

**IMPORTANCE OF REACTION MECHANISMS
IN THE KINETIC EXTRAPOLATION OF HYDROCARBONS MATURATION
EXPERIMENTS TO GEOLOGICAL RESERVOIR CONDITIONS**

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Deep seated, high pressure- hot reservoirs ($T > 200^{\circ}\text{C}$, pressures up to Kbars) are among exploration targets for the petroleum industry. Yet, such unconventional reservoirs present high exploration risks and prediction of the nature and physico-chemical state of their fluids is important. One aspect of this problem is to be able to properly reconstruct the evolution of hydrocarbons in such reservoirs during basin evolution. One approach is to study the thermal stability of petroleum and hydrocarbons by means of laboratory experimentation. Yet, the use of temperatures higher than in nature ($T < 250^{\circ}\text{C}$) and short times (few hours to several weeks) necessitates the use of kinetic models to extrapolate experimental results to geological conditions

We are presenting the advantage of using kinetic modelling with explicit chemical reaction mechanisms to understand the behavior of hydrocarbon mixtures during thermal cracking at laboratory and geological time-temperature-high pressure conditions. Our approach is based on the construction of an evolutive kinetic model based on elementary radical reactions. These reactions are universal to any study of hydrocarbons pyrolysis. Yet high pressure experimentation data are scarce, this is why we conducted numerous high pressure experiments on pure hydrocarbons as well as on their mixtures. For each experiment we compute reaction mechanisms networks which allow the construction of a kinetic model. When the model describes correctly the experiments all important reactions were considered and the kinetic model is validated. The model can be extended with the addition of any new experiments on new reactants. Doing so, cross-reactions between hydrocarbons are taken into account. This model, based on the specific properties of elementary radical reactions can then be extrapolated to geological time-temperature conditions: this is fundamentally different from the extrapolation based on Arrhenius first order rate laws, very commonly applied in geochemistry.

Our results reveal the major kinetic effect of the presence of aromatic hydrocarbons on the thermal stability of alkanes at geological time-temperature conditions. This can be

explained by specific effects related to 1) the structure of the aromatic hydrocarbons (for instance, the presence and size of alkyl substituents on the benzene ring leads to major different reaction pathways), 2) temperature range at which the reactions are considered (change in chemical selectivity) 3) influence of pressure on reaction mechanisms.

Very significant deviations of the behaviour of the hydrocarbons mixtures between experimental and geological time-temperature conditions are evidenced which can absolutely not be predicted by the Arrhenius first order kinetic models. Not taking into account chemical selectivity with temperature drop between experiments and reservoir conditions will lead to major misinterpretation. Finally we will illustrate the use of our model to the prediction of the thermal stability of natural hydrocarbon mixtures at reservoir time-temperature-pressure conditions.