Heavy Petroleum Composition 5: The Compositional and Structural Continuum of Petroleum Revealed

D.C. Podgorski (FSU, Chemistry); Y.E. Corilo (NHMFL, Chemistry); L. Nyadong (NHMFL, Chemistry); V.V. Lobodin (NHMFL, Chemistry); W.K. Robbins (Consultant); A.M. McKenna (NHMFL, Chemistry); A.G. Marshall (FSU, NHMFL, Chemistry); R.P. Rodgers (FSU, NHMFL, Chemistry)

Results and Discussion

Twenty-five years ago, Boduszynski *et al.* proposed that crude oil composition increases gradually and continuously with regard to aromaticity, molecular weight, and heteroatom content, from the light distillates to non-distillables. Prior exhaustive characterization of heavy vacuum gas oil by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) provided compositional data that strongly supports the continuum model. However, when the molecular formulas obtained by FT-ICR MS for the distillates and the asphaltenes from the same parent crude oil are plotted as double bond equivalents (DBE = rings + double bonds to carbon) versus carbon number, a gap appears between the compositional space of "asphaltenes" and "maltenes", in contradiction to the Boduszynski-Altgelt model. Here, a heavy distillate cut (atmospheric equivalent boiling point = 523 - 593 °C) is fractionated according to the number of aromatic rings by HPLC-2. The C7-deasphalted whole oil (C7-DAO), its pentane soluble/insoluble fractions, and each of their ring number fractions are comprehensively characterized by atmospheric pressure photoionization (APPI) FT-ICR MS and MS/MS (see Figure 1). The HPLC-2 fractions from both the C5-soluble and C5-insoluble C7-DAO represent a gradual and continuous progression that fills the compositional "gap" in carbon number and aromaticity between asphaltenes and maltenes as a function of increasing aromatic ring number, as predicted by Boduszynski. Tandem MS results indicate that each ring number fraction comprises both island and archipelago structural motifs. The C5-insoluble C7-DAO components have similar structure but with higher order fused ring core structures and are composed of a higher proportion of archipelago structures than the C5-soluble C7-DAO components. Thus, MS/MS exposes the aromatic building blocks of "maltenic" and "asphaltenic" species (structural continuum) that comprise island and archipelago structural motifs.

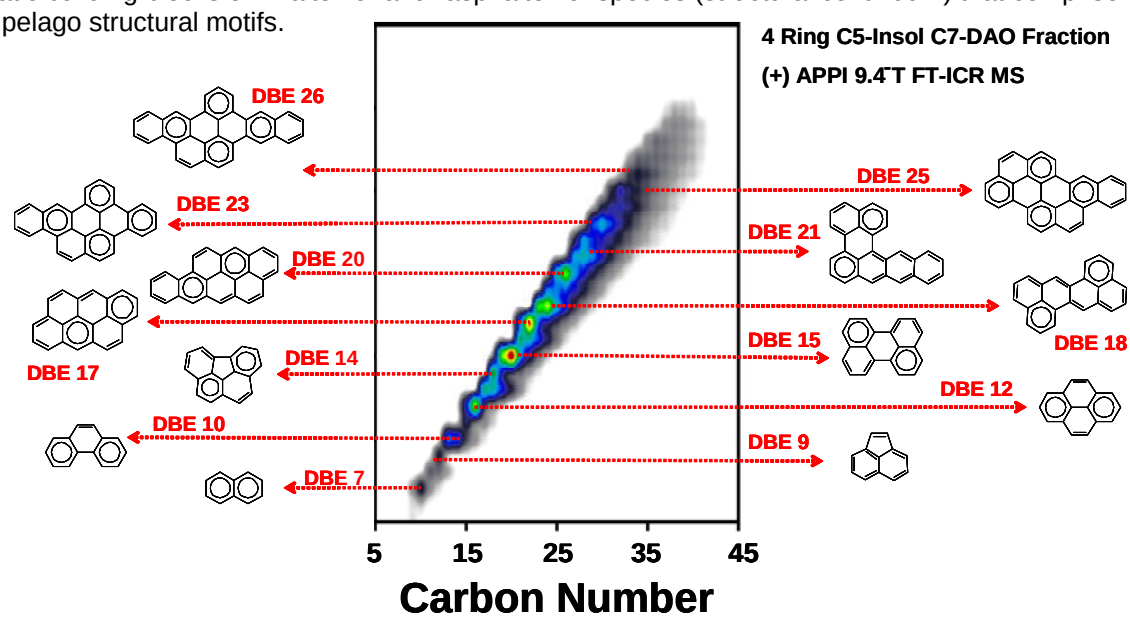

Figure 1. DBE vs. carbon number image of 4-ring C_5-insoluble C_7-de-asphalted oil (DAO) fraction after 500 ms of infrared irradiation. Proposed structures reveal the structural diversity of core components.

Acknowledgments

The work was supported by the National Science Foundation (NSF) Division of Materials Research through DMR-06-54118, the State of Florida, the Florida State University Future Fuels Institute, and BP/The Gulf of Mexico Research Initiative.

References

[1] Podgorski, D. C., *et al.*, Energy & Fuels, **27**, 1268-1276 (2013).