FT-ICR mass spectrometer. Ions were generated externally by an electrospray ionization (ESI) or atmospheric pressure photoionization (APPI) (ThermoFisher) ion source and accumulated for a period of 0.5 – 5 s prior to introduction into the ICR cell. 100 time-domain transients were co-added for each sample and stored for later fast Fourier transformation and frequency-to-mass conversion. The stored time-domain signal was Hanning-apodized and zero-filled once prior to fast Fourier transformation and generation of the magnitude-mode frequency domain spectrum. A custom modular ICR data system (PREDATOR) provides instrument control, data acquisition, and data analysis. Mass spectra were internally calibrated with respect to a known homologous series, class-specific to the ionization method. Homologous series were separated and grouped by nominal Kendrick mass and Kendrick mass defect to facilitate rapid identification, as described elsewhere.

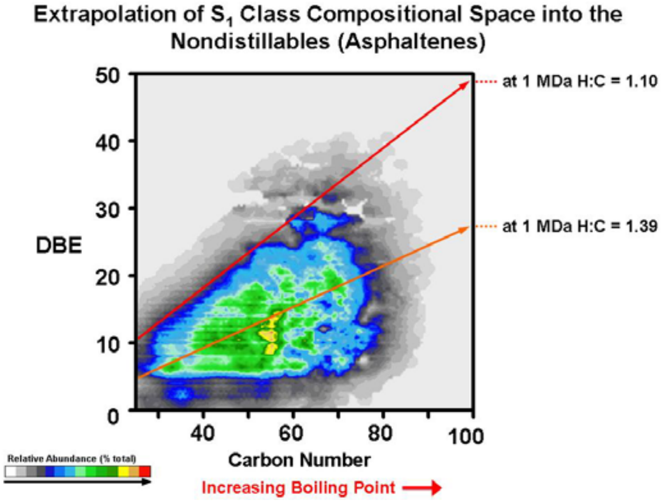

Figure 1. Composite isoabundance contoured plot of DBE (double bond equivalents, number of rings plus double bonds) vs. carbon number for the S_1 class for Middle Eastern heavy crude oil distillation series and residue maltenes.

Results and Discussion

Detailed characterization of an Arabian heavy crude oil distillation series defines maltene compositional space (aromaticity and carbon number) for ~10-25 hydrocarbon and heteroatom-containing classes. Calculation of the hydrogen to carbon (H:C) bounds of the distillable space for all classes identified reveals that projection of the compositional continuum to high carbon number (as high as a megaDalton) can not account for asphaltene bulk H:C ratios (**Figure 1**).

Thus, either asphaltenes are not high molecular weight materials or the continuity model does not apply. Direct asphaltene characterization is hampered by extensive solution phase aggregation at concentrations as low as 50 µg/mL (**Figure 2**). Compositional information for nondistillable and its implications in aggregation will be discussed in detail.

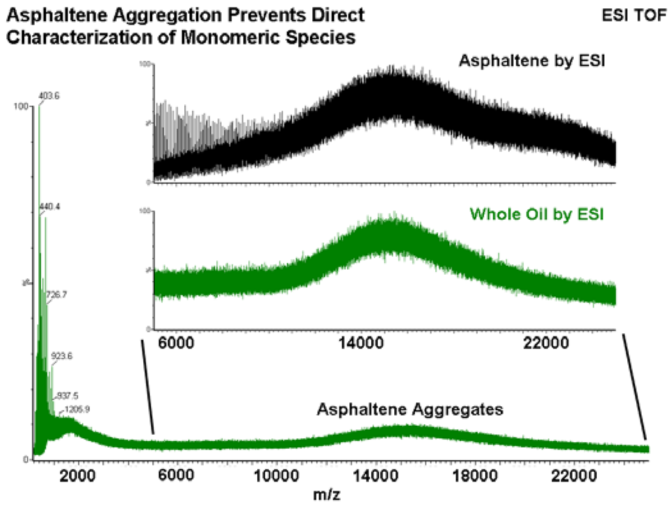

Figure 2. Positive-ion electrospray TOF mass spectrum of Middle Eastern heavy crude oil (bottom) and asphaltenes (top, black) reveal asphaltenic species aggregation at low concentration (50 µg/mL) .

Maltene Chromatographic Fractions. Fractionation and subsequent characterization by (+/-) electrospray and APPI mass spectrometry was performed for the maltene fractions of Middle Eastern heavy crude and its 593^+ ˚C residue. Three distinct FT-ICR mass spectra were collected for each subfraction to reveal compositional differences between the fractions as well as differences between the same classes isolated from the whole crude and residue. Enhanced characterization of the acidic species by negative electrospray ionization was facilitated by modification of the solvent system by the addition of TMAH to increase the ionization efficiency of slightly acidic nitrogen-containing classes (**Figure 3**).

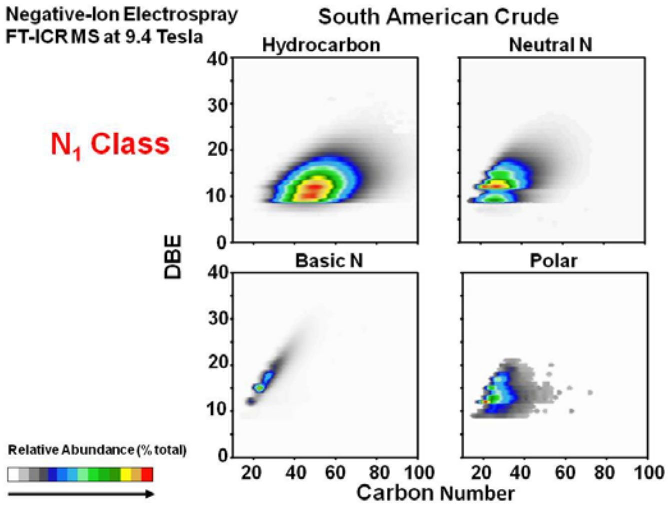

Figure 3. DBE vs. carbon number plots acquired for the N_1 class obtained by negative electrospray ionization FT-ICR MS.

DBE vs. Carbon Number Images. APPI FT-ICR MS analysis of each fraction reveals that the hydrocarbon fraction is composed of alkyl-substituted aromatic hydrocarbons with a low relative abundance of polar components. Non-basic (pyrrolic) nitrogen dominates the neutral nitrogen fraction whereas the basic nitrogen is dominated by pyridinic nitrogen, hydrocarbons, thiophenes and furans. Positive-ion electrospray shows that highly abundant structures with DBE values that correspond to quinoline/acridine shift slightly to lower carbon number with increasing solvent strength. Negative-ion electrospray for the nonpolar fractions shows bimodal DBE distributions consistent with carbazole and benzocarbazole structures with highly aromatic structure dominant in the basic nitrogen fraction. Trends in molecular weight and aromaticity as a function of LC elution across and between each crude oil fraction will be discussed and compared to the overall composition of crude oil.

Conclusions

Detailed compositional analysis of Middle Eastern heavy crude and its residue defines their compositional space in DBE and carbon number as a function of heteroatom class. Comparison of chromatographic fractions and distillate cuts converges on the continuum of crude oil composition proposed by Boduszynski more than 20 years ago.

References

[1] Boduszynski, M. M.; Altgelt, K. H., Composition and Analysis of Heavy Petroleum Fractions. CRC Press: New York, NY, 1994.

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