Microkinetic Modelling of Methane (CH_4) Pyrolysis over Gas-Phase $ZnCl_2$ Catalyst

Computational Assignment
Course - CHE-631
Chemical Reaction Engineering

Name – Soumyo Deep Chowdhury
Roll – 241020033

1. ABSTRACT

Methane pyrolysis is one of the methods to produce hydrogen on a large scale in industries. Methane, upon decomposition, gives Hydrogen which is then used for multiple purposes including energy applications. Here, methane pyrolysis occurs at 1 atm pressure, in the presence of a $ZnCl_2$ (Zinc Chloride) catalyst at 1273 K temperature. The partial pressure of methane and argon gases is 0.45 atm, while for Zinc Chloride it is 0.1 atm. Based upon the reaction kinetics and mechanisms, data on the 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 find out the rate-limiting reaction steps.

2. INTRODUCTION

Steam reforming of hydrocarbons is the primary industrial method for hydrogen production but results in significant CO2 emissions. Methane pyrolysis offers a CO2-free alternative, but it faces challenges, including slow gas-phase reactions and equipment clogging due to carbon formation. However, these issues can be mitigated by using a catalyst. This catalyst can be composed of metals, metallic alloys, or molten salt mixtures. Here, ZnCl2 salt is used as a heterogeneous catalyst.

In this article, we use theory to investigate whether halide vapors are active gas-phase catalysts for methane pyrolysis. Unfortunately, the reaction network converting methane to hydrogen and carbon is very large; therefore, it is impossible to investigate all steps. For this reason we are investigating only the early steps in the process. This is justified by the widely held and reasonable belief that breaking the carbon−hydrogen bond is rate-limiting. The fact that the effective rate is first order in methane partial pressure supports this view.

3 METHODOLOGY

From experimental studies, multiple reaction steps are devised. Here, a total of 24 reaction steps are devised out of which some are unimolecular and other are bimolecular.
Now the rate coefficients for all 24 reactions are calculated based upon the transition state theory, which is stated as:

$$k_{tst} = \left(\sqrt{\frac{K_b T}{2\pi m}}\right) * \left(\frac{Q^{\#}}{\frac{Q^r}{V^{\nu-1}}}\right)$$

Where,
k_{tst} = Rate constant
K_b = Boltzmann constant
m = Mass of the system
V = Volume
ν = 1 for unimolecular reaction and 2 for by molecular reaction.

3.1 Rate Equation

$$Rate = \frac{1}{V}\frac{dN}{dt} = -\sum_{j=1}^{m} k_j \prod_{i=1}^{n} \left(\frac{N_i}{V}\right)^{|\nu_{ij}|} + \sum_{j=1}^{m} k_{-j} \prod_{i=1}^{n} \left(\frac{N_i}{V}\right)^{|\nu_{ij}|}$$

Where,
V = Volume of the reaction mixture
N_i = Moles of species i
k_j = Forward reaction rate constant
k_{-j} = Backward reaction rate constant
ν_{ij} = Stoichiometric coefficient

3.2 Sensitivity Analysis using Degree of Reaction Control:

Now, Sensitivity analysis for methane pyrolysis reaction is done in order to determine which reaction is actually rate limiting. This helps in reducing the computational load by providing the estimate of the equations which actually have impact on the reaction rate.
A method of sensitivity analysis, called Degree of Reaction Control (DRC) is used here to determine the rate-limiting steps from the cluster of reaction steps.
Following is the equation to calculate DRC:

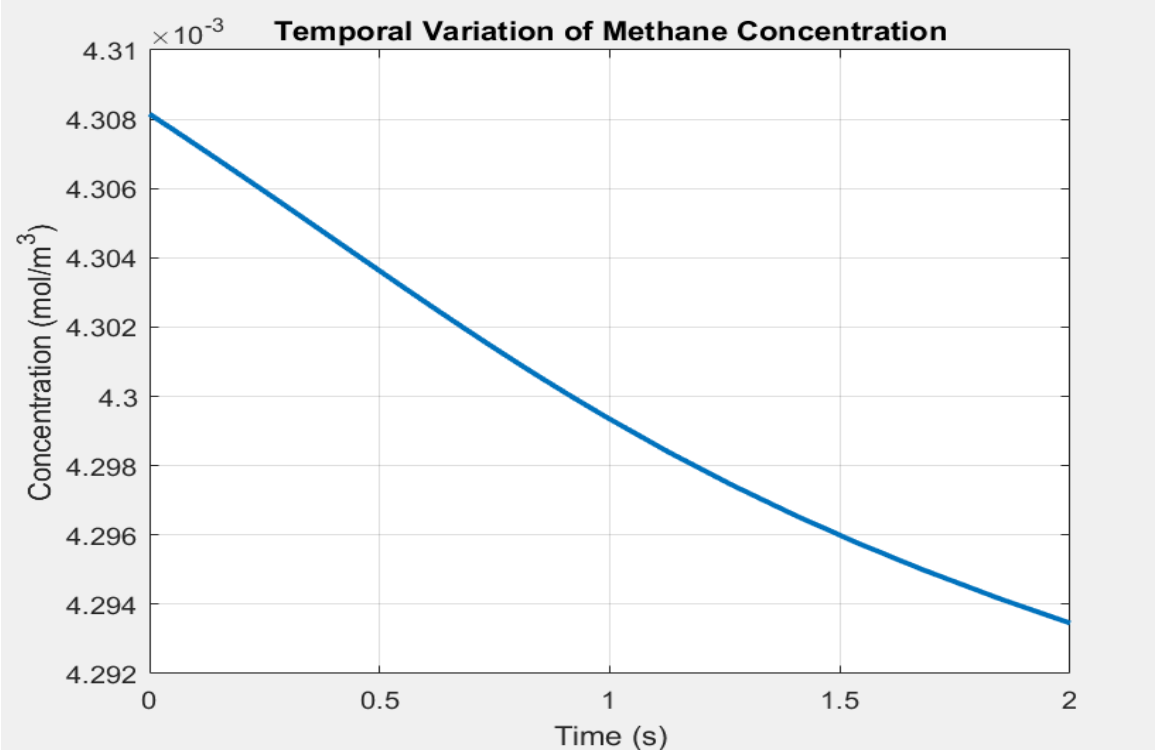
$$X_i = \left(\frac{k_i}{r} * \frac{\partial r}{\partial k_i}\right)_{k_{i\neq j}, K_j} = \left(\frac{\partial[ln(r)]}{\partial[ln(k_i)]}\right)_{k_{i\neq j}, K_j}$$

Where,
Ki = Equilibrium constant for i^{th} reaction
r = Rate of reaction
Xi = DRC Parameter
ki = Rate constant for i^{th} reaction

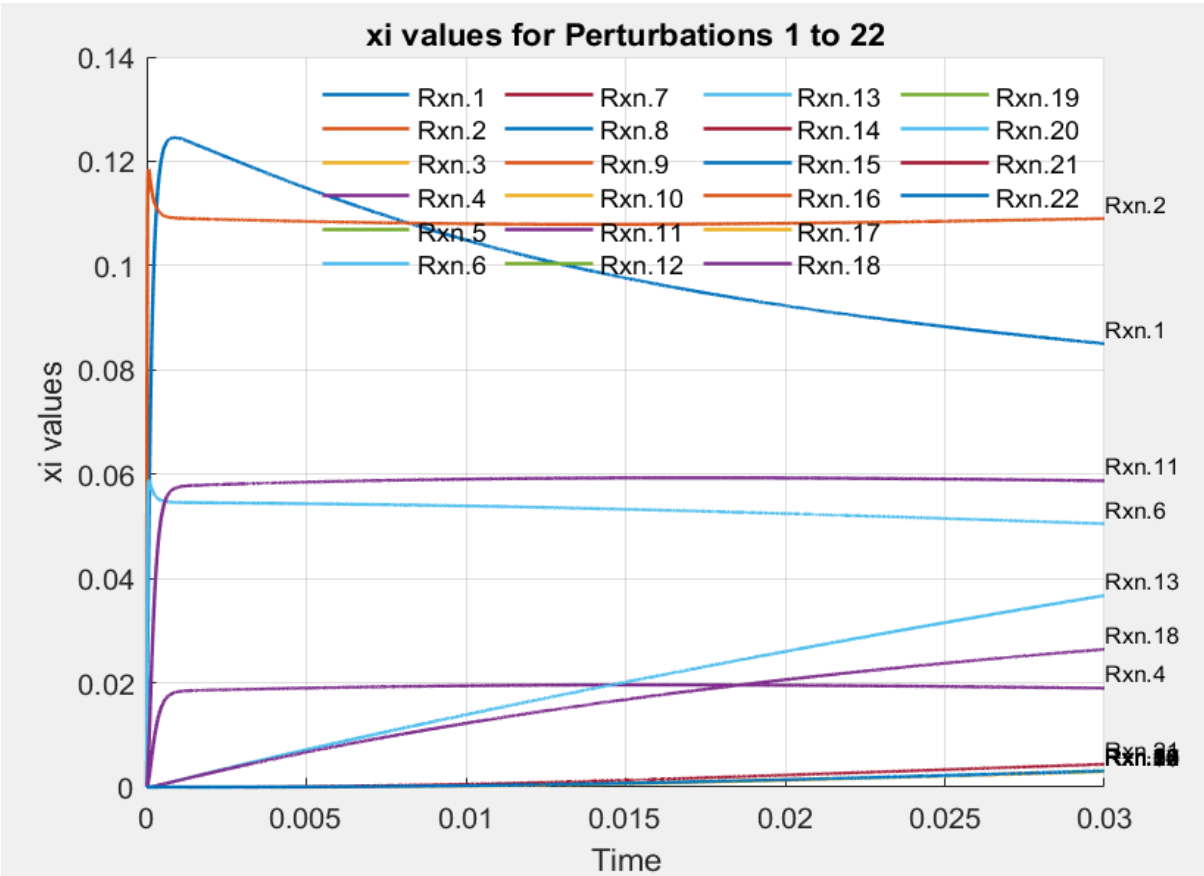
Now, if the value of Xi is non zero for a reaction then that reaction may be rate limiting and if Xi value is zero for a reaction then that reaction will not be rate limiting.

4. RESULTS AND PLOTS

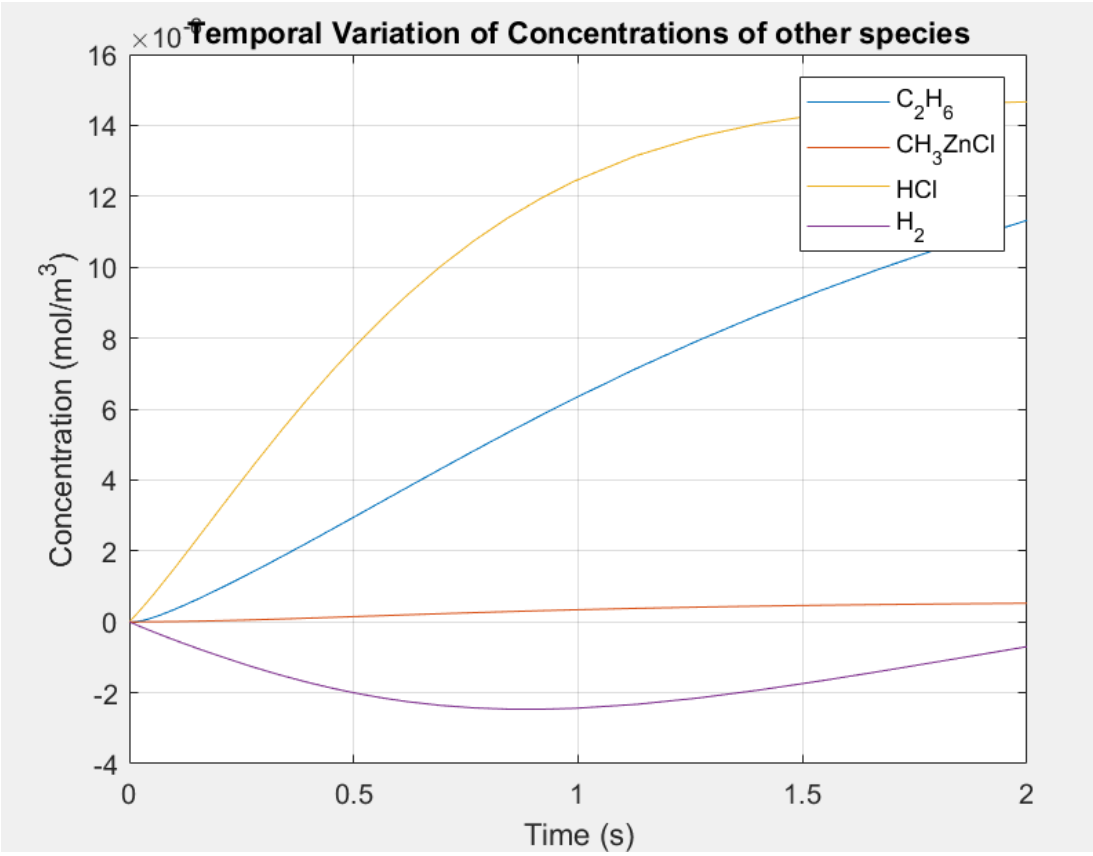
4.1. Methane Degradation Plot:



4.2. Degree of Rate Control Plot:



4.3. Temporal Variation :



5. CONCLUSIONS:

It can be clearly seen that the degradation of methane is exponentially decreasing although the curvature is not deep enough compared to the plot of the research project. It may be due to the short range of time span assumed. Secondly, the intermediate concentrations are hardly visible in the DRC plot due to the less stability of the intermediate steps and hence are immediately consumed to final products and Bi-products as shown in the third and final plot.

In the first plot of degradation of CH_4 due to the pyrolysis of methane. Since methane is the primary reactant so it is usual to see this type of exponentially decaying plot of concentration wrt time. The degradation curve provides a practical view of how quickly methane is converted under given conditions (1 atm and 1273 K with $ZnCl_2$ as a catalyst). If the time span was extended, we might observe a complete depletion trend or a potential leveling off if a product inhibits further reaction.

In the DRC plot, we observe that some species such as Reaction steps **1,2 & 6** are initially dominant but as the reaction proceeds they slow down this is because methane is the primary reactant and the rest are intermediates so they are unstable and hence convert to more stable products. However, we can also see that some reactions are stable and are thus Xi is increasing or constant (for example – **Rxn.11, 13,18**) due to the formation of stable products.