Report of computational assignment on Micro-Kinetic Modelling and Degree of Rate Control

Submitted by

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Problem statement - You are given that Na can act as a gas-phase catalysts for methane pyrolysis and initial decomposition pathways are given in Table 1. Write a code to perform micro-kinetic modeling in Matlab to plot the temporal variation of methane with time (0-2hrs). Take the following initial conditions: PCH4 = 0.45 atm, PAr = 0.45 atm, and PNa = 0.1 atm. The total pressure was fixed at 1 atm and the initial volume of the reactor was taken as 1 litre. Also perform sensitivity analysis based on degree of rate control to find the rate-limiting steps in the whole framework.

Microkinetic modelling - Microkinetic modelling is a computational approach that involves breaking down chemical reactions into elementary steps, assigning rate constants to these steps, and solving a system of differential equations to predict the kinetics of the overall reaction.

For a reaction system containing n species and defined by m equilibrium reactions, the net rate of reaction of any species I (r_I) is defined using the phenomenological rate equation,

$$r_l = \sum_{j=1}^{m} r_{lj} = \frac{1}{V}\frac{dN_l}{dt} = -\sum_{j=1}^{m} k_j \prod_{\substack{i=1 \\ \nu_{ij}<0}}^{n} \left(\frac{N_i}{V}\right)^{|\nu_{ij}|} + \sum_{j=1}^{m} k_{-j} \prod_{\substack{i=1 \\ \nu_{ij}>0}}^{n} \left(\frac{N_i}{V}\right)^{|\nu_{ij}|},$$

N_l - Moles of the l^{th} species

V - Total volume of the reactor

k_j & k_{-j} - Forward rate coefficient and Backward rate coefficient respectively

v_{ij} - Stoichiometric coefficient of the i^{th} species in the j^{th} reaction. v_{ij} in the j^{th} reaction is taken as positive if the ith species is a product, negative if the ith species is a reactant, and zero if the i^{th} species is not present.

Sensitivity Analysis - Sensitivity analysis based on the degree of rate control evaluates the influence of individual reaction steps on the overall system kinetics by calculating the degree of rate control for each step. It is done to find the rate-limiting steps.

The DRC for an elementary step i (X_i) is defined as

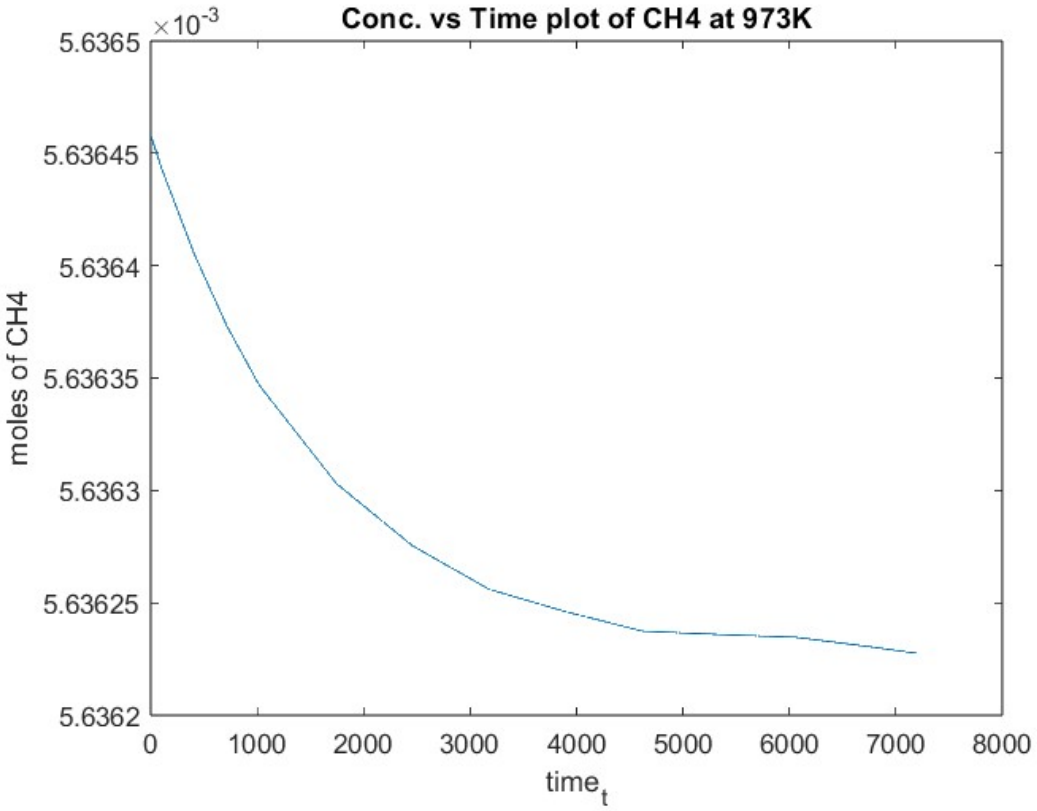
$$X_i = \frac{k_i}{r}\left(\frac{\partial r}{\partial k_i}\right)_{k_{j\neq i},K_j} = \left(\frac{\partial[\ln r]}{\partial[\ln k_i]}\right)_{k_{j\neq i},K_j}$$

k_i - forward rate coefficient

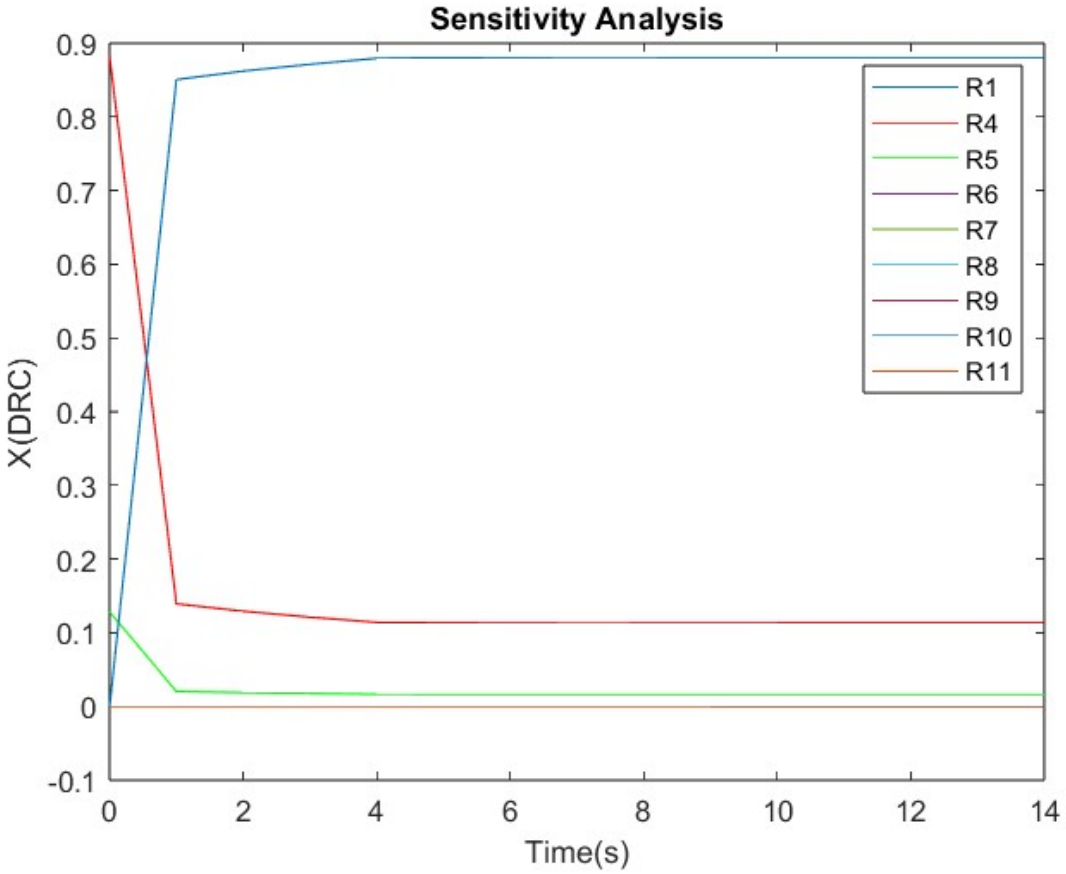
K_j - equilibrium constant

r - net rate of decomposition of reactant

Result



As the reaction proceeds moles of CH_4 is decreasing.



As we can see from the graph, three reactions mainly are the rate-limiting steps.

Thus, these reactions contribute to the overall rate of methane pyrolysis and for rest of the reactions DRC is zero.

That is reactions 1, 4 & 5 contribute to the overall rate of methane pyrolysis.

$$1 \quad CH_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3^{\bullet} + H^{\bullet}$$

$$4 \quad CH_4 + Na \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} NaH + CH_3^{\bullet}$$

$$5 \quad CH_4 + Na \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HNaCH_3$$