

## A comparison of asphaltene model compounds and asphaltenes. The “island” vs. “archipelago” models

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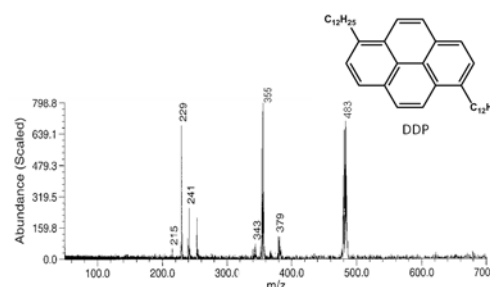
Asphaltenes are defined as the fraction of crude oil that is soluble in toluene and insoluble in n-heptane.[1] Many problems arise from the presence of asphaltenes in crude oil. They are known to foul catalysts during the processing of crude oil, and to precipitate out in equipment, thus increasing regular maintenance needs.[2,3] As light crude oil reserves diminish, creating a shift towards using heavier crude oil reserves containing a higher percentage of asphaltenes, the need to better understand asphaltenes in order to efficiently utilize heavier crude oil reserves has become urgent.

Asphaltene structure is a topic of intense debate. Two different model structures, the “island” model and the “archipelago” model, are being considered. The “island” model features a large aromatic core with alkyl chains branching out. The “archipelago” model contains multiple aromatic cores linked via alkyl chains, and possibly also alkyl chains branching out from the aromatic systems. We have examined several model compounds of both the “island” and “archipelago” variety via laser-induced acoustic desorption combined with electron ionization (LIAD/EI) mass spectrometry (MS), electrospray ionization (ESI) MS, and atmospheric pressure chemical ionization (APCI) MS. The observed fragmentation pathways were compared to those of asphaltenes in order to gain insight into the structures of asphaltenes.

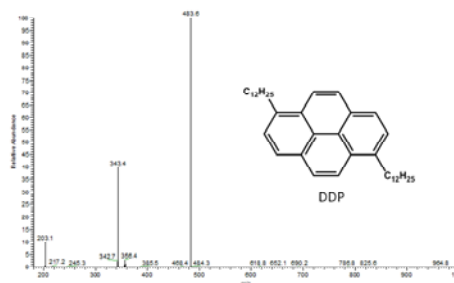
LIAD/EI MS was performed using a 3 T Fourier transform-ion cyclotron resonance (FT-ICR) MS, as described previously [4]. This method has been shown to allow the desorption of asphaltenes and ionization of the gaseous neutral molecules via EI while avoiding the severe limitations that hamper the use of methods such as ESI and MALDI. Most model compounds yielded a stable molecular ion upon LIAD/EI, while a few produced only fragment ions. Energy-resolved studies were conducted to examine the energetic requirements of the different fragmentation pathways for the model compounds. These results were compared to LIAD/EI results obtained for asphaltenes.

The model compounds were also studied using APCI and ESI in a linear quadrupole ion trap (LQIT). ESI could ionize only one of the model compounds, while APCI (with toluene) yielded stable  $[M+H]^+$  for all of the compounds studied. The protonated molecules

were isolated and subjected to collision-activated dissociation (CAD), which yielded a unique fragment ion distribution for each compound. Asphaltenes were also examined using ESI and APCI, and those data were compared to the model compound results.



**Fig. 1.** “Island” model compound DDP. LIAD/EI yields the molecular ion along with fragment ions formed by consecutive losses of  $C_9H_{20}$  from its alkyl chains.



**Fig. 2.** Positive mode APCI spectrum for the model compound DDP. APCI in toluene produces a stable  $[M+H]^+$  (top), and CAD of this ion yields consecutive losses of its entire alkyl chains

This study showed distinct fragmentation characteristics for ions arising from “island” vs. “archipelago” model compounds. These findings will aid in the elucidation of the molecular structures of asphaltenes.

### References

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- [3] Trejo, F.; Centeno, G.; Ancheyta, J., (2004) *Fuel*, 83, 2169-2175.
- [4] Pinkston, D.S., et al. (2009) *Energy Fuels*, 23, 5564-5570