Insight into the thermodynamic model for reforming of methane over nickel catalyst

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Abstract

The reforming of light hydrocarbons to produce synthesis gas, H_2 and CO, is an important intermediate for manufacturing valuable basic chemicals and synthesis fuels. In order to understand these reforming processes better, elementary step reaction mechanisms are developed. In the available literature, the surface reaction mechanisms are usually achieved with the help of reaction kinetic parameters without using the thermochemistry of the species referred to kinetic models due to the unavailability of the thermochemistry of the intermediate species involved in the multi-step reaction mechanism. In this work, investigations are made to obtain the thermochemistry of the intermediate species to establish thermodynamic equilibrium in order to develop a thermodynamic model for steam reforming of methane over nickel. The thermochemistry of the surface bound species is taken from different sources available in the literature and after that a detailed sensitivity analysis is performed to match the results with experiments. The simulation set up is adapted from the literature experiments given in [1]. The results produced with the one-dimensional tool using the thermodynamic model developed in the present investigation consisting of 21 reversible reactions are compared with the kinetic scheme with 42 irreversible reactions from reference simulation along with their experimental results. Both the models show some major differences in the reaction pathways which provides a useful insight into the key rate determining steps and needs further investigations.

Keywords: Nickel-based catalyst; One-dimensional modeling; Thermodynamic model; Steam reforming;

1. Introduction

A crucial chemical process providing synthesis gas (H_2 and CO) is steam reforming of hydrocarbons [2, 3]. The reforming of steam plays an important role as a feedstock in many catalytic processes [1], such as, synthesis of methanol, oxo-synthesis, and Fischer-Tropsch synthesis. The methane or gas (natural) reforming is the most prominent and widely used industrial steam reforming process [1, 3, 4].

There are several kinetic models available in literature to study reforming processes. Quiceno et al. [5] described the steam reforming of methane accompanied by water-gas shift reactions on a $Ni/MgAl_2O_4$ catalyst by intrinsic rate equations derived from a Langmuir-Hinshelwood mechanism. A catalytic sequence for reactions of CH_4 with CO_2 and H_2O on Ni/MgO catalysts is considered by Wei et al. [6]. A microkinetic model for steam reforming reactions over a $Ni/MgAl_2O_4$ catalyst is investigated by Aparicio et al. [7] by reactions for CO_2 reforming of methane and deactivation by carbon formation.

Other investigations focusing on reduction of the cost of synthesis gas production are partial oxidation over noble metal catalysts [8–11] as well as CO_2 reforming [12–14] of natural gas to synthesis gas. Several investigations considered the sequence and interaction of the reaction routes to understand the reaction mechanism of synthesis gas formation from methane. A direct catalytic partial oxidation route has been studies by Hickman et al. [11] and the indirect route in [8–10, 15]. The steps for steam reforming for the catalytic partial oxidation of methane over platinum and rhodium are published in [11, 15–17]. In [18, 19], the reaction kinetics of methane steam reforming over nickel catalyst has been extensively investigated experimentally and theoretically.

All the investigations in literature consider a kinetic model with all the direct/irreversible reactions. The detailed surface reaction mechanism in these models requires specification of Arrhenius parameters for all the forward reactions involved in the mechanism. In these models, even the reverse rates are calculated with the help of kinetic parameters without using the thermochemistry of the intermediate species involved in the mechanism. Hence the equilibrium can be achieved by modifying the Arrhenius parameters. The prime reason to follow this approach is because of the unavailability of the thermodata of the surface species.

However, the optimum approach to establish thermodynamic equilibrium would be to use the thermodata of the surface species to calculate the reverse rate expressions. The Arrhenius parameters are more accurate to define the speed of the reactions whereas the thermochemistry is more important to achieve the equilibrium. This motivated us to develop a thermodynamic model where the kinetic parameters are given only for the forward reactions and then the rate

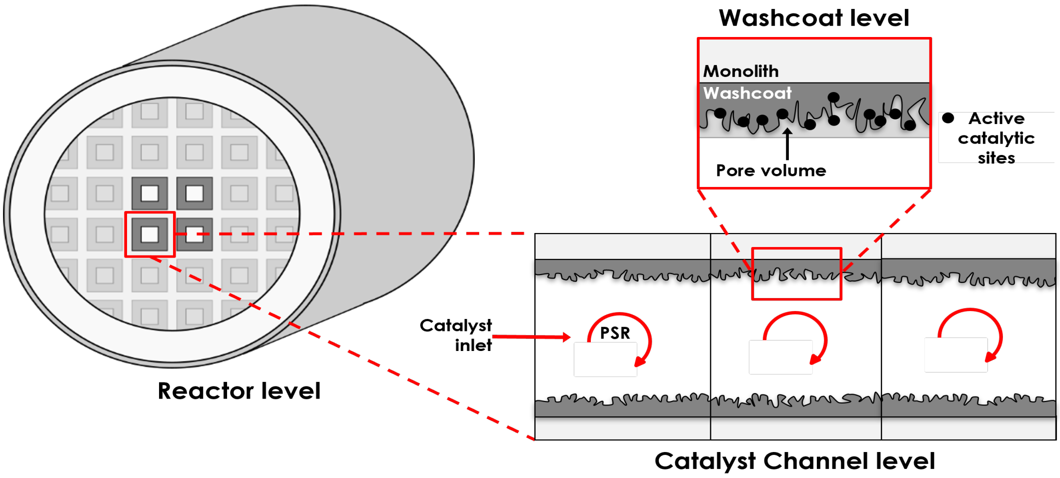

Figure 1: Schematic illustration of the one-dimensional modeling approach

expressions for the reverse reactions can be calculated by using the thermodata of the intermediate species.

The thermochemistry of the intermediate species available from this study can be further directly used in other reforming processes, for instance, dry reforming or oxidative reforming of methane over a nickel catalyst in order to understand and mitigate the coke formation problems encountered in these reforming processes at different conditions.

2. Simulation Set-up

The simulation set-up is taken from Maier at al. [1]. This allows us to re-calculate the results for the kinetic model with the LOGEcat for validation of the model as well as the surface reaction mechanism and later checking the predictive capability for the thermodynamic model. As done in the reference paper [1], the simulations are performed for different reactor conditions in terms of parameter as temperature while keeping the fuel ratio, flow rate and pressure same as [1]. The simulations are carried out at four temperatures, i.e., 920, 1020, 1120, and 1220 K.

The one-dimensional model, LOGEcat [20] is used for the simulations and the model is based on the single-channel 1D catalyst model applicable to the simulations of all standard after-treatment catalytic processes of combustion exhaust gas, for example, three-way catalyst (TWC), diesel oxidation catalysts (DOC), NO_x storage and reduction (NSR) catalysts and selective catalytic reduction (SCR) catalysts.

The single channel divided into a finite number of cells with Δx as their length is shown in Figure 1. As shown in the figure, each cell is treated as a perfectly stirred reactor (PSR). The pressure gradient along with inhomogeneity of the mixture can be neglected because the diameter of the catalytic channel is small. The external diffusion is modeled by a thin layer represented by a separate pore gas zone close to the wall. This pore layer is depicted by the area between the bulk gas and the washcoat as shown in Figure 1. For more details about conservation equations used in the model and the derivations of these equations, we refer the reader to [20, 21] and to understand the modeling approach, to our previous work [22–25].

A single channel being 1.0×10^{-2} m in length with a catalyst radius of 7.5×10^{-3} m which is uniformly divided into 25 cells is considered for the simulations with one layer of washcoat. The overall heat transfer efficiency factor, mass transfer efficiency factor and the efficiency factors for the surface chemistry are taken as one. The surface site density for nickel is 2.6×10^{-5} mol/m^2 [3]. The surface area per catalyst length is selected 6.9×10^{-3} m^2/m by performing the sensitivity analysis to get the results comparable to the reference simulations and experiments. Argon dilution is used similar to [1].

The reaction mechanism for the simulations is taken from Maier et al. [1] which contains 6 gas-phase and 13 surface species in total along with 42 forward reactions referred as kinetic model. After validating the results produces with the LOGEcat using the kinetic model, a thermodynamic model is developed. In this model, only 21 forward reactions are used with the kinetic parameters taken from Maier et al. [1]. The kinetic expressions for the remaining 21 backward reactions are then calculated with the help of the thermochemistry for the intermediate species involved in the surface reaction mechanism. Since the thermochemistry of the surface bound species is not easily available, we have taken the thermodata from different sources [1, 26]. The thermodata from Maier et al. [1] is referred as DETCHEM and from Liu et al. [26] as RMG in upcoming sections.

The heat capacity, entropy and enthalpy for all the intermediate species involved in the surface mechanism have been summarised in [22] in Table 1 for both the sources, DETCHEM as well as RMG. We note that the enthalpy of formation of species vary in a wide range for the two sources, specially for the species, C(s), CH_3(s), CH(s), and CH_4(s). This hints towards the requirement of a further investigation to find the sensitive limits for thermochemistry of all the species. Nevertheless, the most sensitive reactions for dry reforming of methane using a kinetic model and the thermodynamic model have been given in [25], Table 3.

3. Results

The above mentioned 1D model is used to perform the simulations for various temperatures for the steam reforming of methane over a nickel catalyst. The kinetic parameters for the considered 21 forward reactions and the thermochemistry of the 13 surface species are taken from [1].

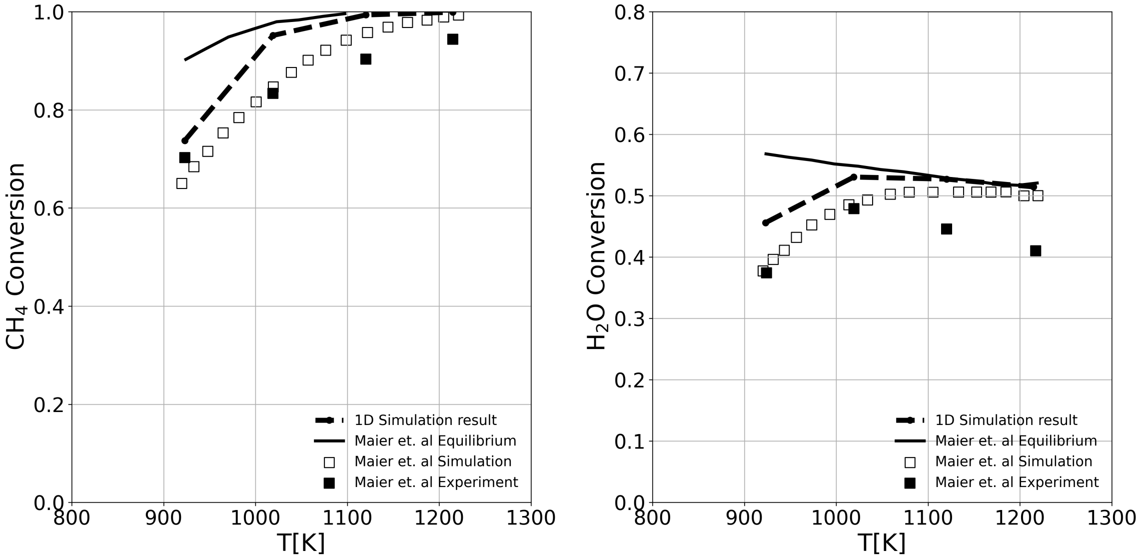

Figure 2: Methane and water conversion as a function of temperature along with the reference data. The 1D simulation results are shown for thermodynamic data from DETCHEM by replacing the species CO(s) from RMG data.

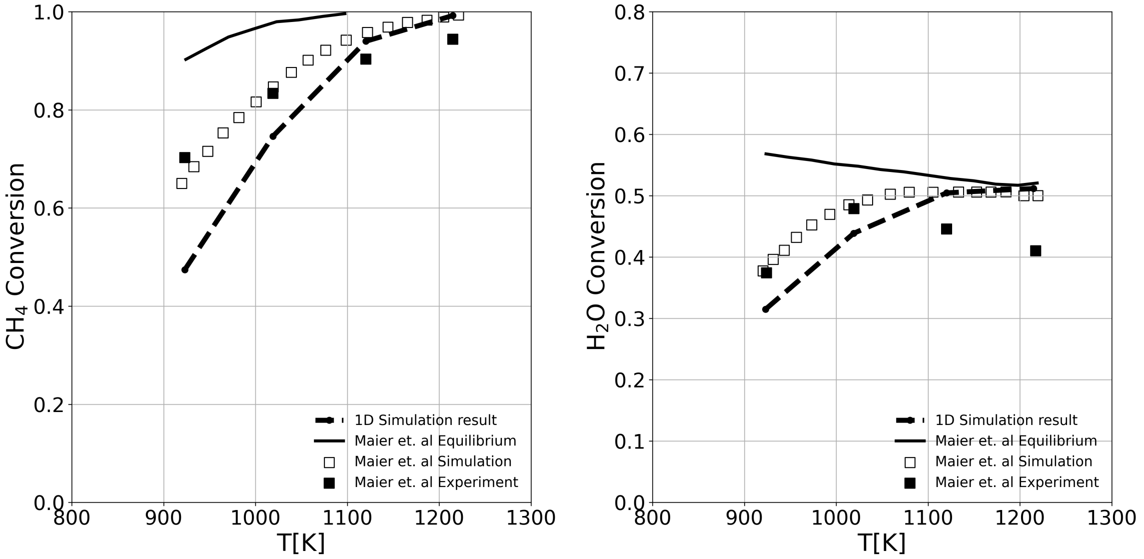

Figure 3: Methane and water conversion as a function of temperature along with the reference data. The 1D simulation results are shown for thermodynamic data from DETCHEM by replacing the species $CO_2(s)$ from RMG data.

As an initial check, we used the thermodata only from DETCHEM and check the methane and water conversion in the considered temperature range. The species concentration showed deviations (under predicted) and this motivated us to take the thermodata from RMG for all the intermediate species where the deviation in the conversion profile was noted more than the previous data set (still under predicted). So, in order to understand the impact of thermodata of the individual species, we next considered the thermodata for all the 13 species from DETCHEM and then replaced the thermodata of species one by one with RMG.

We note that the target for the thermodynamic model, presented in this paper, is to perform close to the reference experiments. However, there are several assumptions to develop the reference kinetic model [1] which is used as the base to develop the thermodynamic model. So, the results for our model are expected to remain close to the reference simulations.

3.1. Influence of CO(s)

The influence of only some of the site species are shown and discussed in this paper. Figure 2 shows the methane and water conversion as a function of temperature using the thermodynamic model along with the reference experiments and simulations with kinetic model from [1]. The thermodynamic model used the thermodynamic data for all the species from DETCHEM [1] and only for the species CO(s), the thermodynamic data is used from RMG [26]. The conversion for both the reactants is over predicted at all the temperatures.

For methane conversion in the range 900-1100 K, the over prediction is significant whereas, for higher temperature (1200 K) thermodynamic equilibrium is achieved. In case

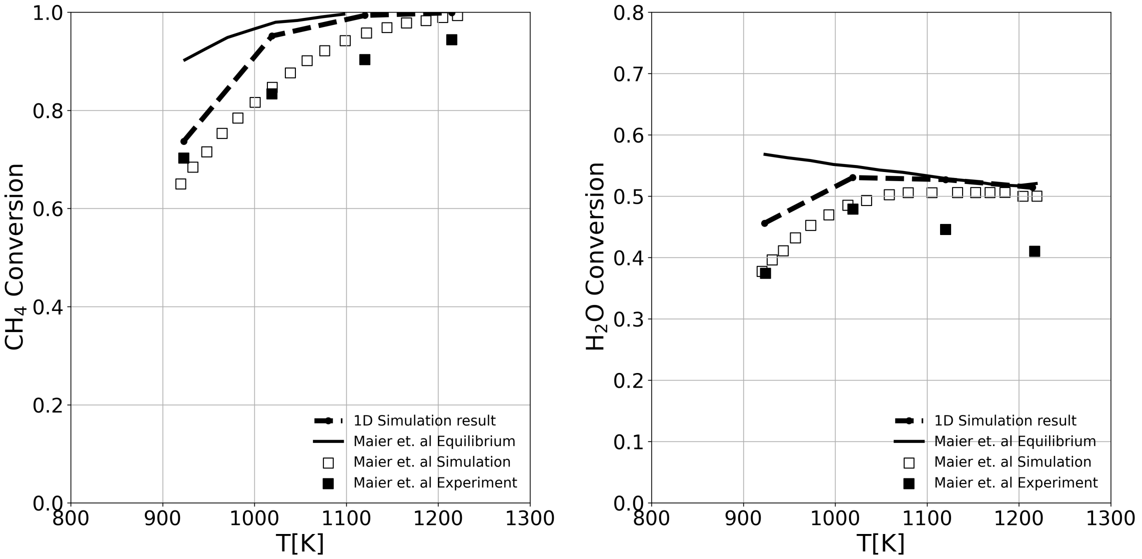

Figure 4: Methane and water conversion as a function of temperature along with the reference data. The 1D simulation results are shown for thermodynamic data from DETCHEM by replacing the species CO(s) and $CO_2(s)$ from RMG data.

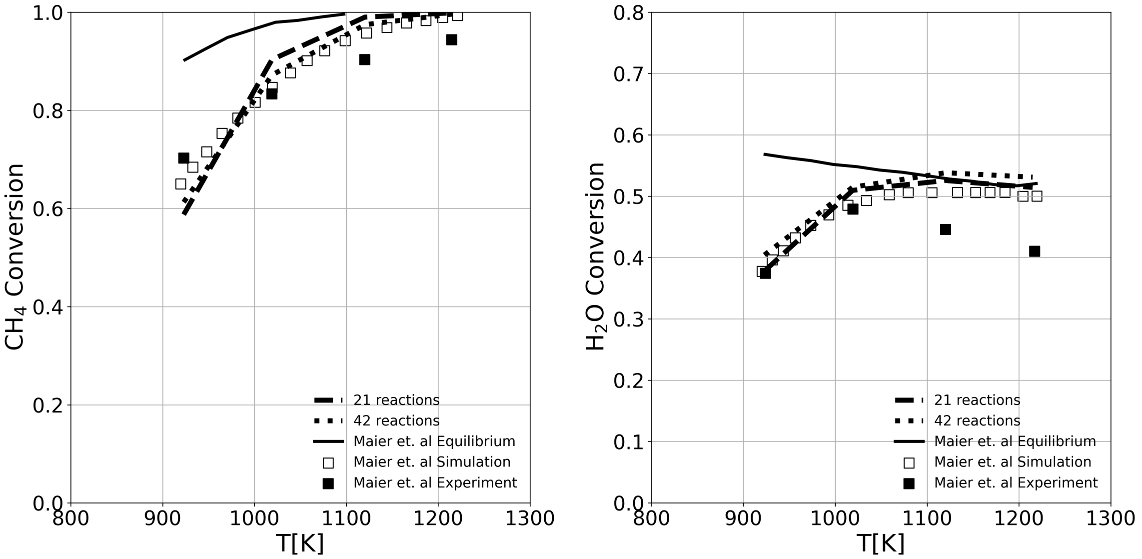

Figure 5: Methane and water conversion as a function of temperature along with the reference data with the kinetic model. All other parameters are kept fixed. 1D simulation results produced with the kinetic model (42 reactions) as well as thermodynamic model (21 reactions) are shown.

of water, the conversion is deviating from the reference simulations at low temperatures and shows agreement at temperatures above 1000 K. The water conversion computed with the 1D model as well as for reference simulations is away from reference experiments, specially at high temperatures.

3.2. Influence of $CO_2(s)$

The influence of the species $CO_2(s)$ shown in Figure 3 is completely different as compared with the CO(s) species. For both the species, methane conversion is in equilibrium at higher temperatures. The conversion of both the reactant species is under predicted at low temperatures by utilizing the thermodata for all the species from DETCHEM [1] and for $CO_2(s)$ species from RMG [26]. However, if the thermodata for both the species, CO(s) and $CO_2(s)$, is taken from RMG [26], shown in Figure 4, while all other species thermodata is taken from DETCHEM [1], then the species conversion is similar to the one explained above in Figure 2.

Such investigation was further performed for all the 13 surface species and we found that out of all the involved site species, CO(s) and $CH_4(s)$ are the most sensitive and play an important role to achieve conversion of the species comparable to the reference experiments. However, a direct replacement of the RMG species with DETCHEM could not compute the conversion correctly. This lead us to perform the enthalpy sensitivity analysis of the most sensitive species. The enthalpy of formation of the species CO(s) (thermodata for this species is taken from RMG) was further increased from 1 to 100 kJ to achieve the reactant conversion comparable with the reference experiments and simulations.

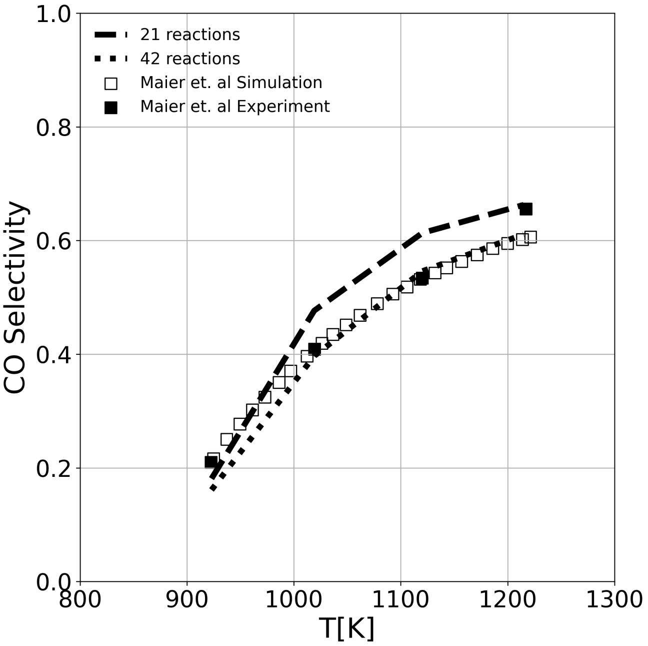

Figure 6: CO selectivity as a function of temperature along with the reference data. The reference data is using the kinetic model while the 1D simulation results are shown for both, the kinetic model and the thermodynamic model.

3.3. Comparison between kinetic and thermodynamic model

Further, the simulations are performed using LOGEcat with the kinetic model taken from Maier at al. [1] and with the thermodynamic model developed in the considered temperature range. Methane and water conversion as a function of temperature along with the reference experiments and simulations with the kinetic model is shown in Figure 5 keeping all other parameters fixed. In this figure, the LOGEcat results are shown for kinetic model using 42 reaction as well as for thermodynamic model using 21 reactions. 1D simulation results produced with the kinetic model (42 reactions) as well as thermodynamic model (21 reactions) are in good agreement with the reference simulations as well as with each other illustrating the the thermochemistry of the surface species is robust and can be used in future for similar investigations where thermodata is an important parameter.

The CO selectivity variation with temperature in methane steam reforming for fixed fuel ratio shown in Figure 6 shows deviations with thermodynamic model calculations. The calculations with LOGEcat using the kinetic model are in good agreement with the reference simulations and experimental data. Various reactions pathways and reaction sensitivity analysis needs to be performed in future to understand the difference in the calculations using the thermodynamic model.

To summarize, the 1D model, LOGEcat, is used to perform the simulations by utilizing already existing kinetic model with 42 irreversible reactions and with the help of new thermodynamic model consisting of 21 reversible reactions. In thermodynamic model, the reverse rates are calculated using the thermochemistry of the intermediate species. The thermochemistry of all the species is taken from [1] except for CO(s), which is taken from RMG [26] and adopted for our model by increasing the enthalpy of formation by 40 kJ to get a better agreement with the reference experiments and simulations.

4. Conclusions

The kinetic models are used to investigate the steam reforming of methane over a nickel catalyst. These models comprise of all the direct or irreversible reactions in the detailed surface reaction mechanism due to the unavailability of the thermochemistry of the intermediate species. For example, in Maier et al. [1], the reforming is studies by using 42 forward reactions. However, in the present work we focus on utilizing the thermochemistry of the surface bound species from different sources to develop a thermodynamic model.

Therefore, only 21 forward reactions are considered in the surface reaction mechanism and the backward reactions are omitted. The rate for backwards reactions are accounted by the thermochemistry of the intermediate species. In our model, the thermochemistry for the species CO(s) is taken from RMG [26] with a increased formation of enthalpy by 40 kJ and for all other species, the thermochemistry is utilized from [1]. A one-dimensional model, LOGEcat is used to perform the simulations. First, the kinetic model with 42 reactions from literature is used to carry out the simulations and then the thermodynamic model with 21 reactions. The results from both the models are compared with literature [1] for different temperatures.

The thermochemistry from different sources shows differences in the conversion of methane and water. The sensitivity analysis on the thermochemistry lead us to find the most sensitive species which can be modified to get the conversion of reactant comparable with the reference experiments and simulations performed with the kinetic model. A further investigation can be performed to find the sensitive limits for the formation of enthalpy of all the species considered to understand the role of thermochemistry in details. The most sensitive reactions can also be figured out by performing the flow analysis in future.

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