THE BIORESISTANCE OF BOUND BIOMARKERS RELEASED FROM ASPHALTENES OF ONE SEQUENCE OF NATURALLY BIODEGRADED OILS

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Introduction

Asphaltenes are generally considered to be composed of condensed aromatic units and aliphatic hydrocarbon moieties, which are mainly derived from the cleavage of covalent bonds in kerogens at an early stage of petroleum generation (Snowdon et al., 2016 and references therein). Previous studies indicated that asphaltenes are more recalcitrant to secondary alterations. Therefore, the biomarkers bound in asphaltenes may provide new insights into organic geochemistry of crude oil, such as the origin, oil-oil or oil-source rock correlation of the oil (Behar et al., 1984).

Flash pyrolysis is one kind of pyrolysis approaches to characterizing the molecular composition and structure of asphaltenes. It is proved that flash pyrolysis is qualified to release bound biomarkers from crude oil asphaltenes. In our study, asphaltenes were separated from a set of tar sand bitumens which possess an identical source origin and similar thermal maturity but experience different degrees of biodegradation. On-line flash pyrolysis directly coupled with gas chromatography–mass spectrometry (Py-GC-MS) was conducted on these asphaltenes. This work nicely afford us an opportunity to study the influence of biodegradation on the bound biomarkers in asphaltenes.

Results

Figure 1a shows the m/z 217 mass chromatograms from GC-MS analysis of the saturate fractions of bitumens with various biodegradation degrees. With the onset of biodegradation (from LH-2 to LH-8), C₂₇–C₂₉ αααα20R steranes were degraded beginning at LH-5 (PM level 5; Peters and Moldowan, 1993), with preferential removal of C₂₇ homologue relative to C₂₈ and C₂₉. However, the GC-MS traces of m/z 217 of the asphaltene pyrolysates are quite similar to each other for all samples (Figure 1b). It suggests that the bound steranes released from asphaltenes by flash pyrolysis may be unaltered during biodegradation. In contrast to the free steroids in the biodegraded bitumens, the distribution of steroid compounds in the asphaltene pyrolysates show well-preserved regular steranes and trace amounts of diasteranes and C₂₇ αββ(20R + 20S) cholestanes. Such significant discrepancies may be due to the fact that steranes in the bitumens have suffered a maturation process and/or a biodegradation process while biomarker profiles in the asphaltene pyrolysates are considered to represent oils at an early and low thermal maturity stage.

Similarly, the free hopanes in bitumens were partly degraded at very heavy biodegradation stage (PM level 8) (figures not shown), with apparent removal of C₂₅ and C₃₀ hopanes. However, the bound hopanoids in asphaltene pyrolysates show very little alteration during biodegradation, and possess lower maturity than the free hopanoids in bitumens.
Figure 1 m/z 217 mass chromatograms of (a) saturate fractions of bitumens and (b) asphaltene pyrolysates released from bitumens with various degrees of biodegradation. The assignments of the different chromatographic peaks are listed in Table 1.

Table 1 Steroid compounds identified in Figure 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>No.</th>
<th>Compounds</th>
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<tbody>
<tr>
<td>1</td>
<td>5α(H)-pregnane</td>
<td>6</td>
<td>C_{28} 5α(H),14β(H),17β(H)-ergostane (20S)</td>
</tr>
<tr>
<td>2</td>
<td>5α(H)-homopregnane</td>
<td>7</td>
<td>C_{28} 5α(H),14α(H),17α(H)-ergostane (20R)</td>
</tr>
<tr>
<td>3</td>
<td>C_{27} 5α(H),14α(H),17α(H)-cholestan (20S)</td>
<td>8</td>
<td>C_{29} 5α(H),14α(H),17α(H)-stigmastane (20S)</td>
</tr>
<tr>
<td>4</td>
<td>C_{27} 5α(H),14α(H),17α(H)-cholestan (20R)</td>
<td>9</td>
<td>C_{29} 5α(H),14β(H),17β(H)-stigmastane (20R+20S)</td>
</tr>
<tr>
<td>5</td>
<td>C_{29} 5α(H),14β(H),17β(H)-ergostane (20R)</td>
<td>10</td>
<td>C_{29} 5α(H),14α(H),17α(H)-stigmastane (20R)</td>
</tr>
</tbody>
</table>

Conclusions

Although some routine biomarker parameters were obviously affected by biodegradation (steranes were altered beginning at heavy biodegradation stage and hopanes were degraded during very heavy to severe biodegradation), the bound hydrocarbon biomarkers released from asphaltenes through flash pyrolysis show the signature of early and low thermal maturity oils. They were almost unaltered during subsequent thermal maturation and biodegradation. This study also demonstrated that the biomarker parameters based on asphaltene pyrolysates can be used as very reliable indices for correlation studies, even when the oils were heavily–severely biodegraded.

References