

## CHARACTERIZATION OF *n*-HEPTANE SOLUBLE FRACTIONS PRODUCED BY MILD DISAGGREGATION OF ASPHALTENES AND ITS RELEVANCE FOR THE STUDY OF PETROLEUM SYSTEMS

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Asphaltenes are the most complex components of crude oils. The term asphaltene is defined operationally; asphaltenes are defined to be toluene soluble and *n*-heptane insoluble (Badre *et al.*, 2006). In general asphaltenes possess fused ring aromaticity, small aliphatic side chains, and polar heteroatom-containing functional groups (e.g., carboxylic acids, carbonyl, phenol, pyrroles and pyridines) inter- and intra-molecularly capable of donating or accepting protons (Gawrys and Kilpatrick, 2005).

These structural features enable asphaltenes to occlude other molecular species hindering their secondary alterations that occur in oil reservoirs which are therefore believed to be remnants of the “original oil” (Behar and Pelet, 1984; Liao and Geng, 2002; Liao *et al.*, 2006a; Liao *et al.*, 2006b).

The purpose of this work was to study four oil samples with different degrees of biodegradation, through the release of biomarkers from asphaltenes. Oil mixtures, oil-oil correlation, oil-source correlation, and effect of migration and secondary alterations had been interpreted from geochemical parameters derived from these “preserved” biomarkers.

The asphaltenes were precipitated and oxidized with NaIO<sub>4</sub>-NaH<sub>2</sub>PO<sub>4</sub> to release the occluded hydrocarbons. The fraction compositions (SARA: saturate hydrocarbon, aromatic hydrocarbon, resin and asphaltene) of the crude oils were determined by TLC-FID analysis. The saturated and aromatic fractions of occluded and crude oils were analysed by GC-MS.

Fig. 1 shows the mass chromatograms (*m/z* 85) of the saturated hydrocarbon fractions of the crude oil and the oxidation products released from the corresponding asphaltenes. The crude oil is heavily depleted, mainly from *n*-alkanes, showing heavy biodegradation process, while the released products of the corresponding asphaltene show a full distribution of *n*-alkanes, from *n*C<sub>15</sub> to *n*C<sub>35</sub>, pointing to the protection effect from biodegradation that can be attributed to the encapsulation by the asphaltene network.

The characteristic mass chromatograms (*m/z* 191) of terpane compounds removed from the asphaltenes showed higher pentacyclic / tricyclic terpanes ratio in relation to the

crude oil sample. This indicates that the occluded hydrocarbons had been little or not affected by alteration process in oil reservoirs, while the hydrocarbons of the crude oil samples had been subjected to secondary alteration processes such as maturation and biodegradation.

The saturated hydrocarbons occluded by asphaltene structures are suggested to represent the original oil derived from kerogens but retained inside asphaltenes over geological time. This method was applied to the study of Brazilian biodegraded crude oils.

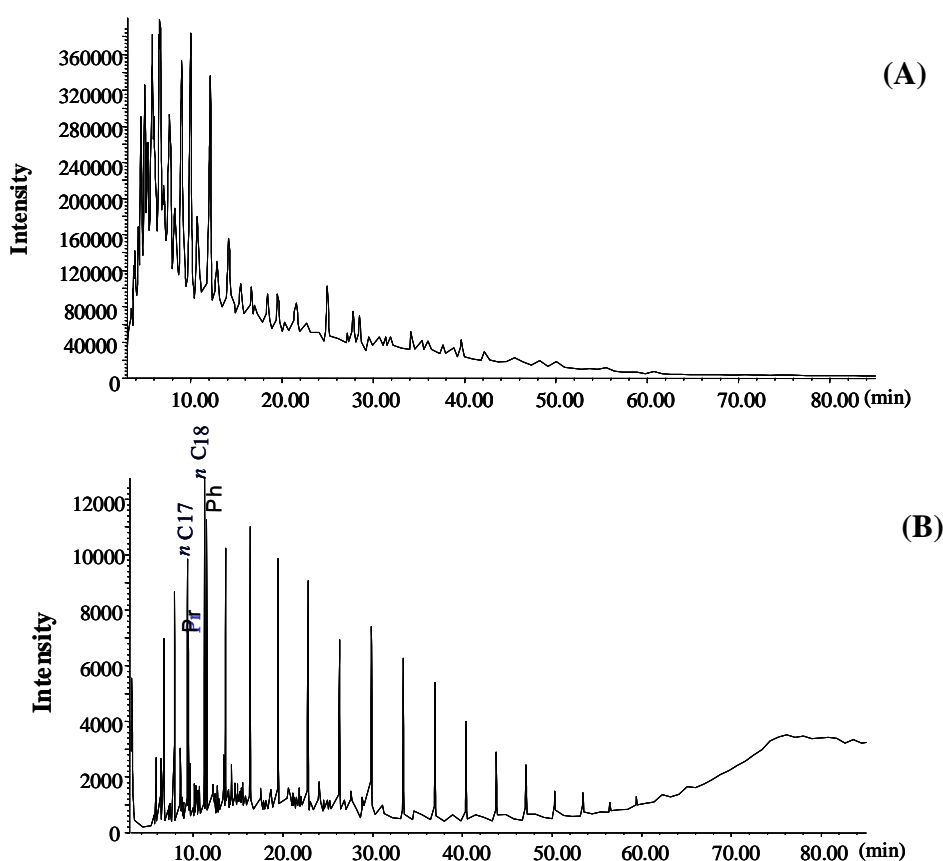


Figure 1. Gas chromatograms ( $m/z$  85) of the saturated hydrocarbons fractions from: (A) crude oil, (B) occluded products of the corresponding asphaltene.

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