

KINETIC PARAMETERS OF THERMAL CRACKING OF SIMPLE HYDROCARBONS: FROM LABORATORY TO GEOLOGICAL TIME-TEMPERATURE CONDITIONS

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Introduction

The prediction of the composition of petroleum, which is submitted to thermal cracking during million years, requires a good knowledge of the reaction kinetics, particularly in deeply buried reservoirs, at high pressure (100-1000 bar) and high temperature (> 200°C). The apparent kinetic parameters (apparent frequency factor A and apparent activation energy E_a) are commonly determined from laboratory pyrolysis at high pressure of crude oils or pure hydrocarbons. The geological time is compensated by higher temperature (350-450°C) than those encountered in reservoir. The global kinetic models derived from experimental results are then computed using geological time-temperature conditions. Due to the complexity of the chemical composition of crude oils, it is easier to derive reliable kinetic parameters from pyrolysis of pure hydrocarbons.

In order to determine precisely the main reaction pathways and obtain reliable predictions, detailed kinetic models of the thermal cracking of pure hydrocarbons or simple mixtures can also be setup. These detailed kinetic models consist of mechanisms made of elementary steps (mainly free-radical reactions) with their fundamental kinetic parameters. That is why they can be extrapolated in the range 100-1000 bar and 150-450°C: the main reaction pathways and the fundamental kinetic parameters remain unchanged. The main advantages of these models are their precision and the possible extrapolation, and the main drawback is the size of the model (several hundred even thousand reactions) which prevents their integration in a basin model.

The study presented here aims at testing if the apparent kinetic parameters are constant in the range 200-400°C, at high pressure, i.e. if the apparent kinetic parameters determined at 400°C can be used at 200°C by extrapolation of the Arrhenius law in a reliable manner. The hydrocarbons studied are linear and branched alkanes, several aromatic compounds (toluene, trimethylbenzene, methylnaphthalene, decylbenzene and tetralin) and cycloalkanes (methylcyclohexane and butylcyclohexane). All free-radical mechanisms used were constructed and validated on experimental data by our team for about 15 years. The detailed models are used to compute the apparent kinetic parameters at 700 bar and two temperatures: 200 and 400°C. The relative scales of stability at 400 and 200°C are setup and compared. Then the kinetic parameters computed at 400°C and then at 200°C are used at 200°C to calculate and compare the conversion after some million years, as well as the half-reaction time. This comparison is performed to highlight the influence of extrapolating kinetic parameters outside the range of temperature in which they were computed.

Example of results

The apparent kinetic parameters which are the most influenced by temperature are those of decylbenzene DB, methylcyclohexane MCH and tetralin. We compared the computed apparent rate constant in the range 200-400°C to the apparent rate constant extrapolated from 400°C by the Arrhenius law (Figure 1). The apparent rate constant of MCH is overestimated

by the extrapolation of the Arrhenius law whereas the opposite is observed for DB and tetralin.

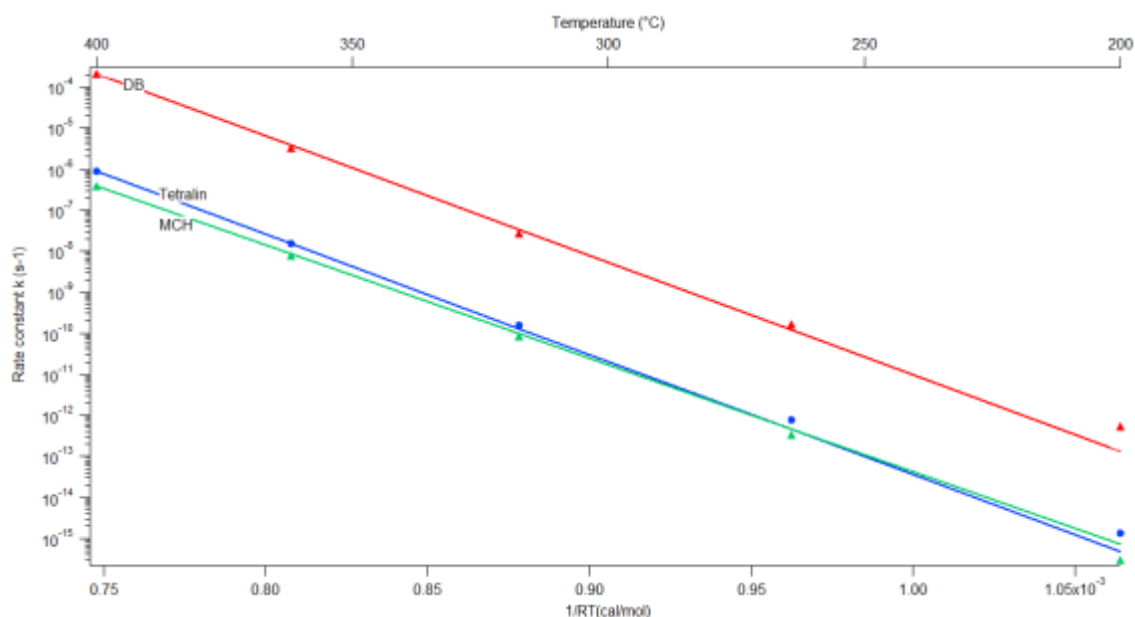


Figure 1 Computed evolution of the rate constants (DB, MCH and tetralin) as a function of temperature compared with the extrapolation of the Arrhenius law from 400°C.

The half-reaction time of MCH at 200°C is more than divided by 2 when it is calculated with the apparent kinetic parameters computed at 400°C instead of 200°C. In the case of DB and tetralin, the reverse phenomenon is observed: the half reaction times are more than tripled when they are calculated with the apparent kinetic parameters computed at 400°C instead of 200°C.

Conclusions

Most of the compounds studied here exhibit apparent kinetic parameters that are slightly or even highly different between 400°C and 200°C. Extrapolating apparent kinetic parameters obtained at 400°C, even when they are only slightly different from those at 200°C, can lead to huge differences in terms of half-reaction times or conversion after some million years. All hydrocarbons studied here (alkanes, monoaromatics and naphthenes) appear more stable at 200°C than it could be inferred by using the apparent kinetic parameters computed at 400°C, except decylbenzene and tetralin which appear much more reactive. To conclude, any extrapolation beyond the original range of temperature of the apparent kinetic parameters has to be undertaken very carefully.