The Compositional and Structural Continuum of Petroleum from Light Distillates to Asphaltenes: The Boduszynski Continuum Theory as Revealed by FT-ICR Mass Spectrometry

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Introduction

In the early 1980s, Boduszynski published a series of manuscripts that addressed the compositional progression of heavy petroleum. Boduszynski concluded that petroleum composition progresses gradually and continuously in aromaticity, molecular weight, and heteroatom concentration as a function of increasing boiling point. The Continuum Model was deduced from field ionization mass spectrometry that lacked the resolution needed to identify elemental compositions for heavy crude oils. However, combined with boiling point trends, molecular weight distributions, and solubility/chromatography behavior, Boduszynski described the Continuum Model of Petroleum. Herein, we revisit the same topic and employ the same analytical methods; however, we use state-of-the-art Fourier Transform Ion Cyclotron Resonance Mass Spectrometers (FT-ICR MS) that can readily resolve and uniquely identify molecular formulas to tens-of-thousands of individual petroleum species in a single analysis.

Experimental

Positive atmospheric pressure photoionization (+APPI) coupled to 9.4 T FT-ICR mass spectrometry and IRMPD were used to analyze distillation cuts, heavy oils, asphaltenes, and extrography.

Results and Discussion

High field FT-ICR mass spectrometry enables to trace the molecular-level changes in complex petroleum samples as a function of increasing boiling point. We have evaluated the Continuum Model from light distillates to asphaltenes, for hundreds-of-thousands of species by FT-ICR MS and found no deviations. The most significant finding over the past two decades of petroleum research at the National High Magnetic Field Laboratory has been what predictions can be made if it is assumed that the Boduszynski Continuum model is correct. For example, the maltene continuum cannot be extrapolated to higher carbon number and match the bulk H/C ratio of asphaltenes. Thus, the maltene continuum fades to higher carbon number and bends back on itself (to decreasing carbon number), as it climbs to higher aromaticity (DBE) to become the asphaltene continuum. This completes the petroleum compositional continuum from the planar PAH line, down to DBE = 0, the saturates. The structures that lie in between complete the structural continuum. The ability to complete the structural continuum was realized by the discovery of highly selective ionization for one structural type (islands) that have a lower tendency to self-associate than archipelago structures. Once removed from the sample, abundant archipelago structures were revealed. Thus, the continuum favors no single structure or composition; ionization in mass spectrometry does. The petroleum structural continuum is composed of abundant island and archipelago species, and like the compositional continuum, it varies by sample. Given that all these molecular features ultimately determine the value of a crude oil, it is not surprising that initial focused efforts in the implementation of such complex information are for refinery models.

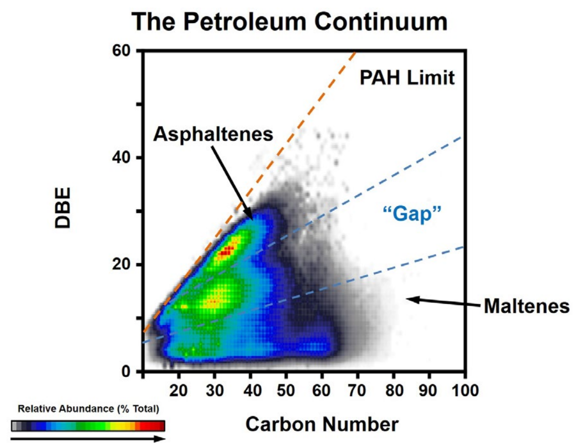

Fig 1. The continuum composition of petroleum: DBE vs. carbon number plots for maltene ring fractions and asphaltene extrography fractions.

Conclusions

It coexists with abundant archipelago structures, and the ratios of each are sample-dependent. the results create a molecular-level map of complex compositional information that reveals relationships between carbon number, aromaticity (DBE), heteroatom content (N, O, S), chemical functionality, ring number, structure (island and archipelago), and boiling point.

Acknowledgements

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Reference

[1] Chacón-Patiño M.L., *et al.*, The Boduszynski Continuum: Contributions to the Understanding of the Molecular Composition of Petroleum, Chapter 6, **1282**, 113–171 (2018).