

## OPEN VERSUS CLOSED-SYSTEM PYROLYSIS KINETICS FOR PRIMARY CRACKING IN SOURCE ROCKS

François Lorant<sup>1</sup>, Françoise Behar<sup>1</sup>, Henrique L. de B. Penteadó<sup>2</sup> & Luiz C. da S. Freitas<sup>2</sup>

<sup>1</sup> Institut Français du Pétrole, 1-4 avenue de Bois Preau, 92852 Rueil-Malmaison, France

<sup>2</sup> Petrobras R&D Center, Cidade Universitária, I. Fundão, 21949-900, Rio de Janeiro, Brazil

**Introduction** - The formation of oil and gas within source rocks is usually represented in basin simulators by a set of empirical rate equations, each of them involving three parameters: two kinetic parameters (the activation energy,  $E_a$ , and the frequency factor,  $A$ ), that both control the temperature-dependency of the reaction rate via the Arrhenius law, and a stoichiometric coefficient that controls the contribution of each reaction to the petroleum potential of the source rock. These parameters, which are source-rock specific, need to be calibrated from case to case. This can efficiently be achieved by means of artificial maturation experiments carried out under controlled temperature and pressure conditions on immature source rock or kerogen samples. Then, assuming bulk rate equations, corresponding kinetic and stoichiometric parameters are tuned to account for results from laboratory experiments, and applied as such in basin simulation. However, an important limitation of this approach is that the values thus assigned to the empirical parameters, and subsequently the uncertainty in the oil and gas windows prediction, directly depend on how far experimental data obtained at high temperatures are representative of geochemical processes that occur in sedimentary basins under lower temperatures.

Experimental simulations of primary cracking can be conducted under various conditions: in open system (*e.g.*, Rock-Eval technique), in dry closed reactors (gold tubes, MSSV: *e.g.* Horsfield et al., 1989), or in closed reactors with addition of water (hydrous-pyrolysis, Lewan, 1994). Unfortunately, these different pyrolysis techniques are not always consistent with each other. For instance, Monthieux (1986) compared open (Rock-Eval), closed (MSSV) and confined (gold tubes) systems for a series of homogenous coals, using various types of measurements to characterize their level of thermal maturation (*i.e.*, atomic analyses, optical microscopy, carbon isotopes, IR spectrometry, hydrogen index, biomarkers). This work showed that natural coalification is better reproduced by high-pressure closed-system pyrolysis techniques, eventually with addition of water, while experiments performed at lower pressure in quartz tubes (MSSV-like techniques) and open-system pyrolyses deviate more often from natural maturation trends. Behar et al. (2003) confirmed some of these conclusions in a similar study performed on an immature coal. Differences in NSO potentials of kerogens between open and closed systems were also described by Behar et al. (1997), and Koopmans et al. (1998) pointed out inconsistencies in the biomarker content of oils

artificially generated in hydrous and anhydrous closed systems. More recently, Lewan and Ruble (2001) reported discrepancies in bulk petroleum formation rates between hydrous pyrolysis and Rock-Eval experiments. However, when looking at the compositions of pyrolysis effluents, it seems that differences between open and closed-system experiments (with or without addition of water) do not affect all chemical fractions with the same magnitude. For instance, Lorant and Behar (2002) showed that the artificial simulation of gas formation is very sensitive to the experimental conditions (*i.e.*, open versus closed system), whereas experimental data of Vinge et al. (2003) suggested that the generation of light oil was not.

In summary, different pyrolysis conditions yield different results, especially when comparing open-system with closed-system techniques. Various petroleum geochemistry laboratories, including IFP since the work of Monthioux (1986), consider that moderate-to-high pressure closed-system pyrolysis experiments constitute the best approach to artificially simulate natural maturation processes. Unfortunately, these experiments are relatively difficult to handle compared to open-system techniques (recovery procedures, data interpretation, etc.) and are also much more expensive and time-consuming. Therefore, closed-system data cannot be generated massively. A way to overcome this limitation would be to entirely generate experimental data from open-system techniques, then to correct both mass balances and reactions rates in relation to closed-system pyrolysis. In order to estimate the feasibility of such an approach, it is necessary (i) to set up a protocol for systematically comparing open and closed-system pyrolyses in terms of kerogen transformation ratio and effluents composition, and (ii) to check if the shift between open and closed systems kinetics is always the same or varies from one kerogen to another.

**Methodology** – The two questions above were addressed by conducting two series of pyrolysis experiments on 8 kerogen concentrates isolated from type I and type II Brazilian source rocks of different ages. In the first series, the rate of conversion of kerogen into hydrocarbon chemical classes was measured as a function of time and temperature in open-system pyrolysis (Rock-Eval based kinetics), according to the protocol proposed by Lorant et al. (2003). Compositional mass balances included the following fractions: C<sub>1</sub>, C<sub>2</sub>-C<sub>5</sub>, C<sub>6</sub>-C<sub>14</sub>Sat, C<sub>6</sub>-C<sub>14</sub>Aro, C<sub>14+</sub>Sat, C<sub>14+</sub>Aro and NSO. In the second series of experiments, the same kerogens were heated under 100 bars in sealed gold tubes filled with nitrogen gas. Pyrolysis effluents were recovered, fractionated and quantified according to the same procedures as those used for open-system experiments. Moreover, for both pyrolysis systems kerogens were submitted to the same thermal conditions, *i.e.*, 225, 250, 275, 300, 325 and 350°C for 3 hours. These experimental conditions were calibrated in order to limit the effects of secondary cracking in closed system. Under such conditions, mass balances from open and closed systems could be compared directly.

**Results** – For both experimental systems, kerogen transformation ratios were calculated by measuring the remaining petroleum potential of all residual kerogens (*i.e.*, extracted pyrolysis residues) via Rock-Eval analysis:  $TR = (100 - w) S_2^r / S_2^0$ , where  $S_2^0$  and  $S_2^r$  are respectively the petroleum potentials of the initial and the residual kerogens, and  $w$  is the kerogen weight loss (in wgt %). In agreement with Lewan and Ruble (2001), we observed that the conversion of kerogen into hydrocarbons was systematically much faster in closed system than in open system (Figure 1). Moreover, this shift appeared to be reproducible from one sample to another, *i.e.*, relationships between open and closed-system transformation ratios straightforwardly followed the same pattern. Assuming a single 1<sup>st</sup>-order reaction, transformation ratios were numerically modeled for different shifts in activation energies, and then compared to experimental data (see curves for different  $E$  values on Figure 1). According to this simple calculation, we estimated that the bulk conversion of kerogen in closed system could be approximated by simply switching activation energies derived from open-system experiments by about -3 to -2 kcal/mole. This rule appeared to be valid whatever the source rock sample.

Regarding compositional mass balances, the following trends were observed systematically. Firstly, significantly more gas was generated in closed system compared to open system, especially more methane. Secondly,  $C_{6+}$  yields were comparable in both systems, although liquids recovered in open system were slightly depleted (by ~ 10%) in NSO compounds compared to those generated in the gold tubes. The proportions of aromatics were comparable, while more aliphatics were formed in open system. These results were consistent with the idea that some secondary cracking of heavy compounds occurs during open-system pyrolysis of kerogen. However, this process, the extent of which appeared to be quite limited, did not account for the differences in gas generation, and was not enough to explain the substantial shift in kerogen conversion rates previously commented.

To conclude, this study showed that systematic differences exist for kerogen cracking in open and closed systems. Once calibrated, these trends might be used to correct open-system data relative to closed-system pyrolysis. However, beyond this practical issue, the origins of these discrepancies are not clearly understood and would deserve further research.

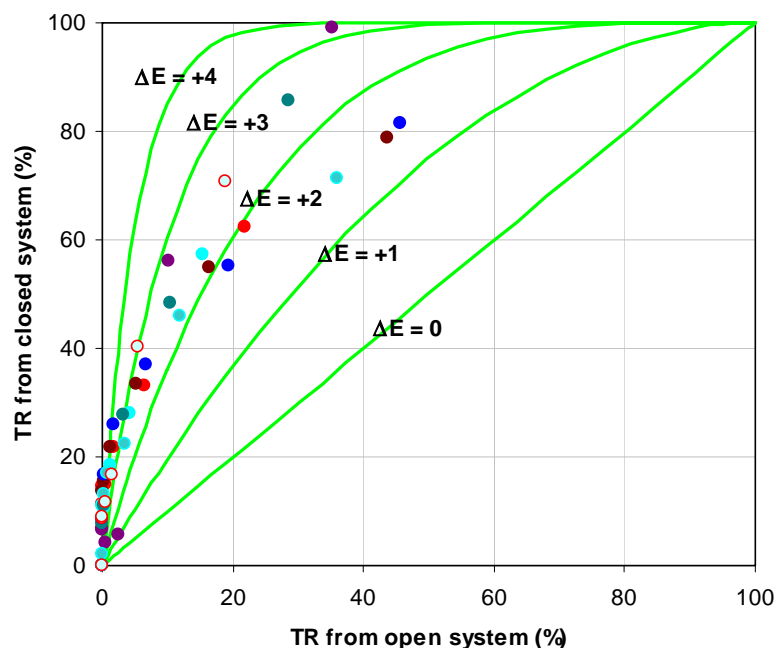


Figure 1 – Comparison of kerogen transformation ratios in open and closed systems for 8 kerogen concentrates (colored series).  $E$  = activation energy difference between open and closed-system kinetics in kcal/mole.

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