NEW PARAMETERS BASED ON O_1 CLASS DISTRIBUTION OBTAINED BY ESI(-) FT-ICR MS TO ASSESS BIODEGRADATION

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Introduction

Petroleomics by Electrospray Ionization (ESI) coupling to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) have been used to assess biodegradation extent, mainly involving the evaluation of O-classes, since the main changes occurred by biodegradation over polar compounds is in oxygen containing species (Rodgers et al., 2005; Kim et al., 2005; Vaz et al., 2014). The production and biodegradation of O-compounds follow a preferential order, and based on this some parameters were already proposed focusing on O_2 class, such as A/C ratio (acyclic to 2-4 cyclic O_2-species) showed by Kim et al. (2005) and SA Index (given by the sum of relative abundance of species with DBE1-6 for the class O_2) presented by Vaz et al (2014).

O_1 heteroatom class, on the other hand, have been less used to assess biodegradation than O_2 class, but can still provide important information about microbial degradation of petroleum. Kim et al. (2005) showed how the distribution of O_1 compounds changes with increasing biodegradation, with some trends observed, such as the diminishing of relative abundance of this species with increasing DBE. In this context, this study has used negative ion mode FT-ICR MS to evaluate the effects of biodegradation on O_1 class in a set of Brazilian crude oils with distinct levels of biodegradation.

The sample suit used in this work comprises 11 crude oils from the following Brazilian Basins: Campos (C02, C07, C12, C17); Santos (SA01); Potiguar (P01); Recôncavo (R02, R03, R04); and Unknown basins (U01, U06). This samples were prior classified in four levels of biodegradation, according Peters and Moldowan scale (Peters and Moldowan, 2005): R02, R04 and U06 with PM level 0-1 (non/very slight); SA01, P01, U01 with PM level 2-3 (slight/moderate); C02, C07, C12 and C17 with PM level 3 (moderate); R03 with PM level 5-10 (heavy/severe). To the FT-ICR MS analysis, the samples (2 mg) were previously dissolved in 1 mL of toluene and then diluted with 1 mL of methanol, containing 0.1% of ammonium hydroxide. Direct infusion ESI-MS in negative ion mode was performed and samples were analyzed by a 7.2T LTQ FT Ultra mass spectrometer (ThermoScientific, Bremen, Germany) with resolving power of 400,000 on 200-1000Da mass range.

Results

O_1 heteroatom class can provide valuable information concerning microbial degradation of petroleum. In general, O_1-compounds abundance decreases with increasing biodegradation (Kim et al., 2005). In this study it was also observed this trend, in which more biodegraded oil samples presented lower O_1 relative abundance (samples C02, C07, C12, C17, PM level 3), reaching to not detected O_1-compounds at heavy/severe levels of biodegradation (sample R03, PM level 5-10).

Generally, O_1-compounds in petroleum begin at DBE 4, likely corresponding to phenols or monoaromatic alcohols (Kim et al., 2005). In this study it was observed that to non/ slightly biodegraded oil samples the DBE 4 class (monoaromatic cores compounds) is the most abundant. However, in moderately biodegraded (PM level 3) oil samples DBE 5 is the DBE class most abundant.

Thought the robustness of A/C ratio calculated from O_2 class (Kim et al., 2005), it is still necessary more parameters to evaluate biodegradation. Therefore, it is proposed herein two new parameters using O_1 heteroatom class to assess biodegradation, the MA1 Index and MA2 Index, calculated by the ratio between DBE 4 over DBE 5 and DBE 7 of O_1 class, respectively. Figure 1 shows the good correlation of these parameters with A/C ratio, in which the coupling of them can be useful to monitor biodegradation. These new indexes are based on the change of DBE relative abundance distribution with increasing biodegradation, in which it can be observed a decreasing in relative abundance of DBE 4 class, since these phenolic and/or benzylic compounds are more readily degraded by microorganisms. According to Kim et al. (2005), this DBE 4 species are nearly absent in severely degraded oils. However, O_1-species with higher DBE values persist in more degraded oils, in which the DBE 5 and DBE 7 are, in general, more abundant to highly biodegraded samples.

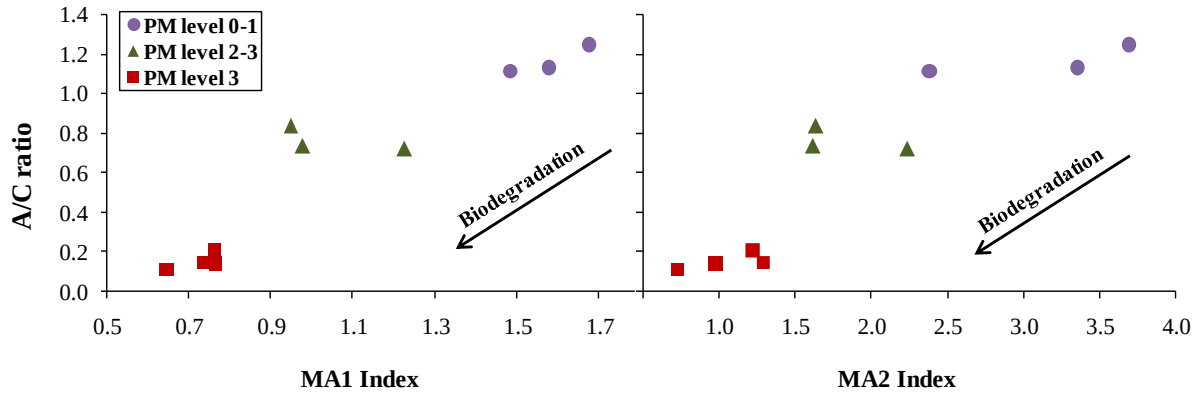

Figure 1 *A/C ratio coupled to new proposed parameters MA1 Index and MA2 Index to assess biodegradation using O_1 class by ESI(-) FT-ICR MS.*

Conclusions

Petroleomics by ESI(-) FT-ICR MS focused on O_1 heteroatom class has shown to be a useful tool to classify Brazilian oils in level of biodegradation, using the new proposed parameters MA1 Index and MA2 Index.

References

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