Computational Assignment

Given that Na can act as a gas-phase catalyst for methane pyrolysis and initial decomposition pathways are given.

Micro-kinetic modelling is performed to study the temporal variation of methane with time.

For a reaction system containing **n** species and defined by **m** equilibrium reactions, the net rate of reaction of any species **l** ($\mathbf{r_l}$) is defined using the phenomenological rate equation,

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

Where,

$\mathbf{N_l}$ - Moles of the $\mathbf{l}^{th}$ species

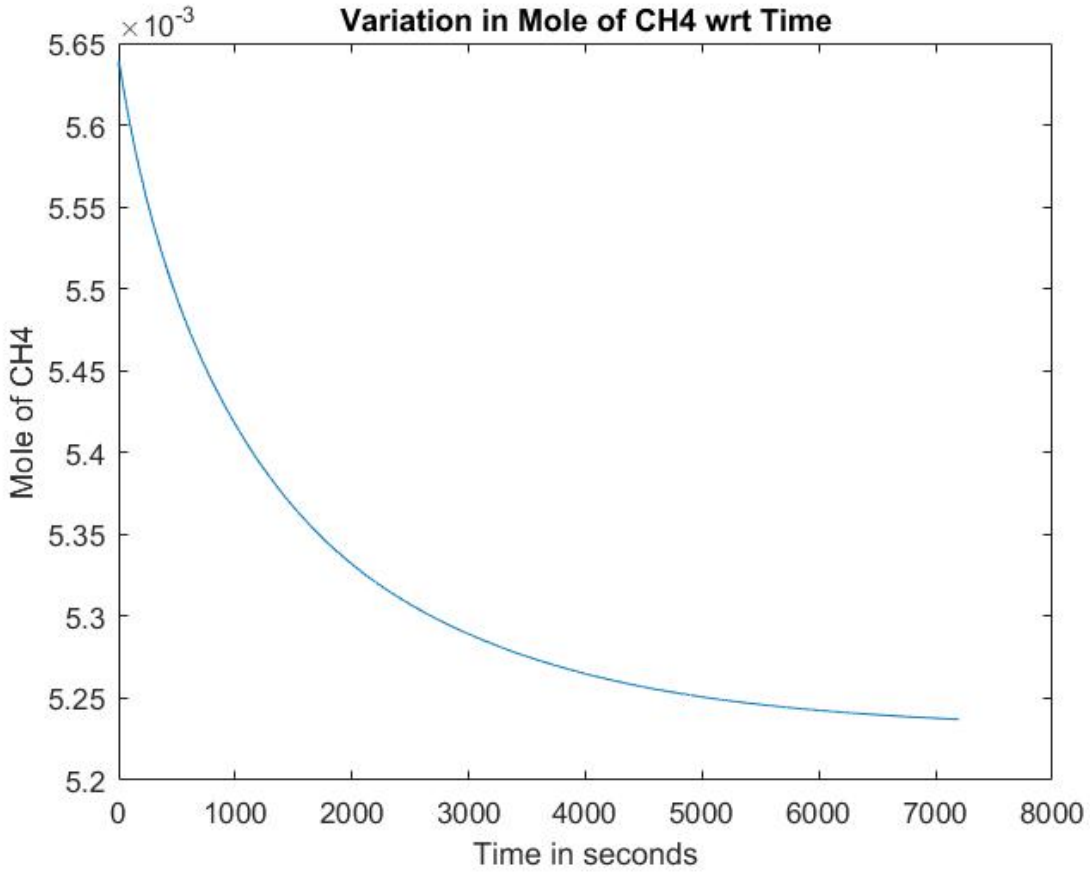
V - Total volume of the reactor

$\mathbf{k_j}$ - Forward rate coefficient

$\mathbf{k_{-j}}$ - Backward rate coefficient

$\mathbf{\nu_{ij}}$ - Stoichiometric coefficient of the $\mathbf{i}^{th}$ species in the $\mathbf{j}^{th}$ reaction. ν_{ij} in the $\mathbf{j}^{th}$ reaction is taken as positive if the **i**th species is a product, negative if the $\mathbf{i}^{th}$ species is a reactant, and zero if the $\mathbf{i}^{th}$ species is not present.

Matlab Result



Analysis

From the graph one can observe as time progresses, mole of methane decreases and become constant after certain time that is equilibrium is reached.

Sensitivity analysis is performed based on Degree of Rate Control(DRC) to find the rate-limiting steps.

DRC predicts the changes in the overall rate of consumption upon small changes in one of the kinetic parameters (in our case kf is increased by 10%).

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

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

Where,

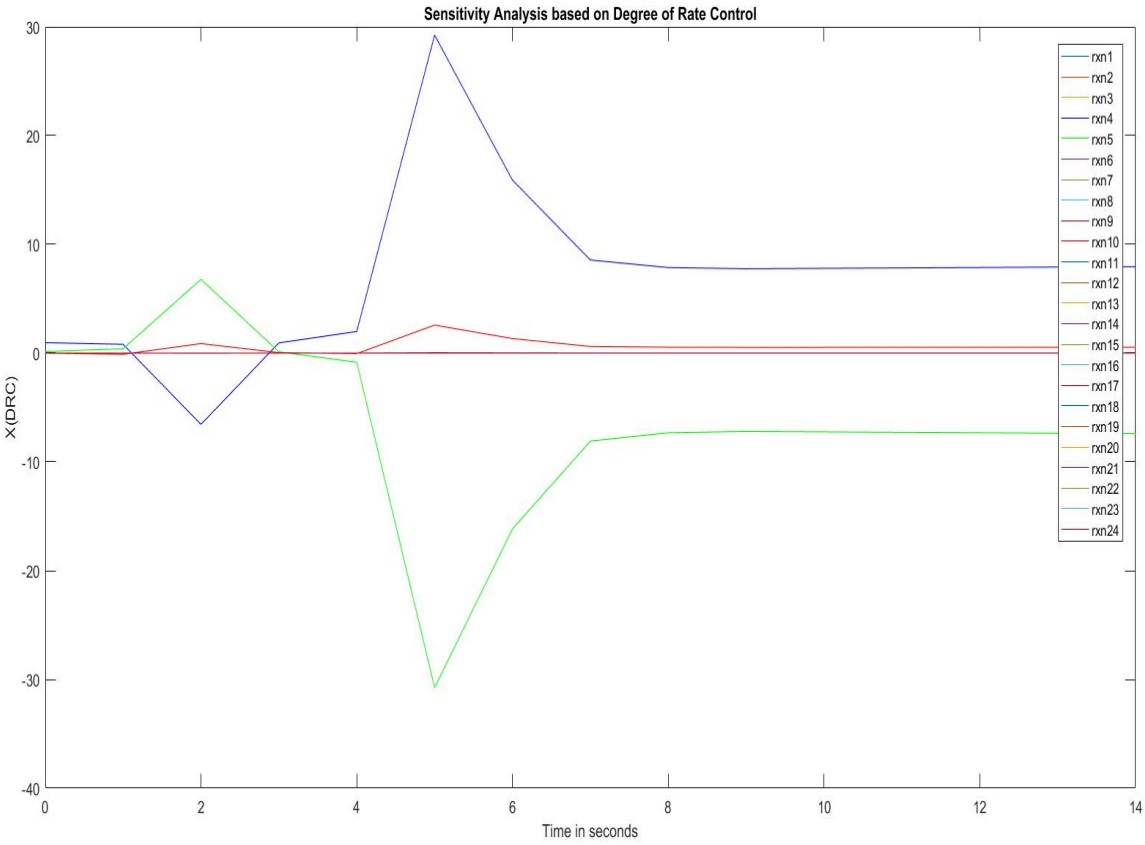
$\mathbf{k_i}$ - Forward rate coefficient of the $\mathbf{i}^{th}$ elementary step

$\mathbf{K_j}$ - Equilibrium constant of the $\mathbf{j}^{th}$ elementary step

r - Net rate of decomposition of CH_4

The partial derivative is evaluated by varying $\boldsymbol{k_i}$ but keeping all the other $\boldsymbol{k_j}$ constant and keeping all the equilibrium constants fixed.

Matlab Result



Analysis

From the graph, it can be observed that three reactions mainly are the rate-limiting steps because DRC is non-zero. That is kinetic parameters of these reactions contribute to the overall rate of methane pyrolysis and rest reactions DRC is zero hence they do not contribute.

Namely, reactions 4, 5 & 10 contribute to the overall rate of methane pyrolysis.

Reactions are:

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

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

$$CH_4 + H^{\bullet} \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} CH_3^{\bullet} + H_2$$

SUBMITTED BY:

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