

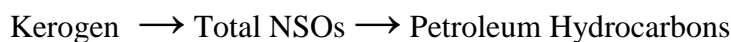
## ROLE OF NSO COMPOUNDS IN PRIMARY CRACKING AND ON KINETIC PARAMETERS DETERMINED BY OPEN- AND CLOSED-SYSTEM PYROLYSIS

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The study of kerogen cracking in either open or closed system enables to understand (i) the main steps of kerogen thermal decomposition and (ii) the mass balances obtained in the two systems. Results show that in both systems, NSOs (i.e., resins and asphaltenes) are major compounds generated from kerogen cracking. In closed-system pyrolysis, these compounds are generated earlier than the main phase of hydrocarbon generation. Thus, the following primary kinetic scheme was established:



This new kinetic scheme takes into account kerogen cracking in both closed- and open-system pyrolysis as shown on Figure 1.

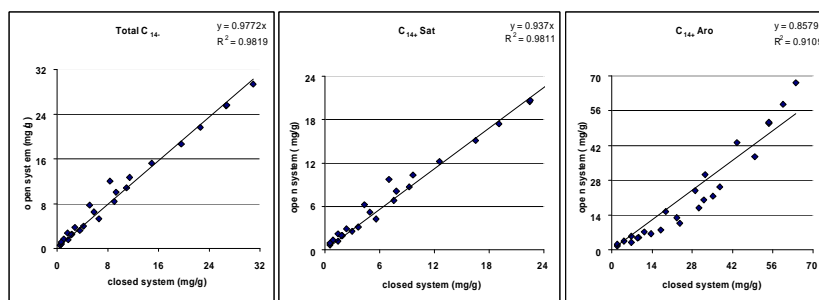
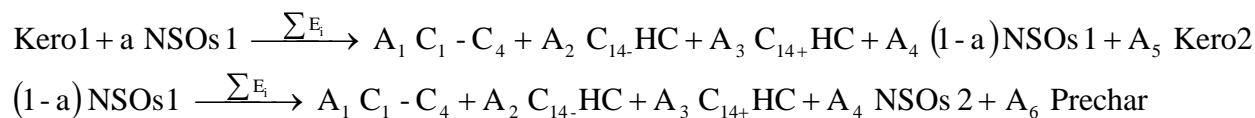


Figure 1. Comparison of yields for different organic classes obtained using kinetics from open system data with those recovered in closed system experiments for Type II kerogen.

In open-system pyrolysis (e.g., Rock Eval), due to the very high content of the NSOs produced at the onset of kerogen cracking, a major part of the generated NSOs are not swept away by the carrier. The NSOs, which cannot be vaporized because of their high molecular weight, remain in the pyrolysis chamber and undergo secondary cracking with increasing severity. Consequently, the kinetics obtained in open-system pyrolysis is a combination of kerogen cracking and the decomposition of NSOs. Thus, two successive reactions might be taken into account for the total conversion of both the kerogen and the total generated NSOs in open-system pyrolysis:



The two-step concept was initially observed in the oil-shale retorting experiments of the early and mid-1900s. Early quantification of the timing of petroleum formation by Tissot and Welte (1984, p. 586) recognized the two steps but for computational reasons combined them into one (i.e., kerogen to oil). Subsequent controversy and discussion has occurred over kinetic parameters based on products from a two-step concept that is readily recognized in hydrous pyrolysis and a combined one-step concept that is typically advocated in open-system nonhydrous pyrolysis (Lewan et al., 2006; Lewan and Ruble, 2002; Lewan, 1998; Burnham, 1998; Ruble et al., 2003; and Curry, 2003). A major implication of this study, based on closed nonhydrous pyrolysis, is that it is critical to engage the two-step concept in evaluating kinetic parameters for natural oil formation.

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