Changes in oil properties with the advance of thermal maturation induced by hydrous pyrolysis for a Brazilian source rock containing a Type-I kerogen

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Introduction and goal
To understand the thermochemical transformation of kerogen with increasing maturation and the compositional variation of the generated products, the petroleum industry has used laboratory pyrolysis experiments to artificially mature source rocks at relatively high temperatures and short times under an inert atmosphere. Because of the use of several pyrolysis conditions, such as open or closed system, hydrous or anhydrous and isothermal or nonisothermal pyrolysis, significant differences are observed in the generated petroleum products. However, the composition of oils generated and expelled in hydrous pyrolysis are the closest to that of natural oils (Lewan, 1997; Ruble et al., 2001; Lewan et al., 2006), and therefore, provide the best method to evaluate changes in oil properties with thermal maturity.

This research investigates changes in expelled oil generated by hydrous pyrolysis from an immature organic-rich lacustrine source rock (TOC=28.8%; HI=892 mg HC/g TOC; 0.3%Ro) of Aptian age from the Araripe Basin (NE-Brazil). The tested sample is representative of a Type-I kerogen and can be considered a reasonable analog for Brazilian lacustrine source rocks of Lower Cretaceous age, which are responsible for most of the oil generated in the Brazilian continental margin.

Analytical Methods
The hydrous pyrolysis experiments were conducted under isothermal conditions at twelve different temperatures for 72 hours (280, 300, 310, 320, 325, 330, 340, 345, 350, 355, 360, 365°C) and at 310, 325, 340, and 355°C for different times (e.g., 12, 24, 30, 36, 48, 72, 96, 104, 120, 132 hours) to simulate the full range of petroleum generation from early bitumen generation to maximum oil generation.

Generated gases were characterized by molecular composition including C1-C6 saturated and unsaturated hydrocarbons, H2S, CO2, O2, N2, He and Ar. The expelled oils were characterized by their bulk properties (sulfur content, API gravity, stable carbon isotopes and SARA fractions) and molecular properties (alkane distribution and biomarker signatures). Product yields in mg/g TOC and gas/oil ratios (GOR m3/m3) were calculated for each experiment. Based on the maximum expelled oil yield at 360°C for 72h, the transformation ratios (TR) for generation of expelled oil were determined for all the experiments. Physico-chemical properties of expelled oils were evaluated in a function of TR (Fig. 1).

Results and Discussion
The petroleum yields (oil + hydrocarbon gases) increase linearly with the advance of transformation ratio at a maximum of 728.23 mg/g TOC. The hydrocarbon gases (C1-CS) generated at the oil peak represent 9% of total (Fig. 1A). The beginning of oil generation stage corresponds to 0.2TR, when the bitumen is effectively decomposed (320-325°C).

In general, the geochemical results indicate that there are some changes in bulk parameters of the expelled oils, mainly related to API gravity, SARA fractions, and whole-oil stable carbon isotopic composition (δ13C). The molecular properties like the distribution of n-paraffins and isoprenoids also change systematically with increasing thermal maturation (Fig. 1B).

However, relatively small variations are observed in gas/oil ratios. GOR initially decreased from 500 to 80 m3/m3 and then remained essentially constant until the oil peak. The high GOR values occur during early bitumen generation at the onset of oil generation (Fig. 1C). Similar trends were obtained by Lewan and Henry (2001) for different types of kerogens (Type-I, -II and -IIS) during the oil generation by hydrous pyrolysis.

Figure 1. Relationship between the geochemical parameters of expelled oils generated by hydrous pyrolysis with their transformation ratios. Yields of expelled oil and hydrocarbon gas are given in mg/g of original TOC (A), molecular ratios (B), and gas/oil ratios in m3/m3 (C).

Variations in the API gravity ranging 22° to 32° show a complex relationship with transformation ratios. As expected, increasing API gravities correlate with increasing saturates and decreasing asphaltenes (Spigolon et al., 2013). Sulfur contents ranging of 0.82 to 1.55 wt% and systematically decrease with the advance of TR. Stable carbon isotope composition (δ13C) of whole oils...
show a 12C depletion with increasing transformation ratio from -30.65‰ for the low temperature (280°C) to -28.48‰ for the high temperature (365°C) for 72 hours.

Although the results show pristane/n-C17 and phytane/n-C18 ratios decrease with increasing transformation ratios, the pristane/phytane ratio remains nearly constant (Fig. 1B). During oil generation, the concentration of Stigmastane in the expelled oils decreases with increase transformation ratio and is associated with low concentrations of 3-4 Methyl(di)amantanes. At maximum oil generation (360°C/72h), the concentration of Stigmastane is zero, and the concentration of diamandoids is still very low, which indicates no oil cracking to gas according to Dahl et al. (1999).

Final Remarks

In the case of Type I kerogen-bearing source rock, bulk properties (API gravity, δ13C, sulfur content, SARA fractions) of expelled oils from the hydrous pyrolysis experiments show some systematic changes during the oil generation stage. Among molecular ratios, pristane/n-C17 and Phytane/n-C18 are strongly controlled by the thermal maturation and show a consistent behavior with the advance of transformation ratios during the oil generation stage. As indicated by gas/oil ratios, biomarkers, and diamandoids, no oil cracking to gas was observed under the experimental conditions employed.

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References


