Advances in Asphaltene Petroleomics. Part 3. Dominance of Island or Archipelago Structural Motif Is Sample Dependent

Chacón-Patiño, M.L. (NHMFL); Rowland, S.M. (NHMFL, FFI) and Rodgers, R.P. (NHMFL, FFI)

Introduction

The controversy around asphaltene structure arises from the inconsistency between the "island model" and the pyrolysis products from asphaltenes. The "archipelago model" is consistent with asphaltene chemistry, but it lacks the support of mass spectrometry. However, recent works that combine separations and high-resolution mass spectrometry (HR-MS) for petroleum characterization demonstrate that compounds that ionize efficiently are preferentially detected and thus preclude the characterization of poorly-ionized species. In this work, we demonstrate that the ratio island/archipelago is sample dependent, being consistent with the cracking behavior of asphaltenes in refinery processes.

Experimental

Positive atmospheric pressure photoionization (+APPI) coupled to 9.4 T FT-ICR mass spectrometry and IRMPD were used to analyze asphaltene extrography fractions from Wyoming deposit and Athabasca bitumen.

Results and Discussion

FT-ICR MS and IRMPD results on Wyoming deposit and Athabasca bitumen demonstrate that the selective separation of compounds with high MIY enables access to difficult-to-ionize species that comprised up to ~70 wt% of the asphaltene samples. The latest eluting fractions present ~50-fold lower MIY and reveal compounds not observed in the whole asphaltenes.

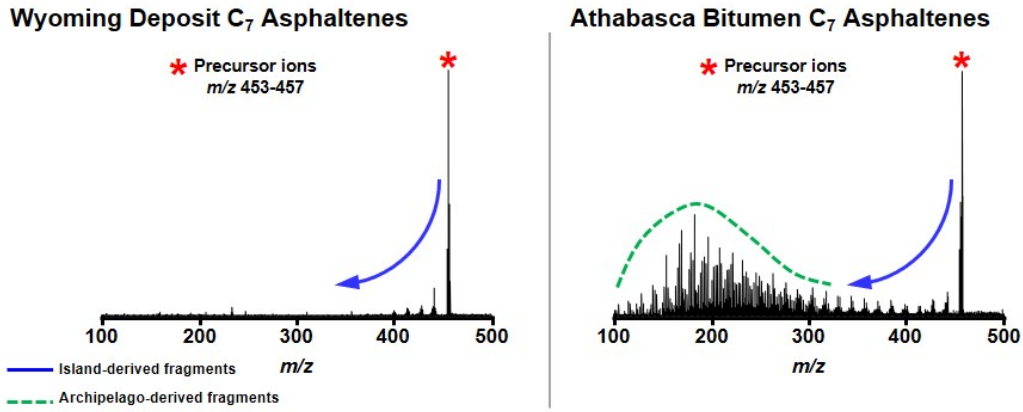

Fig. 1 Fragmentation spectra for (left) Wyoming Deposit C_7 asphaltenes and (right) Athabasca Bitumen C_7 asphaltenes.

These fractions exhibit fragmentation patterns possible only for abundant archipelago motifs. Aggregation tests demonstrate that the decreased MIY of the later-eluting fractions correlates with a higher tendency to self-associate. Hence, MS analyses of the unfractionated samples fail to reveal archipelago species due to the disproportional ionization of non-aggregated island structures. The results demonstrate that island and archipelago structures coexist. The dominance of a particular motif is sample dependent, and the ratio archipelago/island increases as a function of increased m/z, even in island-dominant samples. Island is the dominant structural motif in Wyoming Deposit C_7 asphaltenes; the predominant fragmentation pathway for all extrography fractions consists of loss alkyl chains without significant loss of aromaticity. Conversely, Athabasca Bitumen C_7 asphaltenes exhibit an "atypical" molecular composition. More than 40 wt % of the sample is extracted in the latest extrography fractions, which are composed of difficult-to-ionize species, a fraction of which exhibit atypically low double bond equivalent (DBE = 5−12) and extended homologous series with carbon numbers up to 60. The fragmentation behavior of all Athabasca Bitumen-derived fractions demonstrates a predominant contribution of archipelago motifs.

Conclusions

The ratio island/archipelago is sample dependent, and its accurate quantification should significantly improve the economic value of asphaltene-enriched feedstocks by prediction of yields and optimal conditions for upgrading processes.

Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida.

Reference

[1] Chacón-Patiño M.L., *et al*., Energy &Fuels, **32**(9), 9106-9120 (2018).