Increasing the resolution of biodegradation scales with non-GC experiments


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Introduction

The evolution of organic geochemistry as an autonomous discipline owes acknowledgements to the advances in analytical technology that supported its keys achievements, e.g. gas chromatography (GC) and mass spectrometry. Nowadays, novel analytical techniques with unmatched resolution allow a quasi-molecule-to-molecule analysis of petroleum fluids (petroleomics), which can also offer nice tools for organic geochemistry assessments. One notorious example is the Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), whose analytical features immensely improved the understanding of petroleum compositional complexity, especially in the polar fraction.

Geochemistry assessments based on traditional oil biodegradation scales have the point of view of removed or modified substances (typically hydrocarbons) during the biodegradation process. One of their major drawbacks comes from their inability to classify mixtures (Bennett and Larter, 2008). New scales (i.e. ‘Manco’ scale, Larter et al., 2012) were developed to address these concerns by increasing the scale resolution, although still relying on results coming from traditional gas chromatography – mass spectrometry experiments. Nowadays, FT-ICR MS experiments offer the chance to analyze acid components produced by biodegradation processes. Therefore, new biodegradation metrics can be approached. The present study takes the next step towards a biodegradation scale based on class O2 compounds as analyzed by ultrahigh resolution and accuracy mass spectrometry, which was previously proposed by Vaz et al. (2013). It shows results for heavily biodegraded samples, explores petroleum system implications and shows indications of further developments needed.

Experimental

A set of 14 crude oil samples from the Llanos Orientales Basin, Colombia, were analyzed in a Solarix 9.4 T (Bruker Daltonics, Germany) apparatus using an electrospray ion source operated in the negative ion mode. Mass spectra (m/z 200-1000) were obtained from 200 scans, achieving a resolving power of 530,000 at m/z 400. Data were processed using the Composer software (Sierra Analytics, USA). GC-MS and GC-FID were also used to evaluate typical biodegradation parameters.

Results and Discussion

Whole oil chromatogram, demethylated terpane series (m/z 177) and 25NH/H30 information, when analyzed altogether, show very erratic biodegradation patterns among the samples. Many Llanos Orientales crude oils are composed of variable mixtures of early-charged biodegraded oils from Late Cretaceous source rocks and later charges of oils derived from Tertiary sections (Dzou et al., 1999). Therefore, traditional GC parameters are not sufficient to evaluate differences of biodegradation extent and mixture in these samples.

Previous studies used differences between double bond equivalent (DBE) profiles of class O2 compounds as the basis for two continuous biodegradation parameters, SA Index (∑DBE 1-6) and modified A/C Index (DBE 1 / ∑DBE 2-6), all obtained from FT-ICR MS experiments (Vaz et al., 2013). Briefly, the main effect of biodegradation on DBE profiles is the increase of relative intensities of mono- to pentacyclic saturated acids. In this study, a new sample set of highly biodegraded oils was very suitable to expand the scope of this biodegradation scale (up to 25NH/H30 ratio = 5.36 in m/z 191) (Figure 1).
One important feature arises from the full spectrum that this scale presents, whereby any pattern of oil mixture can be traced and compared to others. Oils with high SA Index values show some level of dispersion that demands more experiments. Nonetheless, these results ultimately suggest that the scale is ready for further testing in other petroleum systems.

The use of this scale in petroleum system studies can also be approached. Estimated impacts of both biodegradation and recharge rates are shown in Figure 2. In case of mixtures, less biodegraded oils have a lower impact on the resulting oil because of their lower acid content. Recharges of pristine oils would affect more the A/C than the SA Index since DBE 1 O2 species are slightly more abundant in them. Experimental efforts to check these and other assumptions are ongoing.

**Conclusions**

The use of high resolution mass spectrometry techniques to probe acid species offers new dimensions to solve common problems of biodegradation scales based on gas chromatography. In this study, the biodegradation scale based on class O2 compounds proposed previously is expanded with a heavily biodegraded crude oils sample set and has its features and impacts explored. The next steps toward a full acceptance would be proofs of its usefulness to petroleum system studies as well as correlations with physical properties, both of which are ongoing efforts.

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**References**