

A Global 4-Step Combustion Modelling Strategy for Hydrogen and Blends of Hydrogen and Natural Gas

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1 Introduction

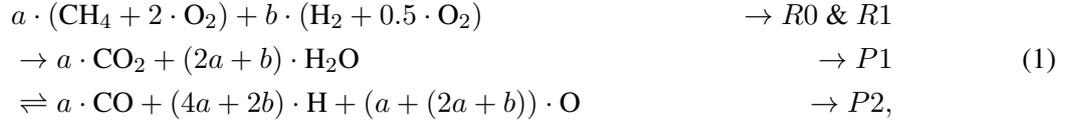
At present, about a third of North America's energy needs are met by natural gas [1]. End uses include a broad range of applications from electricity generation, heating for buildings, and transportation. It is believed that greenhouse gas emissions can be reduced significantly by adopting hydrogen as an energy carrier, or by blending hydrogen with natural gas [2, 3]. Through blending, there is a potential benefit to use existing infrastructure and appliances to deploy, transport, and use hydrogen on a large-scale. Fundamental research is therefore needed to study the safety aspects of how unintended flames in both pure hydrogen-air, and blended mixtures can accelerate and transition to detonation. At the University of Ottawa, research is being carried out to address key knowledge gaps in understanding how flames in blended reactive mixtures involving natural gas and hydrogen can transition to detonation, and what physical parameters control their behaviour and transition to detonation limits. This is being addressed by performing a combination of numerical simulations and experiments, as detailed in two other papers of this conference series [4, 5]. A key aspect of our work is to address the numerical difficulties and challenges of modelling high speed combustion that involve blends of hydrogen and natural gas, of which multi-dimensional simulations can be prohibitively expensive and unattainable unless reduced chemical modelling efforts are undertaken.

In this work, we extend the global 4-step combustion modelling approach of Zhu et al. [6], originally developed for acetylene combustion, to include combustion of fuels that involve blends of hydrogen and methane. Using this approach, our group has recently demonstrated its success at efficiently modelling combustion involving other typical hydrocarbon fuels such as methane, propane, and ethylene [7]. The method was found particularly useful for simulating detonation quenching and re-initiation in methane–oxygen, and was demonstrated to recover experimental observations and key features of the flow field evolution [8]. However, at the time of our previous work, we did not believe this 4-step model could work for hydrogen–oxygen combustion, which we blamed on the significant presence of reactant in the product equilibrium group [7]. In this work, we address the particular challenges of developing a global 4-step combustion model approach for stoichiometric hydrogen combustion using Zhu's method, and assess the performance of the modelling approach. This is in-line with other recent efforts to develop low-cost combustion modelling strategies to study hydrogen detonation dynamics, such as the 3-step chain-branching model approach of Watanabe et al. [9]. What sets the current 4-step global reaction modelling approach apart from other global reaction models is that once it is calibrated to a given mixture composition, there is no need to recalibrate the model for different thermodynamics states.

2 The 4-Step Combustion Model Approach

In the 4-step combustion model approach, we consider only the evolution of 4 reactive global species, namely R_0 , R_1 , P_1 , and P_2 . For the purpose of our investigation into blends of hydrogen–methane, we

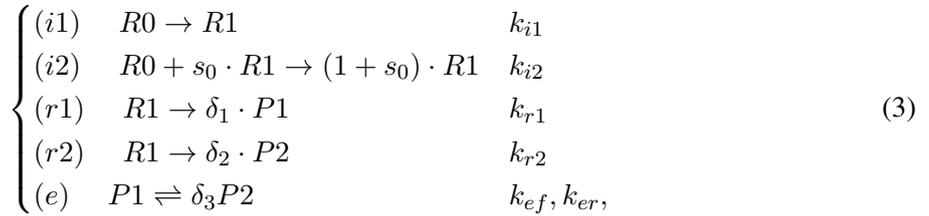
generalize the four species as



where a stoichiometric fuel blend ratio (FBR) is defined by

$$\text{FBR} = \frac{X_{\text{H}_2}}{X_{\text{H}_2} + X_{\text{CH}_4}} = \frac{b}{a + b}, \tag{2}$$

where X refers to the mole fraction of the species indicated. The reaction paths, and corresponding reaction rates and orders, were acquired by modeling the reaction as having two thermally neutral induction regime paths, two irreversible exothermic reaction paths that convert R to $P1$ and $P2$ separately, and an additional equilibrium step between $P1$ and $P2$. The reaction scheme can be summarized as



where the absolute reaction rate constants k_{i1} , k_{i2} , k_{r1} , k_{r2} , k_{ef} , and k_{er} depend on the local thermal state of the mixture, while the stoichiometry coefficients are: $\delta_1 = W_R/W_{P1}$, $\delta_2 = W_R/W_{P2}$, $\delta_3 = W_{P1}/W_{P2}$, where W_i is the molecular weight of the i th species group, and s_0 is the reaction order of the induction step. The species $R1$ in the model plays the role of an activated reactant meant to replace the numerous radicals and intermediate species that are formed during a typical combustion process from reactants to products. Complete details of the combustion model, including the calibrated parameters and model performance at capturing zero- and one-dimensional combustion problems for typical hydrocarbon fuels, are found elsewhere [6, 7]. In this study, the models have been calibrated to the Foundational Fuel Chemistry (FFCM) version 1.0 reaction model [10], whose application is intended to be used for both hydrogen and methane combustion.

3 Challenges Extending the Model to Hydrogen

In general, the procedure for calibrating the blended fuel mixtures, $\text{FBR} < 1$, was a straight forward procedure as previously documented [6, 7]. However, for calibration to $\text{FBR} = 1$, the first challenge encountered was in determining an equilibrium solution at constant temperature and density for species R , $P1$ and $P2$. The system of equations that must be solved to determine the equilibrium state is given by

$$\begin{bmatrix} H_R & H_{P1} & H_{P2} \\ W_R & W_{P1} & W_{P2} \\ 1 & 1 & 1 \end{bmatrix} \cdot \begin{bmatrix} X_R \\ X_{P1} \\ X_{P2} \end{bmatrix} = \begin{bmatrix} H \\ W \\ 1 \end{bmatrix}, \tag{4}$$

or equivalently the system of equations $\mathbf{Ax} = \mathbf{b}$. Here, the molar enthalpy (H) and molecular weight (W) of the mixture are determined by the detailed reaction mechanism using Cantera [11]. We found that as $\text{FBR} \rightarrow 1$, a significant amount of R was present in the equilibrium of products, which we originally assumed was a limitation of the model. At the time, we used the `numpy.matrix` python class to perform matrix inversion to obtain the solution vector $\mathbf{x} = \mathbf{A}^{-1}\mathbf{b}$, which was found to produce negative and greater than unity solutions for some mole fractions, especially at high temperatures and densities. This is shown in Fig. 1a. To address this issue, we instead chose to perform the matrix inversion using

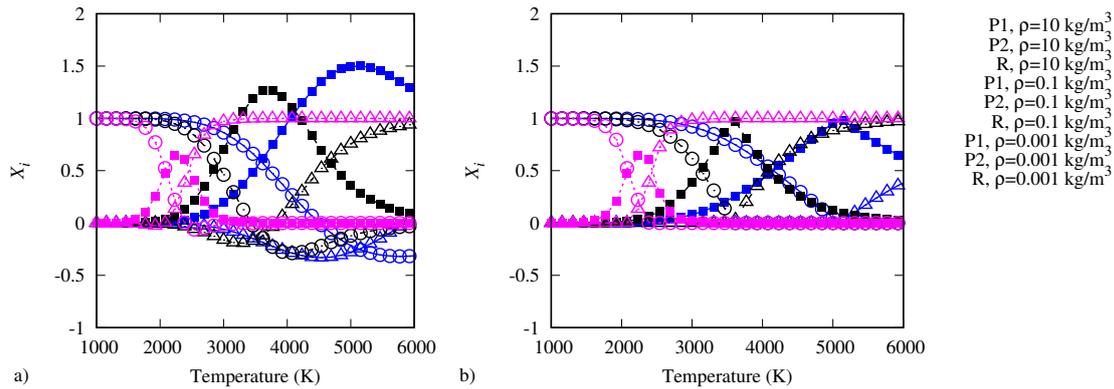


Figure 1: Equilibrium mole fractions for $FBR = 1$ found using a) the `numpy.matrix` python class vs. b) least square minimization method found in the `scipy.optimize` class.

the least square minimization in the `scipy.optimize` class, where bounds on the solution vector can be enforced, i.e. $0 \leq x \leq 1$. Figure 1b shows the resulting equilibrium solutions for R , $P1$, $P2$. Using this approach, X_R can then be redistributed equally into X_{P1} and X_{P2} , which permits the calibration of the equilibrium reaction rates, k_{ef} and k_{er} , following the usual approach [6]. We do note, however, that the redistribution of R may likely lead to some error in the equilibrium products enthalpy or molecular weight. At present, we estimate that errors in predicted H and W are generally within 1%, but enthalpy errors can also be as high as 10 to 100% when the equilibrium $X_R \rightarrow 1$.

The next major challenge encountered in developing the model parameters for $FBR = 1$ was to ensure that the presence of the k_{r2} reaction didn't produce nonphysical endothermic reactions. When calibrating the reaction rates, we found that at the lowest densities and initial temperatures, even small magnitudes of k_{r2} at the start of a reaction could cause it to go endothermic rather than exothermic. Our solution to overcome this problem was to simply set $k_{r2} = 0$ in the low temperature region, when $T < 2500$ K. This cut-off function is shown with respect to our curve fits in Fig. 2. Once the reaction rates were appropriately calibrated, the induction reaction rate, k_i , was calibrated following the usual approach [6].

4 Model Characteristics

Upon appropriate calibration of the equilibrium, reaction, and induction rates, the model was able to reproduce the expected ignition delay times across a wide range of initial temperatures and densities of

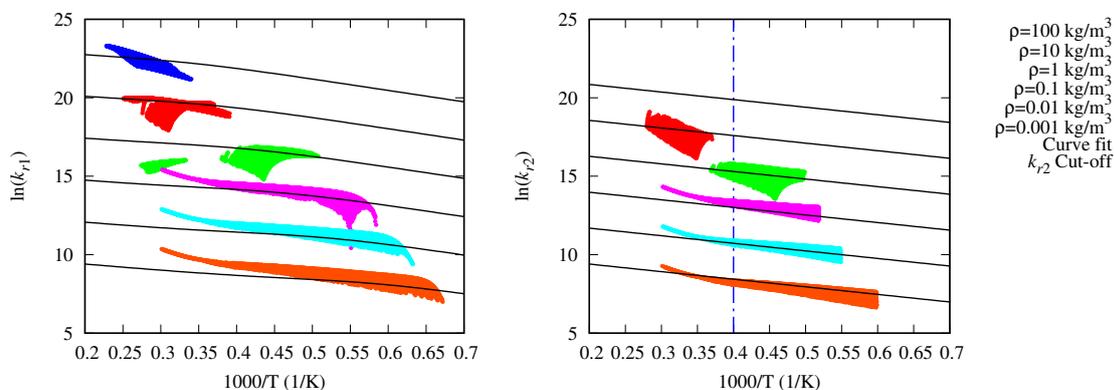


Figure 2: Reaction rates for $FBR = 1$ and the temperature and density dependent curve-fits for a) k_{r1} and b) k_{r2} .

interest ($700 \leq T \leq 2500$ K and $0.001 \leq \rho \leq 100$ kg/m³), as shown in Fig. 3a. Also shown in Fig. 3b, is the model ability to capture the induction to reaction time ratio (t_i/t_r) at densities of $\rho \geq 0.01$ kg/m³, well above the range of practical densities in high speed combustion. This ratio is a particular indicator of how well the reaction stiffness is captured in terms of how long the induction period is compared to the exothermic reaction pulse. Moreover, this ratio has been shown to be an important parameter that controls the multidimensional cellular stability of detonation waves [12].

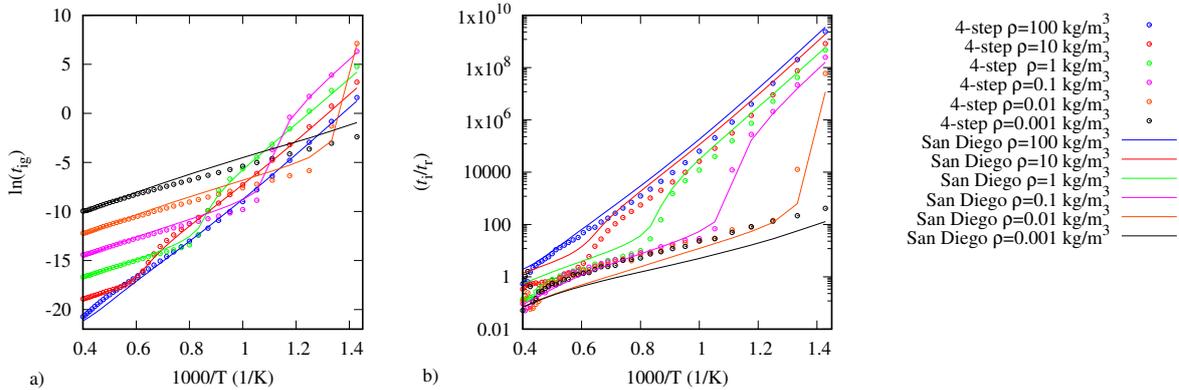


Figure 3: a) Ignition delay times (t_{ig}) and b) induction to reaction time ratio (t_i/t_r) for FBR = 1.

Then, to demonstrate the versatility of the 4-step combustion model approach, the theoretical Chapman-Jouguet (CJ) speeds were calculated using the procedure for several FBR values at $T_0 = 300$ K and a wide range of pressures, using both the 4-step combustion model and detailed reaction mechanisms. The detailed chemistry solutions are obtained using the Shock and Detonation Toolbox libraries [13], while the same applied minimum-wave speed algorithm is used to obtain the four-step model solutions, with the added assumption that only products P1 and P2 exist in equilibrium at the CJ state. In general, the 4-step combustion model captures well the expected CJ-speeds compared to the detailed reaction model. We do note, however, that the 4-step combustion model predictions tended to be about 1% to 2% faster than the value predicted using the detailed reaction mechanism. This difference can be attributed to slight differences in the mixture composition. We also note that our 4-step CJ-solution is based on the frozen sound speed, $c = \gamma RT$, while the solution for the detailed chemistry calculation is based on the evaluation of the equilibrium sound speed in the products.

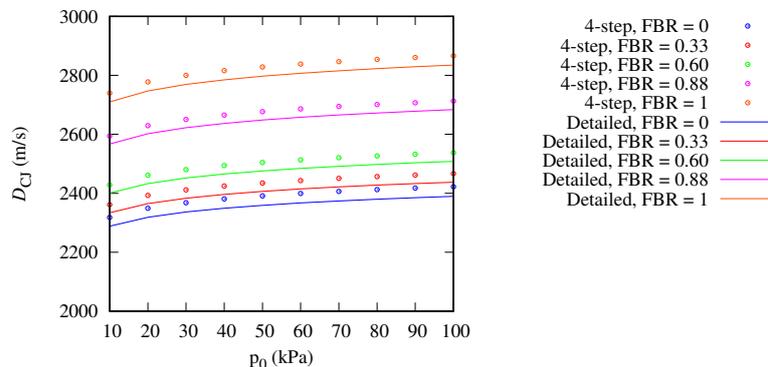


Figure 4: Theoretical Chapman-Jouguet detonation speeds calculated for various FBR and pressures, at $T_0 = 300$ K, using the 4-step combustion model and compared to detailed chemical mechanisms [14, 15].

5 Two-Dimensional Simulations of Hydrogen Detonation Propagation

Finally, to assess the performance of the 4-step model, two-dimensional simulations of detonation propagation were performed for $2\text{H}_2 + \text{O}_2 + 7\text{Ar}$ at $p_0 = 6.67$ kPa, consistent with past simulations of Oran et al. [16]. Here we solve Eulers equations of motion for reactive systems using the 4-step combustion model approach, and compare to a detailed chemistry approach that uses only the relevant hydrogen combustion reactions of the San Diego mechanism [15] (11 species, 23 reactions) - although we expect similar results if using the FFCM-1 mechanism. Specific details of the numerical methods used to simulate detonation waves using these combustion mechanisms are found elsewhere [8, 17]. The domain considered for both simulations is 1.44 m long by 6 cm high, initialized with a ZND profile in the first 3 cm of the domain. Six levels of adaptive mesh refinement was used, where the finest resolution was $117.2 \mu\text{m}$ for both simulations. Both simulations used the same refinement criteria, where cells were refined in zones of density changes between grid levels were in excess of 0.1%. The resulting numerical sootfoil images, obtained by recording locations of maximum pressure, for both simulations are compared in Fig. 5. Clearly, the 4-step model performs well at capturing the expected cellular structure of the wave, in terms of the regularity and the cell size obtained by the end of the domain. In terms of performance, the simulation using the detailed San Diego mechanism took 38.2 hrs to compute on a 16-core AMD Ryzen 9 CPU, while the 4-step model approach only took 11.3 hrs using the same computer and number of cores. Solutions were obtained for both simulations using a total of about 1.2 million computational cells by the time the wave reached near the end of the domain.

6 Conclusion

In this work, we extended the global 4-step combustion modelling approach [6,7] to include combustion of fuels blends involving hydrogen and methane. We were able to address key difficulties in the calibration process as the fuel blend ratio approached that of pure hydrogen–oxygen combustion. The first challenge consisted of using a robust solver for the system of equations applying the appropriate bounds to solving the system of equations that determines the equilibrium state in terms of the global species R , $P1$, and $P2$. The second challenge was to develop a strategy to avoid endothermic reactions from concurring during the production of product group $P2$. Upon addressing these challenges, a model was developed that matched the ignition delay times and induction to reaction time ratios when compared to detailed chemistry. Moreover, the detonation velocities were recovered across the entire range of fuel blend ratios. Finally, two-dimensional simulations were carried out for $2\text{H}_2 + \text{O}_2 + 7\text{Ar}$ at $p_0 = 6.67$ kPa. Here we compared both the 4-step combustion model, calibrated to the FFCM-1 model [10], with

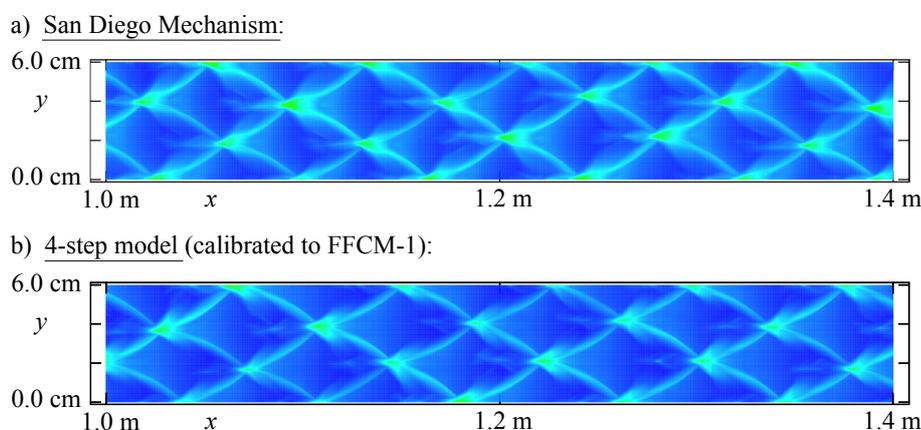


Figure 5: Numerical soot foils for detonation waves propagating in $2\text{H}_2 + \text{O}_2 + 7\text{Ar}$ at $p_0 = 6.67$ kPa, computed using a) the San Diego reaction mechanism [15], and b) the global 4-step combustion model for FBR = 1.

results obtained using the detailed hydrogen portion of the San Diego mechanism [15]. We found that the 4-step combustion modelling approach was more than three times as fast to compute, and recovered the same cellular structure as its detailed chemistry counterpart. However, the real savings is expected for blended fuels, where detailed chemical mechanisms that include hydrocarbon combustion take much longer to compute compared to hydrogen. For example, the FFCM-1 mechanism contains 38 species and 291 reactions, while the complete Konnov mechanism [14] has even more, at 127 species and 1207 reactions. The proposed strategy here thus presents a novel strategy to simulate combustion of blended fuels, where application of detailed chemistry models may be too prohibitive.

This research was supported by UL Research Institutes, and also the Natural Sciences and Engineering Research Council of Canada (NSERC), funding reference number RGPIN-2023-03691. Details of the model parameters are available upon request to the corresponding author.

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