

## **THERMAL STABILITY OF SOURCE ROCK AND OIL ASPHALTENES : COMPARISON WITH KEROGEN KINETICS IN OPEN SYSTEM PYROLYSIS**

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The aim of this work is to determine kinetic parameters during the thermal cracking of asphaltenes in laboratory conditions. Artificial maturation of asphaltenes can be performed either in open system for comparison with kerogen cracking or in closed system for comparison with oil cracking. Therefore, it was checked that asphaltenes kinetics are similar in both pyrolysis systems. Then, a standard Type II kerogen was artificially matured in closed system in order to cover a range of conversion from 10 to 90 %. Both the residual kerogen and the generated asphaltenes were recovered in each experiment and submitted to open pyrolysis in order to derive their bulk kinetic parameters : the distribution of activation energy and the frequency factor. Results show that the global rate constant for asphaltenes cracking is systematically faster than that of the associated kerogen. It is worth noting that global kinetics derived from open system experiments, are based on the conversion defined by a partial amount of the generated products. Indeed, the formation of char, which participates to the conversion of kerogen is not taken into account. Therefore, the global conversion might substantially be modified if char formation is much faster or slower for kerogen and asphaltenes. For kerogen cracking, it is very difficult to specifically determine the amount of char because the char formation from secondary cracking of asphaltenes, (Behar et al., 1991, 1997) may overlap kerogen cracking. Fortunately, it is not the case for asphaltenes; thus, closed pyrolysis experiments were carried out in order to derive kinetic parameters for the total asphaltenes conversion and resulting char formation. Following this research strategy, it is possible to calculate the global asphaltenes kinetics as follows :

- decrease of the amount of asphaltenes in closed system experiments
- sum of the char formation kinetics obtained in closed system experiments with generated products kinetics in open system.

Results show that the two possibilities lead to very similar results. This proves that kinetic parameters obtained either in open or closed system for asphaltenes cracking are similar and confirms that asphaltenes decompose earlier than kerogen in open system.

Consequently, during primary cracking, when kerogen is submitted to open system pyrolysis, it is likely that most of the asphaltenes are decomposed at the same time : thus, the effluents include the pyrolysis products from both kerogen and asphaltenes decomposition. When kinetic parameters are extrapolated to geological conditions, asphaltenes undergo secondary cracking before the migration threshold is reached, and depending on the time necessary for starting primary migration, the expelled fluid will be more or less depleted in asphaltenes.

However, in theory, one may expect that product generated from a reactant is more stable than the reactant itself, thus it is necessary to check these preliminary results. These results may re open the debate for the choice of pyrolysis system for artificially mature kerogen as already discussed by Lewan and Ruble (2001).

In a second step, kinetic parameters of Type II conventional oil asphaltenes were also determined in open and closed pyrolysis system and compared to those of kerogens and asphaltenes artificially matured in closed system. For oil asphaltenes, bulk rate constant are slower than immature asphaltenes generated from kerogen but similar to those associated to kerogen having reached a transformation ratio higher than 50 %. This confirms that expelled asphaltenes from source rocks have already undergone secondary cracking before expulsion and are good indicators of the maturity stage of the corresponding kerogen when the main phase of expulsion occurs. However, kinetic parameters of asphaltenes are different when determined in open or closed pyrolysis system. This observation has direct implication for the extrapolation to geological conditions : if those determined in closed system lead to consistent prediction, those obtained in open system shifts the asphaltenes window to too high temperatures.

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