Detonation analysis using detailed reaction mechanisms

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Abstract: Validation of detailed reaction mechanisms through the comparison of constant volume explosion simulation and shock tube induction time data has been conducted for hydrogen, ethylene, and propane fuels. Steady, one-dimensional detonation and constant volume explosion simulations with the validated mechanisms provide the reaction zone structure, reaction time scales, and effective activation energies.

Key words: Detonation, Detailed reaction mechanisms, Induction time, Shock tube

1. Introduction

Computational simulation is extensively used to study the gasdynamics and chemistry of gaseous detonations. Detailed reaction mechanisms consisting of a comprehensive set of reaction rates attempt to represent all chemical processes within a given system. One, two, or three step models of the global chemical behavior represent the most simplistic mechanisms. In between are reduced reaction mechanisms derived systematically from detailed reaction mechanisms.

Simulations of steady, one-dimensional detonation models with detailed reaction mechanisms have been possible for many years. Unsteady, one-dimensional simulations are beginning to use the smallest detailed reaction mechanisms, while most unsteady and all multi-dimensional simulations resort to the less complex mechanisms. Given significantly increased computational power over time these higher fidelity simulations will incorporate detailed reaction mechanisms. Confidence must be established in the accuracy of all simulations through validation with experiments.

This effort considers the adequacy of existing detailed reaction mechanisms for use in detonation simulation. The chemical systems chosen include those of hydrogen, ethylene, and propane fuels. Shock tube induction time data and detailed reaction mechanisms are compiled from the literature. The mechanisms are used in constant volume explosion simulations under the thermodynamic conditions corresponding to the shock tube data. A quantitative measure of reaction mechanism accuracy is obtained by comparing the experimental and simulated induction times. Errors associated with the experimental data, constant volume approximation, and reaction mechanisms are highlighted.

One validated mechanism is selected with which to perform steady, one-dimensional detonation and constant volume explosion simulations for the reaction zone structure, characteristic reaction scales, and effective activation energies. The quantity of experimental data considered, as well as simulation and analysis data generated, precludes complete presentation in this paper. Refer to Schultz and Shepherd (1999) for a detailed accounting of all information.

2. Reaction mechanism validation

2.1. Shock tube data

Chemical reaction experiments in shock tubes most closely represent the type of initial and thermodynamic conditions associated with detonations. Data from such experiments often include a measurement of the chemical induction time of the shocked mixture. The induction time is qualitatively defined as the relatively thermally neutral period of radical species concentration growth, beginning with shock heating and compression of the fluid particle and ending with the onset of thermal explosion. A variety of quantitative experimental induction time definitions exist, usually associated with an initial rise or maxima in signals including pressure, radiation absorption, or radiation emission from a chemical species.

A database of shock tube induction time measurements has been compiled from the literature and personal communication for hydrogen, ethylene, and propane oxidation. The conditions spanned by the experimental data are summarized in Table 1. All of the experimental thermodynamic data are presented in Fig. 1, along with boxes enclosing the post-shock thermodynamic conditions occuring in atmospheric initial condition cellular detonations for the fuels, equivalence ratios, and diluents considered in Section 3 of this paper. In general the data are sparse for all fuels at detonation post-shock thermodynamic conditions.

An ideal shock tube experiment occurs in one-dimensional, inviscid flow behind either the incident

Table 1. Shock tube data summary

Mixture	# Sets	# Points	ϕ	% Diluent	P (atm)	T (K)
$H_2/O_2/Ar/N_2$	14	940	0.06-9.0	0.0-99.9	0.15-87.0	775-2650
$C_2H_4/O_2/Ar$	7	530	0.12-4.0	70-99	0.2-12.0	900-2350
$C_3H_8/O_2/Ar/N_2$	6	370	0.06-2.0	76-99	0.6-21.8	1000-1700

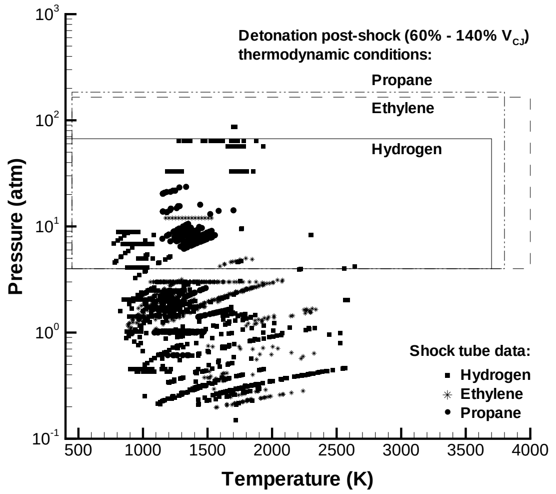

Figure 1. Shock tube data and atmospheric initial condition detonation post-shock (60% - 140% V$_{CJ}$) thermodynamic conditions.

or reflected shock. Shock tube experiments depart from ideality when consideration is given to viscous, heat transfer, and non-equilibrium effects. These complicating experimental aspects are discussed by Schott and Getzinger (1973) and are typically manifested through non-uniform flow properties and reduced test time. In addition, two distinct modes of ignition (weak and strong) have been observed in shock tube experiments by Meyer and Oppenheim (1971). The weak ignition mode occurs at relatively low temperatures and is characterized by a non-uniform distribution of local reaction centers, introducing large variability in induction time measurements.

Difficulties with ascertaining the experimental uncertainty include a general lack of error analysis accompanying the original shock tube data presentation and because the data originates from many different sources utilizing an equally diverse array of techniques and diagnostics. The approach followed here is one of considering the scatter between induction time data points conforming to a specific criterion within a given shock tube data set. The definition of scatter between two data points in this context is taken as the logarithm of the ratio of the induction times. The criterion requires that two data points be associated with the same mixture at pressures and temperatures within 10% and 5K, respectively. The requirement for less than 10% pressure difference is arbitrary, and corresponds to an induction time effect which is not discernable from the shock tube data sets in which pressure was the variable parameter.

A 5K temperature difference is also arbitrary, and intended to permit comparison of data points which have very small differences in temperature due either to experimental uncertainty or as a result of the data processing imposed by the present investigation. Estimates of temperature uncertainty available in the literature range from a few degrees to tens of degrees. The induction time data point comparisons are made within particular shock tube data sets, and therefore consistent deviations in temperature estimates from the actual should provide small relative errors between estimated temperatures. For induction time behavior described by an Arrhenius expression, a 5K temperature variation results in a scatter value of 0.09 in the worst case scenario of high activation energy and low temperature.

The results of the induction time scatter analysis for all shock tube data sets are presented in Fig. 2. A significant rise in the level of scatter is noticeable at relatively low temperatures. This corresponds to the regime in which the induction time is most sensitive to temperature, the weak mode of ignition dominates, and long induction times exacerbate the experimental non-idealities previously mentioned. Most induction time scatter falls below the 0.3 level for all fuels, with hydrogen data scatter approaching the order of magnitude level (1.0) at temperatures below 1000K.

2.2. Constant volume explosion simulations

Nineteen detailed reaction mechanisms were collected from the literature, all applicable to hydrogen oxidation and progressively smaller subsets capable of handling ethylene and propane oxidation. Constant volume explosion simulations were carried out with a FORTRAN program incorporating thermodynamic data and detailed reaction mechanisms through the Chemkin II chemical kinetics package (Kee et al. (1989)), and the *ddebdf* integrator (Shampine and Watts (1979)) for stiff ordinary differential equation systems. The program evolves the

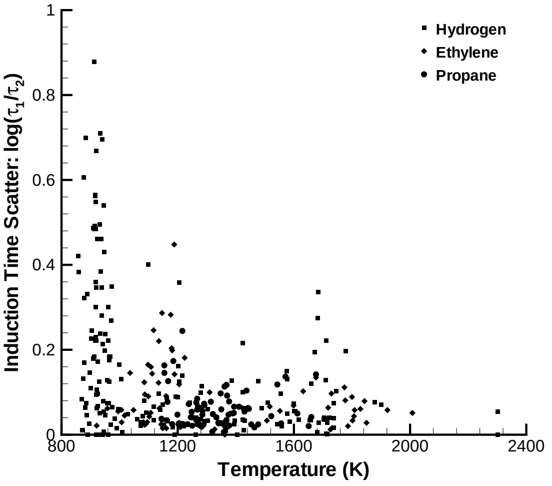

Figure 2. Shock tube induction time data scatter between experiments with the same mixture, and pressures and temperatures within 10% and 5K, respectively

energy and species equations for a stationary, fixed volume fluid particle. A simulation corresponding to each shock tube experiment was performed for every applicable reaction mechanism with initial conditions consisting of the gas mixture composition, post-shock pressure, and post-shock temperature. The evolution of temperature, temperature rate of change, and some species for one constant volume explosion simulation are presented in Figs. 3-4. The end of the induction period is defined as the time corresponding to the maximum rate of temperature change, and is approximately the time of maximum OH concentration. Absolute and relative numerical tolerance constraints of 1x10^{-9} and 1x10^{-10}, respectively, were imposed on the integrator for all simulations. These tolerances were varied over three orders of magnitude to check the effect of numerical integration error on the calculated induction time. Maximum deviations of ±10% were found for the longest induction times.

Imposing a constant volume constraint decreases the induction time due to elevated thermal energy which would otherwise be accounted for by expansion of the reacting fluid. This constraint becomes more realistic as the reaction time decreases relative to the expansion time. Given post-shock acoustic speeds of 700-1000m/s and reaction length scales of millimeters to centimeters (representative of conditions found in shock tube experiments), characteristic expansion times are on the order of 1-100μs. The constant volume approximation is further aided by high diluent concentration limiting the pressure and temperature rise (within 1.5% of the initial values for the case of Figs. 3-4).

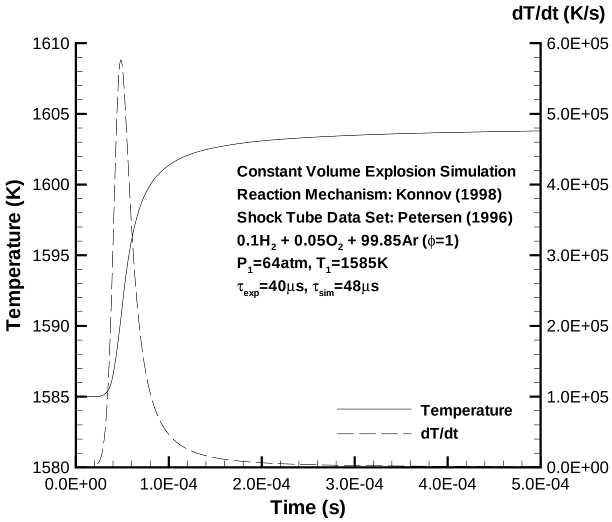

Figure 3. Temperature and temperature rate of change evolution for representative constant volume explosion simulation

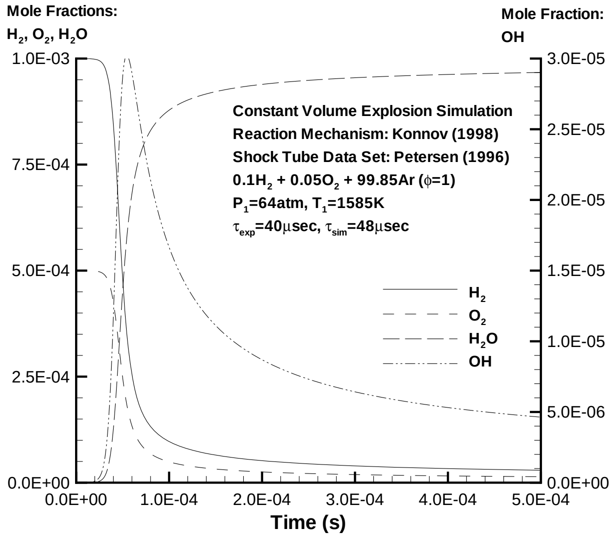

Figure 4. Species evolution for representative constant volume explosion simulation

The constant volume approximation can be evaluated by considering it to provide a lower induction time bound, with a constant pressure process representing an upper bound. Constant pressure explosion simulations were conducted to quantitatively assess the constant volume approximation. The maximum discrepancy, defined by the logarithm of the ratio of the constant pressure to the constant volume induction time, between the two types of simulations was 0.23. As anticipated from one-step chemistry induction time analysis, this discrepancy represents a factor close to the ratio of specific heats.

2.3. Validation results

The constant volume explosion simulation induction time data was compared to the experimental data for all reaction mechanisms and shock tube data conditions. The statistical average error between simulated and experimental induction time data is defined by

$$\mathrm{AverageError} = \frac{1}{\mathrm{N}} \sum_{\mathrm{i=1}}^{\mathrm{N}} \log\left(\frac{\tau_{\mathrm{s,i}}}{\tau_{\mathrm{e,i}}}\right) \qquad (1)$$

where $\tau_{s,i}$ is the i-th simulated induction time, $\tau_{e,i}$ is the i-th experimental induction time, and N is the total number of data points for the particular reaction mechanism, fuel, and temperature range under consideration. A value of 1.0 indicates that the simulated induction times were on average an order of magnitude greater than the experimental induction times. Figure 5 is a plot of the average error versus temperature range for the Konnov (1998) reaction mechanism. The error bars indicate one standard deviation of the average error, representing the range in which 70% of the error lies on a point-by-point comparison basis.

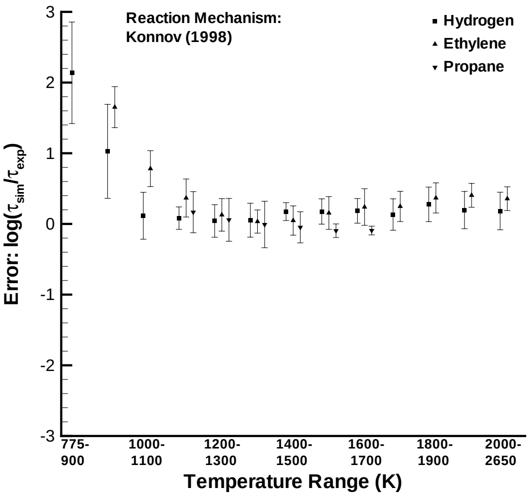

Figure 5. Induction time comparison between constant volume explosion simulations with Konnov (1998) reaction mechanism and shock tube experiments

Simulations with all mechanisms typically overpredict the induction time at all temperatures and follow a decreasing error trend as the temperature increases, regardless of the type of fuel. The Konnov (1998) mechanism exhibited the lowest error over the broadest range of temperatures among the mechanisms which were applicable to all three fuels. The average error provides a quantitative assessment of the accuracy of the mechanism in simulating the chemistry for a particular subset of shock tube conditions. However, the average error presented includes errors associated with experiments, the constant volume gasdynamic model, numerical integration, and the reaction mechanism. The present effort has quantified all of these errors to some extent, and can be summarized as follows for the Konnov (1998) mechanism results.

Numerical integration error was found to be negligible relative to the other error sources at all temperatures. The experimental scatter and constant volume approximation errors for temperatures below 1200K are significantly less than the error between simulated and experimental induction times, indicating that the chemistry is not accurately described by the reaction mechanism. At temperatures above 1200K the experimental and constant volume approximation errors are on the order of the error between simulated and experimental induction times, providing confidence that the reaction mechanism accurately describes the chemistry. Simulated induction times were no greater than an average factor of 1.25 above the experimental induction times at these temperatures.

3. Detonation simulations

Simulations were conducted for ZND detonation waves to obtain the reaction zone structure (evolution of species, velocity, and thermodynamic variables) and characteristic reaction time scales. The FORTRAN program is based on the steady, one-dimensional reactive Euler equations and utilizes the same chemical kinetics package and stiff ordinary differential equation integrator as the constant volume explosion code. Initial conditions consist of the mixture composition, atmospheric initial pressure and temperature, and V_{CJ} shock velocity. The validated reaction mechanism of Konnov (1998) was used for all simulations. Parameters varied include fuel (hydrogen, ethylene, propane), equivalence ratio, diluent (argon, carbon dioxide, helium, nitrogen), and diluent concentration. All but a few of the simulations involved post-shock temperatures within the validation range (above 1200K) where the simulated to experimental induction times were found to be within a factor of 1.25.

The reaction time is defined as the time from the shock to the maximum temperature gradient. This value is plotted versus equivalence ratio for fuel/oxygen and fuel/air mixtures in Fig. 6. Reaction times for the fuel/air mixtures exhibit a minimum near stoichiometric, sharply increase towards the lean side, and gradually rise for rich conditions. Fuel/oxygen mixture curves are relatively flat, with almost all reaction times less than 1μs. There is a clear hierarchy of reaction times in the fuel/air mixtures, increasing from hydrogen to ethylene and finally propane, which depends upon the equivalence ratio for the fuel/oxygen mixtures.

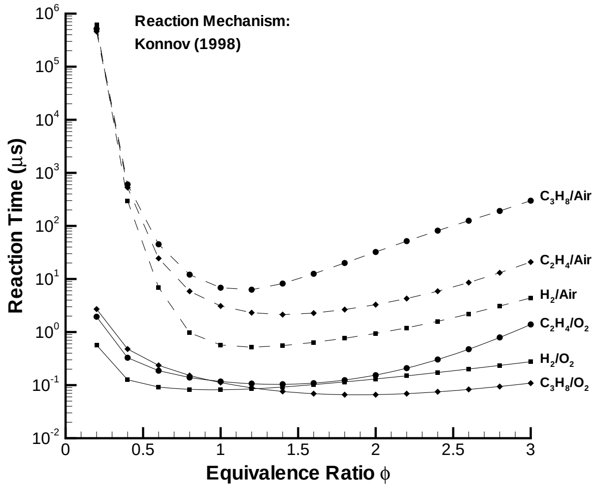

Figure 6. Steady, one-dimensional detonation reaction times for fuel/oxygen and fuel/air mixtures at atmospheric initial conditions with varying equivalence ratio

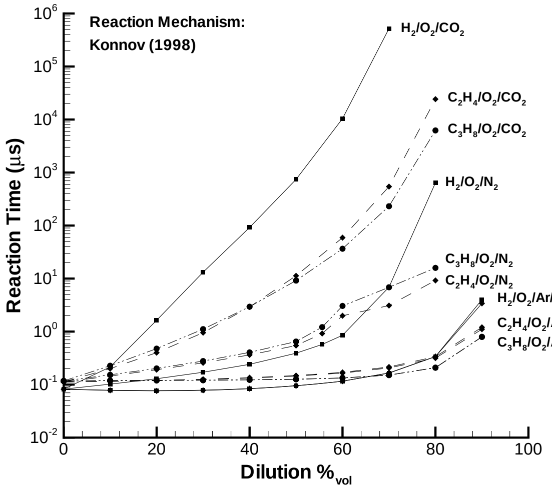

Figure 7. Steady, one-dimensional detonation reaction times for stoichiometric fuel/oxygen/diluent mixtures at atmospheric initial conditions with varying dilution

The reaction time versus percent diluent data for stoichiometric mixtures are presented in Fig. 7. Hydrogen is the most sensitive fuel to dilution. The argon and helium diluents have a thermal inhibiting effect and are quantitatively identical in their effect on the reaction time. Addition of these monatomic gases to a fuel/oxygen mixture decreases the energy release, decreases the heat capacity, and raises the post-shock temperature over a wide range of dilution, maintaining relatively constant reaction time over the same range. Carbon dioxide increases the reaction time most significantly for all fuels, followed by nitrogen. The effect of carbon dioxide is primarily thermal, as shown by Shepherd (1986) in which the thermal and kinetic effects of this diluent were investigated. The almost exact correspondence of reaction times computed with mechanisms with and without nitrogen as a chemically active species indicates that nitrogen also has primarily a thermal effect.

Constant volume explosion simulations can be used to estimate effective activation energies which are indicative of the reaction zone sensitivity to thermodynamic perturbation. Assuming that the global chemical behavior can be represented by an Arrhenius induction time expression, the effective activation energy parameter (θ) is defined by

$$\theta = \frac{E}{RT_{vN}} = \frac{1}{T_{vN}} \left(\frac{\ln \tau_2 - \ln \tau_1}{\frac{1}{T_2} - \frac{1}{T_1}} \right) \tag{2}$$

where E/R is the effective activation temperature, T_{vN} is the post-shock temperature, and two constant volume explosion simulations corresponding to (T_1,τ_1) and (T_2,τ_2) are run for each data point. Initial conditions are generated by varying the shock velocity off V_{CJ} by ±1% to perturb the post-shock thermodynamic conditions. Activation parameters resulting from shock velocity perturbations of ±2% were within 5obtained with the ±1% variation for most cases.

Activation energy parameters are plotted versus equivalence ratio for fuel/oxygen and fuel/air mixtures in Fig. 8. Activation parameters are generally greater for fuel/air mixtures relative to the corresponding fuel/oxygen mixture. Hydrogen mixtures exhibit minimum activation parameters near the stoichiometric condition which increase in the lean and rich directions. Ethylene mixtures have a minimum on the rich side, while propane mixtures demonstrate more complex activation parameter behavior and exhibit no such tendency.

The activation parameters versus percent diluent data for stoichiometric mixtures are presented in Fig. 9. Dilution of these mixtures with argon or helium has the same quantitative effect and results in a slight decrease (10% maximum) of the activation parameter, due to competition between activation temperature and post-shock temperature which both tend to increasing with diluent concentration. Carbon dioxide and nitrogen diluents significantly increase the activation parameter of all mixtures, while the concentration of diluent required to raise the activation parameter and magnitude by which it is increased varies greatly between the three fuels. Note that these two diluents result in complex variations in activation parameter behavior and do not always monotonously increase the activation parameter.

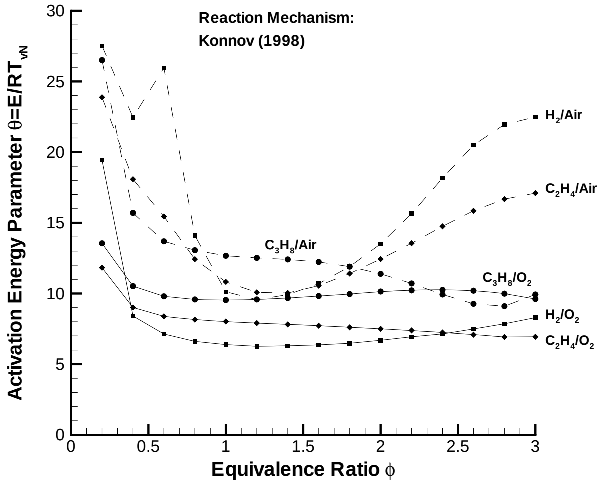

Figure 8. Effective detonation activation parameters for fuel/oxygen and fuel/air mixtures at atmospheric initial conditions with varying equivalence ratio

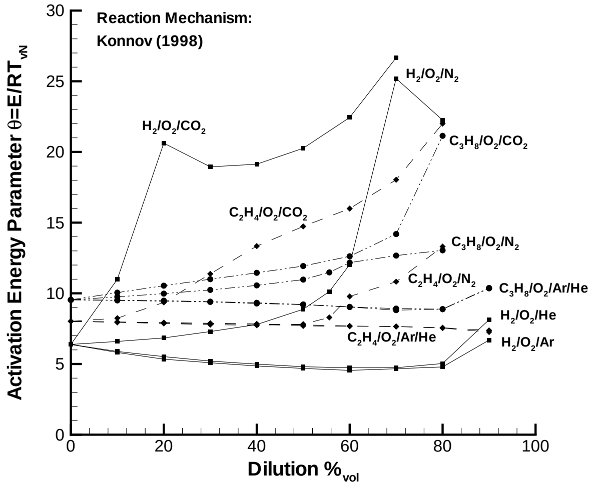

Figure 9. Effective detonation activation parameters for stoichiometric fuel/oxygen/diluent mixtures at atmospheric initial conditions with varying dilution

4. Conclusions

A comprehensive detailed reaction mechanism validation has been conducted for hydrogen, ethylene, and propane fuel oxidation through the comparison of constant volume explosion simulation and experimental shock tube induction time data. Uncertainties associated with the experimental data, numerical integration, the constant volume approximation, and the reaction mechanism chemistry have been elucidated. The Konnov (1998) mechanism simulated the experimental induction time data to within an average factor of 1.25 for temperatures above 1200K.

Steady, one-dimensional detonation and constant volume explosion simulations were performed with the validated reaction mechanisms to provide the reaction zone structure, reaction time scales, and effective activation energies for hydrogen, ethylene, and propane mixtures under a variety of conditions. Reaction time and activation energy data along with discussion of trends have been presented for a wide range of equivalence ratio and diluent type and concentration.

Future work in the area of detailed reaction mechanism validation will include parametric investigations of the existing shock tube database and extension to other hydrocarbon fuels. Additional shock tube data is required at detonation post-shock thermodynamic conditions for all fuels, and experimental uncertainties should be extensively addressed. Finally, unsteady one-dimensional simulations with detailed reaction mechanisms will be the next computational milestone to achieve for more accurate validation efforts.

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