



Chemical kinetic model uncertainty minimization through laminar flame speed measurements



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ABSTRACT

Laminar flame speed measurements were carried for mixture of air with eight C₃₋₄ hydrocarbons (propene, propane, 1,3-butadiene, 1-butene, 2-butene, *iso*-butene, *n*-butane, and *iso*-butane) at the room temperature and ambient pressure. Along with C₁₋₂ hydrocarbon data reported in a recent study, the entire dataset was used to demonstrate how laminar flame speed data can be utilized to explore and minimize the uncertainties in a reaction model for foundation fuels. The USC Mech II kinetic model was chosen as a case study. The method of uncertainty minimization using polynomial chaos expansions (MUM-PCE) (Sheen and Wang, 2011) was employed to constrain the model uncertainty for laminar flame speed predictions. Results demonstrate that a reaction model constrained only by the laminar flame speed values of methane/air flames notably reduces the uncertainty in the predictions of the laminar flame speeds of C₃ and C₄ alkanes, because the key chemical pathways of all of these flames are similar to each other. The uncertainty in model predictions for flames of unsaturated C₃₋₄ hydrocarbons remain significant without considering fuel specific laminar flame speeds in the constraining target data set, because the secondary rate controlling reaction steps are different from those in the saturated alkanes. It is shown that the constraints provided by the laminar flame speeds of the foundation fuels could reduce notably the uncertainties in the predictions of laminar flame speeds of C₄ alcohol/air mixtures. Furthermore, it is demonstrated that an accurate prediction of the laminar flame speed of a particular C₄ alcohol/air mixture is better achieved through measurements for key molecular intermediates formed during the pyrolysis and oxidation of the parent fuel.

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1. Introduction

Reliable chemical kinetic models for the combustion of foundation fuels are a key component towards rational design of practical combustors. The hierarchical nature of combustion chemistry means that the high-temperature reactions of a basis set compounds, including H₂, CO, and C_{*n*}H_{*m*}, form the kinetic foundation for the combustion reactions of higher hydrocarbons. Here, *n* is typically around four [1] although, depending on the fuel structure and composition, aromatic species such as benzene and toluene, may also belong to this set of species. This set of fuels will be referred to as the foundational fuels, and a corresponding reaction model is called foundational fuel chemistry model. During

the combustion of large hydrocarbons, foundational fuel species are formed as intermediates; their oxidation is usually the rate controlling process.

Flame properties of H₂, CO, and C₁₋₂ hydrocarbons have been intensively studied over the last several decades (e.g., [2–6]). Efforts that use laminar flame speeds, *S*_{*l*}⁰, or other global combustion properties to test kinetic models have even a longer history (e.g., [7–14]). The chemistry of C₃₋₄ unsaturated hydrocarbons has also garnered attention [3]. These species are often the key intermediates in high-temperature oxidation of large hydrocarbons (e.g., [15,16]) and bio-derived alcohols (e.g., [17–19]). It has been demonstrated, for example, that uncertainties in the reaction kinetics of intermediates, such as *iso*-butene (*i*-C₄H₈) and propene (C₃H₆) can impact model predictions of *iso*-octane combustion properties [15,16]. In the oxidation of *iso*- and *tert*-butanol, *i*-C₄H₈ was found to be one of the key intermediates (e.g., [19,20]); and our ability

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to predict the flame properties of these alcohols relies on the accuracy of chemistry specific to $i\text{-C}_4\text{H}_8$ and reactions of H_2/CO species.

Reaction model development proceeds in two initial steps. A set of reactions and their rate parameters is compiled first. The model is then tested against a set of experimental measurements. For every rate parameter, there exists an associated uncertainty [21], which collectively manifests either as uncertainties in the model prediction of a combustion phenomenon or as quantitative experiment-model disagreements [22]. In practice, the as-compiled model is often tuned to bring predictions and measurements into agreement, and in a vast majority of instances the tuning is performed in an ad hoc manner. In most cases, the experimental datasets chosen for validation cover too small a thermodynamic condition space [23], and different modeling studies often use different experimental measurements that may or may not overlap each other. For this reason there still exist large discrepancies in predictions made by available reaction models even for the most basic combustion properties such as S_u° [24]. For large fuels, the matter is complicated by the fact that when experiment-model discrepancy arises, it is often difficult to assess the cause for such discrepancy owing to difficulties in isolating the uncertainties that can originate from the fuel specific kinetics and the foundation fuel chemistry. Here, fuel specific kinetics refers to pathway and rates of the parent fuel outside the foundational fuel chemistry set.

To effectively isolate the uncertainties in the fuel specific kinetics and foundation fuel chemistry, it is essential to first understand and minimize the contribution of kinetic uncertainties derived from the foundation model. Within this foundation fuel chemistry model the oxidation kinetics of unsaturated hydrocarbons have been studied to a far lesser degree than straight chain n -alkanes. The purpose of the present study is to supplement the earlier works [24,25], as it presents a self-consistent set of S_u° data of 12 relevant C_{1-4} hydrocarbons. Specifically, measurements were made for S_u° of mixtures of eight hydrocarbons with air at atmospheric pressure. These are C_3H_6 , propane (C_3H_8), 1,3-butadiene (1,3- C_4H_6), 1-butene (1- C_4H_8), 2-butene (2- C_4H_8), $i\text{-C}_4\text{H}_8$, n -butane ($n\text{-C}_4\text{H}_{10}$), and $iso\text{-butane}$ ($i\text{-C}_4\text{H}_{10}$). Comparisons were made against archival data [2–4,24–32]. Moreover, we demonstrate how this set of experiments can be used to constrain foundation fuel chemistry models, using USC Mech II [33] as the test case of this demonstration.

The Method of Uncertainty Minimization using Polynomial Chaos Expansions (MUM-PCE) [23,34] was applied to constrain the aforementioned kinetic model with the intent to better understand the role of S_u° measurements in model uncertainty constraining. Utilizing the experimental S_u° datasets, several questions critical to the utility of the S_u° data were explored. Firstly, the consistency of various sets of experimental data is addressed in the context of situations where large discrepancies can exist between experimental results for the same combustion phenomena. Next, the discrepancies in the available S_u° data and their impact are discussed. Finally, we examine the question of which set of experimental data considered provides the most critical quantitative information to predicting a flame phenomenon of a fuel outside of the current experimental target sets, using flames of butanol isomers as test cases.

It should be noted that there are many discrepancies among the available experimental S_u° data. The scatters in literature data are, in fact, generally larger than the uncertainties reported in the respective publications. It is beyond the scope of this paper to make substantive arguments about which of these measurements is correct. Rather, the focus of this paper is on finding a measurement set that is self-consistent, based on our best current understanding of the measured values and the uncertainty in those measurements, and then determining how the data set and its uncertainty impact the reaction model.

2. Experimental method

All S_u° measurements were carried out in the counterflow configuration at atmospheric pressure, $p = 1$ atm and at an unburned reactant temperature, $T_u = 298$ K. The burner nozzle diameters and nozzle-to-nozzle separation distance were both 1.4 cm. S_u° 's were determined using the twin-flame technique [35,36] over a wide range of equivalence ratios, ϕ . Flow velocities were measured using particle image velocimetry. The flow was seeded with droplets of silicone oil by a high efficiency nebulizer. The minimum axial flow velocity upstream of the flame was defined as the reference flame speed, $S_{u,\text{ref}}$, and the maximum absolute value of the velocity gradient upstream of the flame is defined as the strain rate, K . S_u° 's were determined through nonlinear extrapolations of $S_{u,\text{ref}}$ to $K = 0$ using a computationally-assisted approach [37]. Samples of the extrapolation method are presented in Fig. S1 of the Supplementary material (SPM).

The purities of hydrocarbon reagents used were 99.0%. To determine S_u° 's of 2- C_4H_8 /air mixtures, a mixture of 70% $cis\text{-}2\text{-C}_4\text{H}_8$ and 30% $trans\text{-}2\text{-C}_4\text{H}_8$ was used. With the exception of C_4 hydrocarbons, sonic nozzles were used to meter the mass flow rates of gases. The C_4 hydrocarbons were metered using Teledyne Hastings mass flow controllers. Both sonic nozzles and mass flow controllers were calibrated using a wet gas meter, a soap bubble flow meter, or a DryCal meter which has an accuracy better than 1%. Uncertainties in S_u° 's were determined by the 2σ standard deviations of $S_{u,\text{ref}}$'s based on sampling errors in $S_{u,\text{ref}}$, and have been discussed in an earlier study [38]. In general the uncertainties for fuel lean and rich mixtures are larger than those for near-stoichiometric mixtures. Overall, the uncertainty in ϕ was determined to be within 1%.

3. Reaction models

Primary analyses were carried out using USC Mech II [33]. The reaction model consists of 111 species and 784 elementary reactions, and describes the high temperature oxidation kinetics of H_2/CO and $\text{C}_1\text{-C}_4$ hydrocarbons. The model has been tested against shock-tube ignition delay times, S_u° 's, and speciation measurements in flow reactors, shock tubes, and burner stabilized flames for a wide range of small hydrocarbon fuels, including benzene and toluene. Although a systematic optimization was made for the H_2/CO kinetic subset [39], USC Mech II as a whole is not tuned to fit specific sets of data. For the current optimization study, the rate parameters of the H_2/CO subset were restored to their nominal values listed in Ref. [39]. Additionally, the rate parameter for $\text{OH} + \text{HO}_2 \leftrightarrow \text{H}_2\text{O} + \text{O}_2$ was revised using the expression of Baulch et al. [40], which was shown to represent more accurately the experimental studies [41,42]. For the reaction $\text{H} + \text{O}_2 + \text{M} \leftrightarrow \text{HO}_2 + \text{M}$, the collision efficiency of H_2O was taken to be an active, optimization parameter.

The reaction model just described is referred to as the unconstrained or prior model. Uncertainty factors for the Arrhenius pre-factors in USC Mech II are provided in the supplementary material of Ref. [34]. These factors were taken either in consultation with literature (e.g., [40,43]) or through evaluation [23,34]. The coupled uncertainty in the activation energy and the pressure fall-off parameters was not considered in the present work.

Several representative literature models (summarized in Table 1) were chosen to demonstrate the degree of spread in S_u° predictions by literature models. In all cases, these are some of the well-documented and frequently used reaction models. Unless otherwise indicated, we shall use the abbreviated names for these models in discussion thereafter.

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