

## Trapping of Paraffin and Molecular Breakdown as Supporting Evidence for Rosary-Type Structure of Asphaltenes

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In this communication trapping of paraffin by asphaltenes, detected by Laser Desorption Ionization Mass Spectra (LDIMS) and breakdown of asphaltenes by a commercial catalyst are presented and discussed. LDIMS shows clearly the presence of a paraffin family with molecular mass ranging from 480 to 640. The evidence presented here suggests very strongly that paraffin is trapped by asphaltene molecules. Catalytic treatment of asphaltenes (dissolved in toluene, %) afforded a mixture of a heptane's soluble low molecular mass compound and unconverted asphaltene. The results suggest rupture of relatively weak aliphatic bonds. These LDIMS and catalytic results have been found consistent with the proposed Rosary-Type (RT) structure of asphaltenes (Acevedo *et al*, 2007)

### Experimental

Asphaltenes were flocculated from the crude oil after addition of 40 heptane volumes to a 1:1 (v/v) toluene-crude oil mixture as described elsewhere ((Acevedo *et al*, 1.985)

. The solid obtained was thoroughly washed with boiling heptane to remove resins and other compounds such as paraffin. For simplicity this mixture will be referred here as resins. Resins were recovered after heptane distillation under vacuum.

A commercial mixture of molybdenum and nickel oxides supported on alumina was converted to metallic sulfurs by treatment under H<sub>2</sub> S atmosphere, 400°C, 4 h in a glass microreactor. The solid obtained (0.25 g) and an asphaltene solution in toluene (3.33 %), were placed inside a Parr reactor. The mixture was pressurized with hydrogen (480 psi) and heated (heating rate: 30°/min) under stirring to 320°C during four hours. After this time, the reactor was cooled, opened, the catalyst was filtered and the solvent was evaporated under vacuum. The resulting solid contains about 72% of material soluble in heptane. This will be referred to as CN3 sample.

LDI mass spectra were recorded using an Applied Biosystems apparatus (MALDI-TOF Voyager DE-STR) as described earlier (Acevedo *et al*, 2005). Molecular weight measurements were performed after optimization of laser shots (LS) for maximum volatilization and minimum fragmentation. VPO  $M_n$  values were determined in nitrobenzene at 100°C  $M_n$ .

### Results and Discussion

In view of high complexity of asphaltene mixture molecular models are usually employed to represent it. These models are constructed from a minimum experimental data and hence experiments should be designed to check whether the models could account for general properties such as solubility, molecular trapping, aging, swelling and molecular breakdown. The issue is discussed fully in a recent paper (Acevedo *et al*, 2007) where all these properties were accounted for in terms of RT structures such as the one shown in Figure 1. The theme of this structure is that the polycyclic systems are joined between them by aliphatic bridges, resulting in a flexible structure capable of folding upon itself as shown in Figure 2 for one of the many possible conformers.

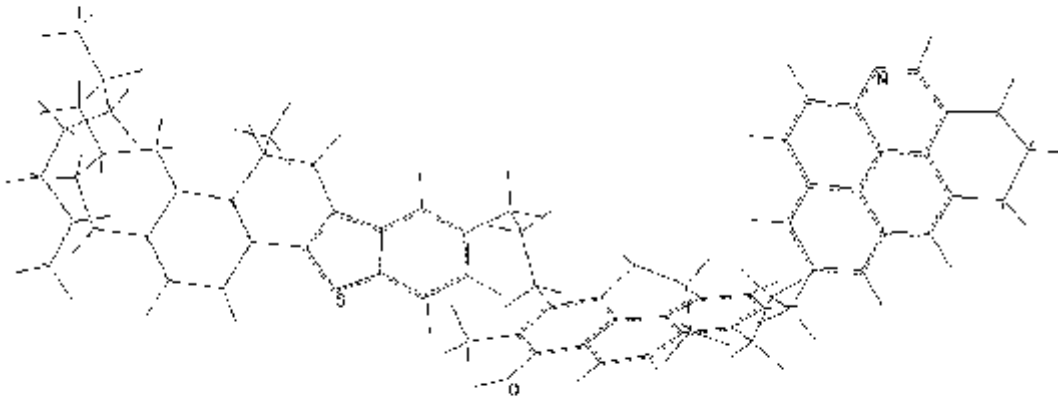


Figure 1. Molecular Model of asphaltene. Molecular mass: 995; molecular formula:  $C_{71}H_{79}NOS$ ; H/C: 1.11. Geometry was obtained using the molecular mechanics procedure described (Acevedo *et al*, 2007).

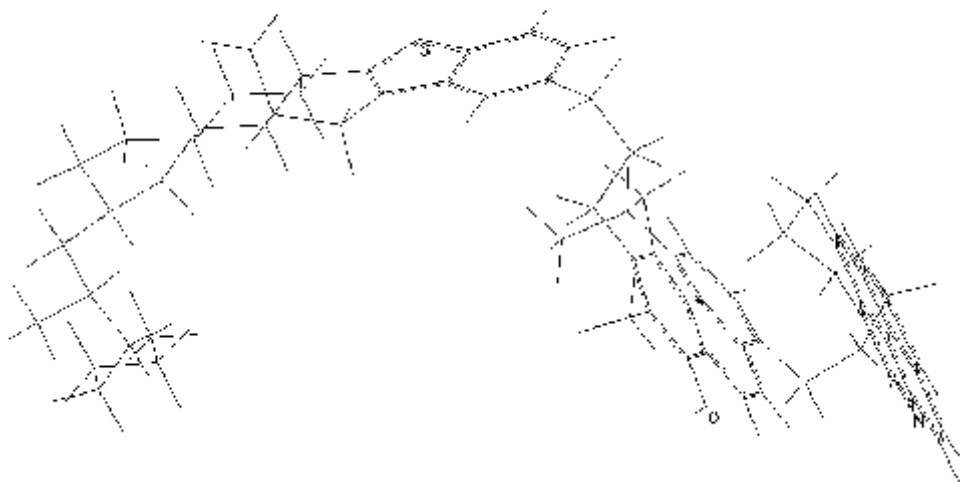


Figure 2. Folded conformer corresponding to the Molecular Model of Figure 1.

The mass spectra of resins and paraffines extracted from the asphaltenes is shown in Figure 3. These spectra were almost identical with the one taken to sample CN3 obtained from the asphaltene catalyses described above.

### Fraction CN4 : Resin

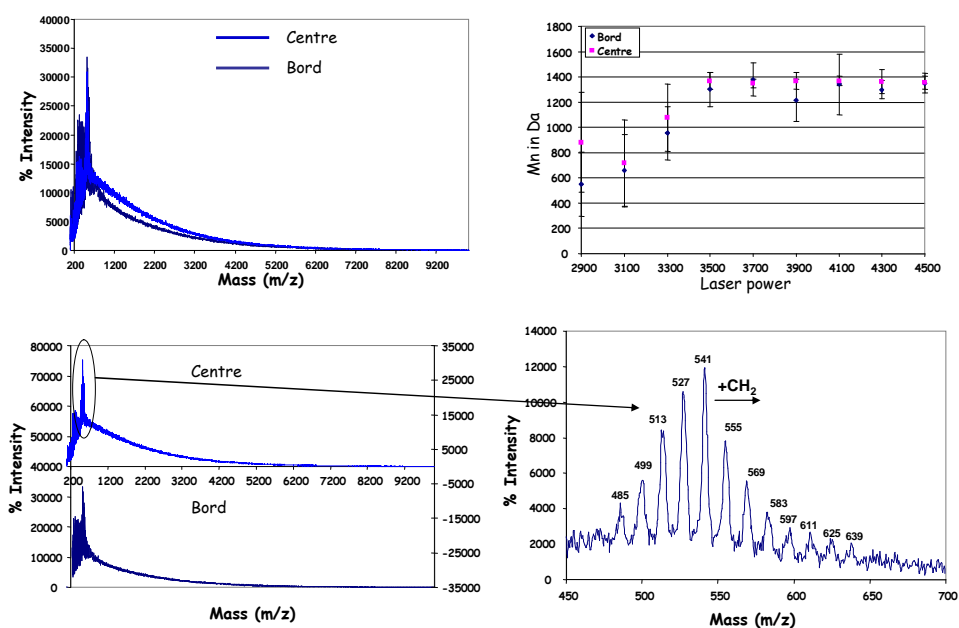
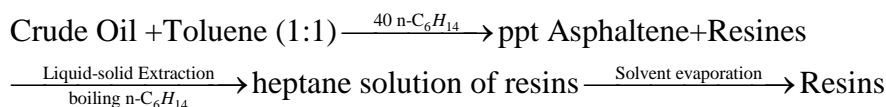


Figure 3. LDIMS of resins extracted from asphaltenes (see: Experimental). Closewise: resins spectra taken from border and centre of sample holder. Molecular mass of sample as a function of LS power (polymerization). Resins spectra showing paraffin presence and family of paraffin. Very similar spectra with paraffin presence was obtained for fraction C3.

The number average molecular mass  $M_n$  for resins and for sample CN3 measured by VPO and LDIMS were both close to 500, indicating that the expected breakdown of relatively weak bonds in the asphaltenes has occurred. In fact mild catalytic conditions were selected with this purpose in mind. In the model above (Figure 1) these weak bonds would be those containing carbon atoms  $\Gamma$  to the aromatic rings. Because of folding and unfolding, asphaltene molecules could trap other molecules present in the crude and Figure 3 illustrates the case for paraffines. As described in the experimental the following scheme was used to the isolate resins:



Hence, the paraffines identified in the mass spectra of Figure 3 should come from the asphaltenes. Washing of precipitate with boiling heptane removes then from the asphaltenes and are then found in the final resins sample. The same paraffinic pattern was found in sample CN3 and presence of paraffines was also detected in the LDIMS of asphaltenes.

As proposed earlier asphaltenes form host-guest complexes with molecules such as free radicals and porphyrines ((Acevedo *et al*, 2007). Evidence for the presence of long paraffines was reported (Simm and Steedman, 1980) and more recently (Graciaa *et al*, 20006). The above results reinforce this thesis and we believe that in this case the paraffin could coil around the asphaltene molecule. In such a case it is easy to understand why is so difficult to remove it from the asphaltenes.

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