To perform sensitivity analysis with Degree of Rate Control to find rate limiting step for methane pyrolysis by gas phase catalyst Na

Department Of Chemical Engineering
Indian Institute of Technology,
Kanpur

Name: Bhumesh Panchal
Roll No.: 231020008
Course: CHE631A (Chemical Reaction Engineering)
Guide: Prof. Vishal Agarwal

Abstract:

For the large-scale production of H_2 Methane pyrolysis is widely used in today's era. One mole of Methane consists 2 moles of H_2 which is released on decomposition of Methane. H_2 is used as fuel for the energy requirements. Here, pyrolysis of Methane is carried out at 1 atmosphere pressure, in the presence of gas phase catalyst Na (Sodium) at 973 K temperature. Partial pressure of methane and argon(inert) gases is 0.45 atmosphere, while for Na(sodium) it is 0.45 atm. Based upon the reaction kinetics and mechanisms, a data of concentration of CH_4 vs time is calculated and plotted. Also, the sensitivity analysis of all the reaction schemes involved in methane pyrolysis is carried out using Degree of Reaction Control (DRC) and plotted as a function of time to determine the rate-limiting step in the reaction steps.

Introduction:

H_2 can be produced by steam reforming of hydrocarbons which leads to emission of CO_2, also by electrolysis of H_2O which is again energy intensive.
So, methane pyrolysis came into picture with CO_2 free alternative but the process tackle with slow rates and clogging of carbon over the equipment surface. This can be overcome by use of catalyst. Catalyst can be metals or molten salts. Here, sodium(Na) is used as heterogenous(gas phase) catalyst.

Procedure:

From the performed experiments for the given reaction it is found that there are 24 elementary steps occur some are of 1st order and some are of 2nd order.
Rate constants for each forward and backwards reactions are given.

Rate Equation:

$$\text{Rate} = \frac{1}{V}\left(\frac{dN_i}{dt}\right) = -\sum_{i=1}^{24} k_i \prod_{j=1}^{16}\left(\frac{N_j}{V}\right)^{|v_{ji}|} + \sum_{i=1}^{24} k_{-i} \prod_{j=1}^{16}\left(\frac{N_j}{V}\right)^{|v_{ji}|}$$

Where,
V= volume of reaction mixture
i= suffix for rate constants
j= suffix for species
N_i= moles of species i
v_{ji}= stoichiometric coefficient

Sensitivity Analysis by Degree of Rate control

To determine the rate limiting step sensitivity analysis can be done for the given problem. If DRC of ith reaction having zero value then reaction is not rate limiting step.

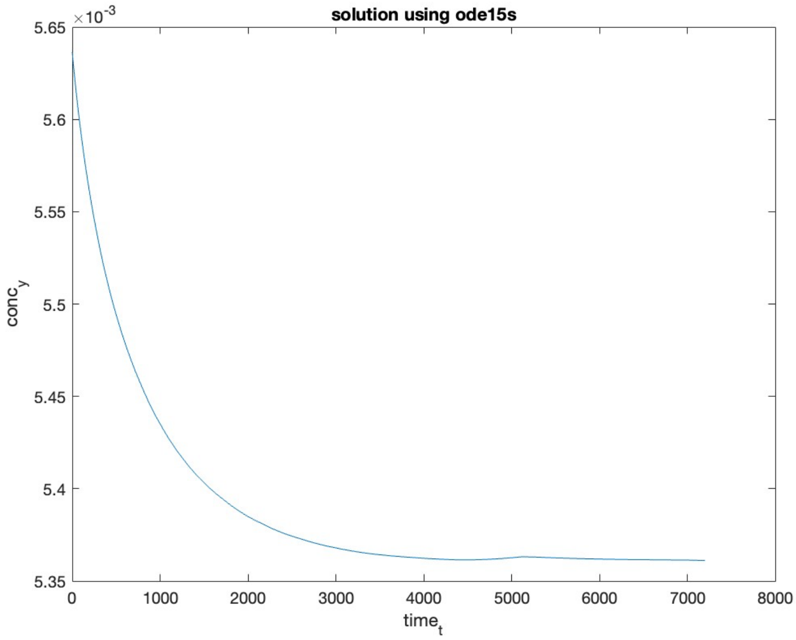
DRC can be defined by the following equation,

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

Where,
X_i= degree of rate control for ith reaction
r= rate of reaction
K_j= Equilibrium constant for jth reaction

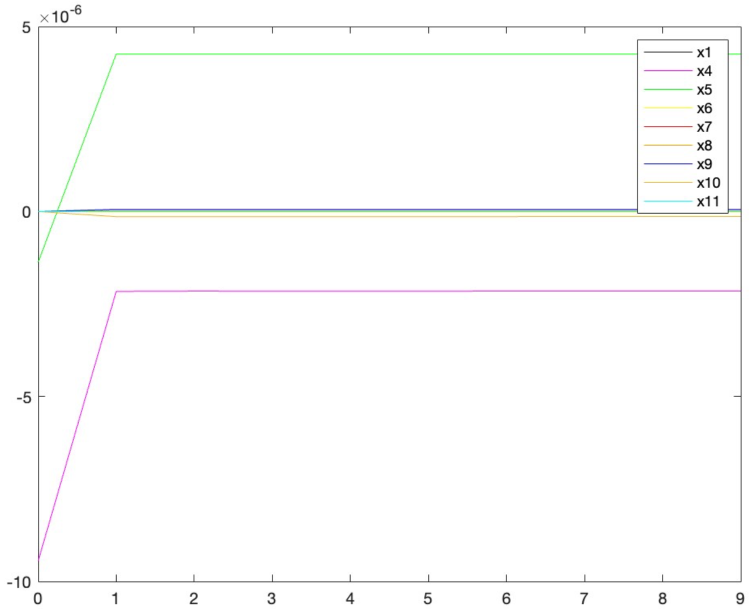
Results and Plots:

1) CH_4 moles v/s Time(sec)



It seen from the graph that as time increases the concentration of CH_4 decreases.

2) DRC: X_i v/s time(sec)



From the graph it is seen that X_4,X_5 and X_8 having non zero value. So from the expression of DRC we can say that reaction 4,5 and 8 are the rale limiting reaction