COMPOSITIONAL KINETICS FROM OPEN-SYSTEM PYROLYSIS AND THEIR EFFECTS ON PETROLEUM SYSTEMS ANALYSIS : THE RECÔNCAVO BASIN CASE STUDY.

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Compositional kinetic parameters obtained for primary cracking of kerogens constitute one of the main basis for the simulation of the quantity, quality and timing of petroleum generation. These parameters are essential for the comprehension of the petroleum charge evolution in mass balance studies.

The spacial distribution of petroleum composition generated within a given source rock unit is usually associated with its thermal maturity gradient. However, part of this variability may also be due to differences in kinetics and petroleum potential composition. Unfortunately, data relative to this latter issue are rarely available for basin modeling studies, where at best only one set of compositional kinetic parameters is used for each source rock unit, regardless of lateral and vertical organic heterogeneities. In order to better assess the effect of organic matter heterogeneity within the same source rock on the petroleum compositional mass balance, an extensive kinetic study was performed in the Early Cretaceous lacustrine basal section of the Recôncavo Basin, Brazil. Twelve samples from two recognized source rocks, theTauá and Gomo members from the Candeias Formation, were selected along the three principal tectonic domains: the southern, central and northeastearn compartments of the basin.

Kerogen concentrates were prepared from each selected sample, then characterized by elemental analysis and Rock Eval analysis. Bulk and compositional kinetics were derived from open system experiments, according to the methodology suggested by Lorant et al. (2003). Compositional mass balances included the following chemical classes : CH_4; C_2-C_5; C_6-C_{14} Sat, C_6-C_{14} Aro, C_{14+}Sat, C_{14+}Aro and NSO.

While both Tauá and Gomo members were deposited in the same lacustrine environment, differences in H/C and O/C are observed among the selected kerogens (Figure 1), mostly due to the local oxidation of organic matter during deposition. Regarding bulk kinetics of kerogens, both source rocks were quite homogeneous (Figure 2), exhibiting a quasi-mono-energetic behavior with a main activation energy around 54 kcal/ mole, for frequency factors in the range $7.7 * 10^{13}$ s^{-1} to $1.4 * 10^{14}$ s^{-1} . In details, however, oxidized

facies were slightly more reactive in the early stages of petroleum generation than other kerogens (see curves 1, 2 and 3 in Figure 2). In fact, the greatest differences among kerogens from each structural domain and source rock units were observed for the composition of pyrolysis effluents, especially the NSO content and the Sat/Aro ratio in the C_{14+} fraction. The magnitude of these variations is illustrated in Figure 3, for the production of hydrocarbons from the Tauá source rock at the Southern Compartment . For this simulation, the frequency factor obtained for bulk kinetics was adopted for all chemical classes.

Another interesting result from this work was the relatively high abundance of NSO compounds in the effluents from primary cracking. Such a feature was already observed in open pyrolysis C_6^+ effluents obtained from other kinds of kerogens (Lorant et al., 2003). Hence, petroleum compositions predicted from primary cracking kinetics based on open system data were significantly different from those of trapped petroleum in the Recôncavo Basin, which is 50 to 90% enriched in saturates (Gaglianone & Trindade, 1988; Penteado, 1999; Penteado & Behar, 2000; Aguiar & Penteado, 2004). This discrepancy can be explained by the efect of retention of most heavy compounds (NSO) within source rocks, which undergo an early secondary cracking during thermal maturation. Consequently, the next step to correctly reproduce the petroleum compositional mass balance in the Recôncavo Basin will be the determination of retention coefficients for NSO compounds, as well as class-specific secondary cracking parameters in the petroleum system simulations as proposed by Penteado (1999).

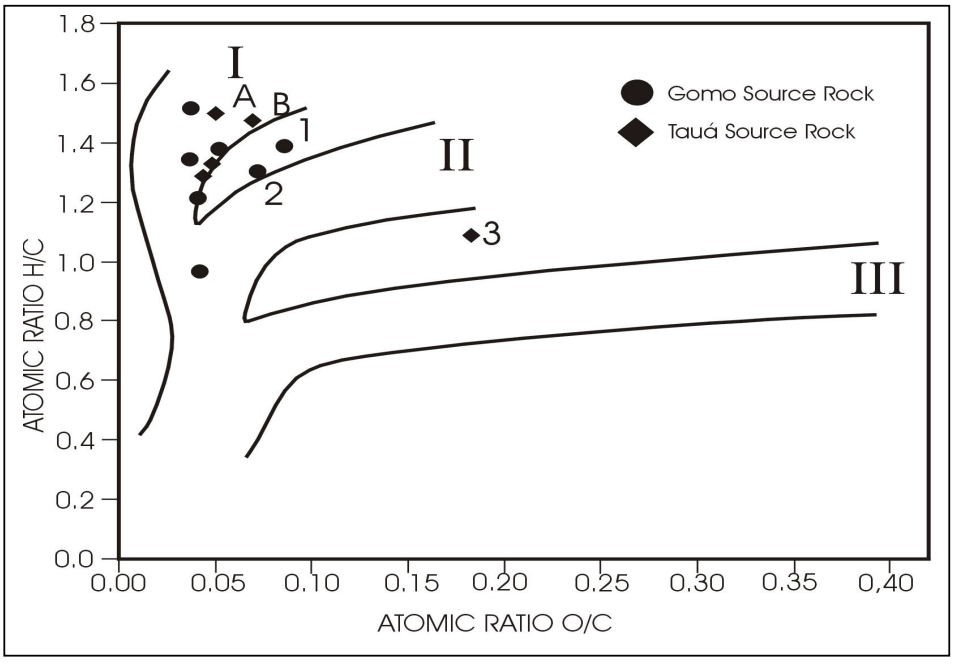

Figure 1 – Position of immature kerogens from the Gomo and Tauá source rocks in a van Krevelen diagram. Oxidized samples are identified by numbers. Tauá samples displayed in Figure 3 are identified by letters.

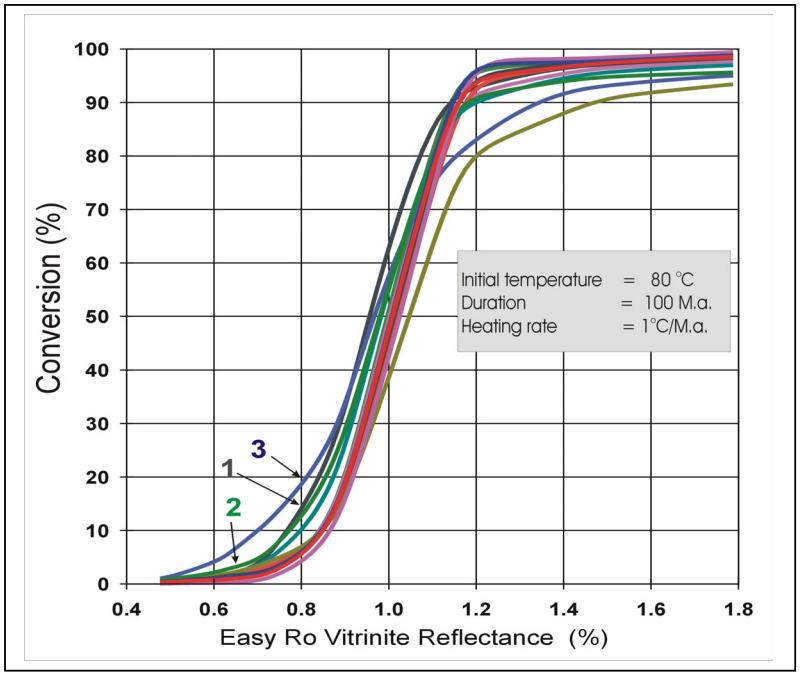

Figure 2 – Simulated transformation ratios for primary cracking of kerogens from the Recôncavo Basin.

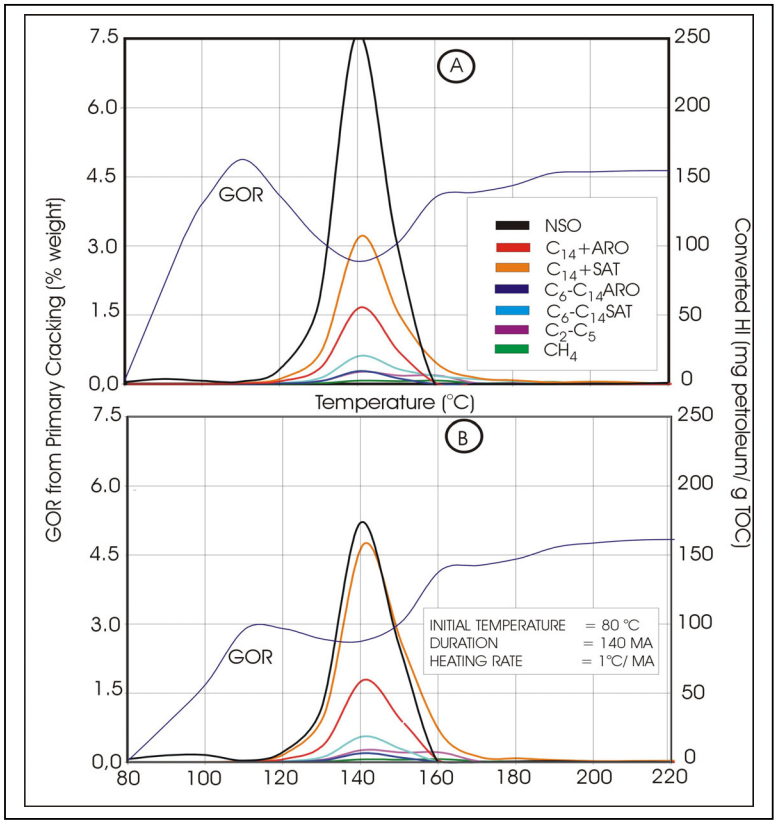

Figure 03 – Rates of petroleum components generation based on compositional kinetics of two samples from the Tauá Member in the Southern Compartment of the Recôncavo Basin.

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