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Effect of artificial maturation at different types of potential source rocks: Focusing on polar compounds evaluation by FT-ICR-MS technique

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Introduction

Generation and expulsion of oil from organic sedimentary rocks have been achieved in the laboratory by a technique known as hydrous pyrolysis. This technique maintains a liquid water phase in contact with organic sedimentary rocks during their heating at subcritical water temperatures. The expelled oil accumulates on the water surface and contains measurable hydrocarbons. The pyrolysate expelled by this technique is more closely analogous to crude oil expelled in the natural system than that techniques that employer carrier gases, cryogenic traps, or solvent extraction methods. In hydrous pyrolysis systems, it was observed that the pyrolysis products from kerogen or lignite degradation are dominated by heteroatomic compounds, called ‘NSOs’, of very high molecular weight (Lewan 2002).

Experimental

A Type I kerogen from Tremembé Formation, Taubaté Basin, Brazil and Type III from Mamu Formation, Benin Flank Basin (Nigeria) was object of this study. For type I kerogen the hydrous pyrolysis experiments were performed at different Temperatures (T = 300, 310, 320, 340, 350, 355 e 360°C) and fixed time (t = 72 h) giving up a total of seven samples of expelled oil (Binotto et al 2010). Eight samples of expelled oil from Type III kerogen was obtained fixing the T(340°C) and varying the hydrous pyrolysis time t (1, 2.5, 5, 10,20,50,100 e 200)h. The expelled oil samples (~ 1 mg) were dissolved in 10 mL of toluene, and 0.5 mL of the resulting solution were transferred to a 1 mL vial and diluted with 0.5 mL of methanol containing 0.2% ammonium hydroxide. The general ESI conditions were as follows: capillary voltage of 3.10 kV, tube lens -100 V and flow rate of 3 µL min-1. Ultrahigh resolution MS was performed using a Thermo Scientific 7.2 Tesla Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT Ultra, ThermoScientific, Bremen, Germany). A scan range of m/z 200–1000 was used, and one scan of 100 microscans was collected in each run.

Results and Discussion

The ESI (-) FT-ICR mass spectra and the class profile (Figure 1) of original extracts of Type I and III kerogen show significant compositional differences. The Type III kerogen presents a distribution of low molecular weight compounds that not checked for Type I, which have high mass molecular profile Similar results were reported by Salmon et al (2011) in the studies of molecular characterization by ESI FT-ICR (-) MS of sample of kerogen Type I from Green River formation. The extract of Type III is characterized by a greater diversity of classes of heteroatom-containing compounds, while kerogen Type I show basically oxygen and nitrogen-containing compounds.

To achieve a better understanding of the polar components composition at expelled oil, samples from kerogen Type I and Type III were selected and their hydrous pyrolysis products at different temperatures were analyzed by negative-ion electrospray Fourier transform ion cyclotron resonance mass spectrometry (ESI(−) FT-ICR MS). FT-ICR MS provides significant mass resolving power, m/ mΔ50%> 200,000 (mΔ50% is the mass spectral full peak width at half-height), from 225 <m/z< 1000, enabling the differentiation of compounds with the same nominal mass but differing exact masses with an accuracy within < 0.3 ppm. ESI is the most commonly used ionization technique for liquid samples, and it selectively ionizes nonvolatile acidic and basic compounds in crude oils and their related derivatives without the interference of nonpolar compounds, such as hydrocarbons.

The changes observed on NSO profile and in the distribution of the series (DBE- double bond equivalent) within a specific class during hydrous pyrolysis in different conditions are illustrated in Figure 2.

Figure 1. ESI (-) FT-ICR mass spectra and acidic NSO classes profile of extracts of two different kerogen type
The heteroatom class distribution for the oils obtained from Type I kerogen at different temperatures and hydrous pyrolysis time (t) of 72 h and the comparison of O Class DBE distribution from oils generated during Exp1 in two extreme temperatures (T = 320 and 360°C) are presented. It is showed that the relative abundance of O2 class increases while O3 and O4 decreases with temperature increasing. The changes observed for O-containing compounds are related to a sequence of dehydration and/or decarboxylation reactions. The changes observed in DBE distribution of O class show an increase on the relative intensity of series with higher DBE values for the oil generated at higher temperature. These series, DBE 7 to 17, correspond to compounds with a larger number of aromatic and naphthenic cores. These results confirm the well-known occurrence of aromatization reactions, justifying the observed shift to higher DBE values.

Conclusions
The NSO composition of two kerogen (Type I and III) revealed by ESI(−) FT-ICR MS shows significant differences. Also, compositional changes were easily observed on oils generated during hydrous pyrolysis experiments in different temperature and time conditions. These results strongly encourage the application of FT-ICR MS as an analytical tool for kinetic studies monitoring during artificial maturation experiments.

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