

The compositional continuum of petroleum

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Proposed over 20 years ago, the Boduszynski model describes the progression of petroleum composition as a function of atmospheric equivalent boiling point [1]. Based on his model, Boduszynski concluded that "most of petroleum components do not exceed a molecular weight of about 2000." He acknowledged that the results are controversial: "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 Boduszynski's 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 that contradict many previously published assertions about petroleum molecular weight and composition.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables detailed characterization of complex petroleum samples at the level of elemental composition assignment. Ultrahigh resolution (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 non-boiling species. Here we present our cumulative efforts in heavy oil characterization by (+/-) electrospray and atmospheric pressure photoionization FT-ICR mass spectrometry, and summarize class, type, and molecular weight trends for distillable / non-distillable petroleum species, and compare the results to proposed asphaltene structural models.

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

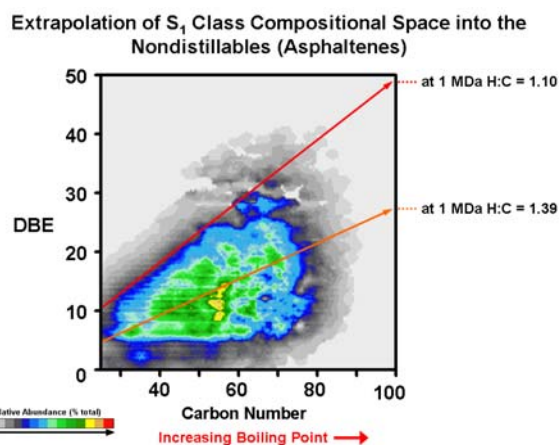


Fig. 1. Composite isoabundance contoured plot for the S₁ class for Arabian heavy crude oil distillation series / residue.

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 $\mu\text{g/mL}$ (Figure 2). Compositional information for nondistillables and its implications in aggregation will be discussed in detail. (Supported by NSF DMR 06-54118 & the State of Florida.)

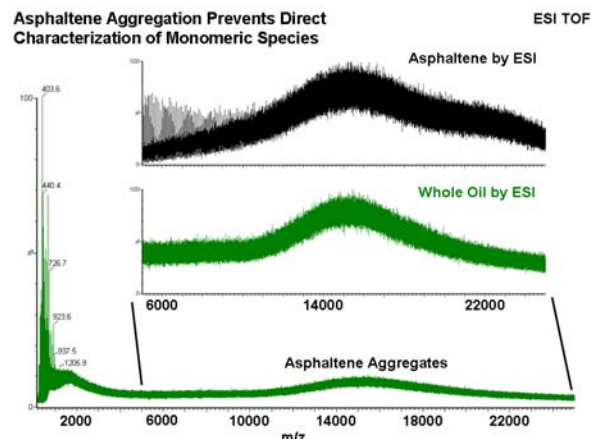


Fig. 2. (+) ESI TOF mass spectrum of Arabian heavy crude oil (bottom) and asphaltenes (top, black) reveal asphaltenic species aggregated at low concentration (50 $\mu\text{g/mL}$).

References

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