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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) (D.A. Sheen and H. Wang, Combust. Flame 2011, 158, 2358–2374) 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 flames 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.

Keyword: Laminar flame speeds, uncertainty quantification, kinetics, chemical model development, alkanes, alkenes

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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 H_2 , CO , and C_nH_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 H_2 , CO , and C_{1-2} hydrocarbons have been intensively studied over the last several decades (e.g., [2-6]). Efforts that use laminar flame speeds, S_u° , or other global combustion properties to test kinetic models have even a longer history (e.g., [7-14]). The chemistry of C_{3-4} unsaturated hydrocarbons has also garnered attention. 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 ($i\text{-C}_4\text{H}_8$) and propene (C_3H_6) can impact model predictions of *iso*-octane combustion properties [15, 16]. In the oxidation of *iso*- and *tert*-butanol, $i\text{-C}_4\text{H}_8$ was found to be one of the key intermediates (e.g., [19, 20]); and our ability 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*- C_4H_8 , *n*-butane ($n-C_4H_{10}$), and *iso*-butane (*i*- C_4H_{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.

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5 Firstly, the consistency of various sets of experimental data is addressed in the context of
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7 situations where large discrepancies can exist between experimental results for the same
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9 combustion phenomena. Next, the discrepancies in the available S_u° data and their impact are
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11 discussed. Finally, we examine the question of which set of experimental data considered
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13 provides the most critical quantitative information to predicting a flame phenomenon of a fuel
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15 outside of the current experimental target sets, using flames of butanol isomers as test cases.
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18 It should be noted that there are many discrepancies among the available experimental S_u°
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20 data. The scatters in literature data are, in fact, generally larger than the uncertainties reported in
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22 the respective publications. It is beyond the scope of this paper to make substantive arguments
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24 about which of these measurements is correct. Rather, the focus of this paper is on finding a
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26 measurement set that is self-consistent, based on our best current understanding of the measured
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28 values and the uncertainty in those measurements, and then determining how the data set and its
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30 uncertainty impact the reaction model.
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33 34 35 **2. Experimental Method**

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37 All S_u° measurements were carried out in the counterflow configuration at atmospheric
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39 pressure, $p = 1$ atm and at an unburned reactant temperature, $T_u = 298$ K. The burner nozzle
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41 diameters and nozzle-to-nozzle separation distance were both 1.4 cm. S_u° 's were determined
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43 using the twin-flame technique [35, 36] over a wide range of equivalence ratios, ϕ . Flow
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45 velocities were measured using particle image velocimetry. The flow was seeded with droplets of
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47 silicone oil by a high efficiency nebulizer. The minimum axial flow velocity upstream of the
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49 flame was defined as the reference flame speed, $S_{u,\text{ref}}$, and the maximum absolute value of the
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51 velocity gradient upstream of the flame is defined as the strain rate, K . S_u° 's were determined
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53 through nonlinear extrapolations of $S_{u,\text{ref}}$ to $K = 0$ using a computationally-assisted approach [37].
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55 Samples of the extrapolation method are presented in Fig. S1 of the Supplementary Material
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57 (SPM).
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The purities of hydrocarbon reagents used were 99.0%. To determine S_u° 's of 2-C₄H₈/air mixtures, a mixture of 70% *cis*-2-C₄H₈ and 30% *trans*-2-C₄H₈ was used. With the exception of C₄ hydrocarbons, sonic nozzles were used to meter the mass flow rates of gases. The C₄ 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 H₂/CO and C₁-C₄ 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 H₂/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 H₂/CO subset were restored to their nominal values listed in Ref. [39]. Additionally, the rate parameter for OH + HO₂ $\leftrightarrow$ H₂O + O₂ 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 H + O₂ + M $\leftrightarrow$ HO₂ + M, the collision efficiency of H₂O 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.

4. Computational Details

MUM-PCE was employed to evaluate the prior model against experimental datasets of S_u° 's of mixtures of C₁-C₄ hydrocarbons with air. The model was represented by a multivariate polynomial response surface at each selected experimental condition. The reaction pre-factors were ranked in order of their uncertainty-weighted sensitivity coefficients for each experimental target. S_u° 's were computed using the PREMIX code [50] along with the Sandia CHEMKIN [51] and the transport subroutine libraries [52]. The transport parameters were based on an updated library with changes made to the binary diffusion coefficients involving H and H₂ [53, 54]. The computations used windward differencing and multicomponent transport formulations with at least 600 adaptive grid points to cover a computational domain of 15 cm.

Prediction uncertainty was quantified by the stochastic spectral expansion method [55-57] and the model was constrained by experimental data. It should be noted that the model posterior uncertainty space strongly depends on the uncertainties of the experimental measurements [23]. The posterior model uncertainties were quantified by MUM-PCE, which has been discussed extensively in previous work [22, 23, 34]. Briefly, each rate coefficient is normalized as a factorial variable [21],

$$x_i = \frac{\ln(k_i / k_{i,0})}{\ln f_i}, \quad (1)$$

where k_i is the rate coefficient of the i^{th} reaction, $k_{i,0}$ is its nominal value, and f_i is its span or the uncertainty factor of the rate coefficient. Thus $x_i = 0$ represents the nominal rate value, and $x_i = -1$ and $+1$ are the lower $k_i = k_{i,0} / f_i$ and upper $k_i = k_{i,0} \times f_i$ bounds of uncertainty in $k_{i,0}$, respectively. In this formulation, simple multipliers for Arrhenius pre-factors were treated, although temperature and pressure dependence in the rate expression may be important for consideration. In the current work, these dependencies were not considered because the S_u° targets do not give enough resolution to warrant such an exercise.

In MUM-PCE, the kinetic parameter and its associated uncertainty is expressed as a polynomial expansion of m basis random variables,

$$x_i = x_i^{(0)} + \sum_{j=1}^m \alpha_{ij} \xi_j, \quad (2)$$

where α_i is the vector of expansion coefficient, ξ_j is the j^{th} basis variable, m is the number of basis variables considered in the expansion, and $\mathbf{x}^{(0)}$ is the vector of normalized rate coefficients, which are zero for a prior model and can be non-zero upon model optimization.

The solution mapping technique was used to map the solutions of differential equations in the form of an algebraic expansion or a response surface [21]. MUM-PCE assumes that the dependency of flame speed prediction on the factorial variables, $S_u^\circ(\mathbf{x})$, can be approximated by a second-order polynomial [23]:

$$S_u^\circ(\mathbf{x}) = S_{u,0}^\circ + \sum_{i=1}^{N_r} a_i x_i + \sum_{i=1}^{N_r} \sum_{j \geq i}^{N_r} b_{ij} x_i x_j, \quad (3)$$

where $S_{u,0}^\circ$ is the nominal flame speed value and N_r represents the number of active parameters. The coefficients a_i and b_{ij} were determined by a regression test against computational experiments from the Sensitivity-Analysis-Based (SAB) method [58]. The accuracy of the response surface is verified by comparing S_u° calculated using the PREMIX flame code against the calculations made using the polynomial predictions of S_u° . The 45° diagonal line plot shown in Fig. S2 of SPM shows a sample of such response surfaces and demonstrates that the accuracy of the response surface is excellent. The mean error between the response surface prediction and

the directly computed S_u° is $< 0.5 \%$ within the hyper-dimensional space defined by the span values of the respective rate coefficients. The maximum error is well below the uncertainty of the experimental data, as will be discussed later.

Combining solution mapping and spectral expansion methods for uncertainty propagation, Eq. (4) provides the prediction of S_u° of the r^{th} experiment with its associated uncertainty contributed by each rate coefficient uncertainty in the model,

$$S_{u,r}^\circ(\xi) = S_{u,r}^\circ(\mathbf{x}^{(0)}) + \sum_{i=1}^m \hat{a}_{r,i} \xi_i + \sum_{i=1}^m \sum_{j=i}^m \hat{\beta}_{r,ij} \xi_i \xi_j. \quad (4)$$

The model prediction uncertainty σ_r is determined from the coefficients in Eq. (4) as:

$$\begin{aligned} \sigma_r^2(x) &= E\left[\left\{S_{u,r}^\circ(\xi)\right\}^2\right] - E^2\left[S_{u,r}^\circ(\xi)\right] \\ &= \sum_{i=1}^m \hat{\alpha}_{r,i}^2 + 2 \sum_{i=1}^m \hat{\beta}_{r,ii}^2 + \sum_{i=1}^{m-1} \sum_{j=i+1}^m \hat{\beta}_{r,ij}^2. \end{aligned} \quad (5)$$

Due to optimization against the experimental target set, the factorial variables are updated to the values best able to fit the given experimental measurements, denoted as $\mathbf{x}^*$. The best-fit values will have an expansion in terms of the basis random variables:

$$x_i^* = x_i^{(0)*} + \sum_{j=1}^m \alpha_{ij}^* \xi_j. \quad (6)$$

The best-fit factorial variables $\mathbf{x}^{(0)*}$ are found by solving the least-squares optimization problem,

$$\Phi(\mathbf{x}^{(0)*}) = \min_{\mathbf{x}^{(0)}} \left\{ \sum_{r=1}^{N_e} \left[\frac{S_{u,r}^\circ(\mathbf{x}^{(0)}) - S_{u,r}^{\circ, \text{obs}}}{\sigma_r^{\text{obs}}} \right]^2 + \sum_{n=1}^{N_r} \left[\frac{x_n}{\sigma_n} \right]^2 \right\}. \quad (7)$$

In the above equation, $S_{u,r}^{\circ, \text{obs}}$ is the r^{th} flame speed target and σ_r^{obs} its uncertainty, and N_e is the total number of experimental measurements. $\mathbf{x}^{(0)*}$ is then an optimal set of rate coefficients by minimizing the least-squares difference between the model predictions and the experimental measurements, weighted by experimental uncertainty. The second term of Eq. (7) comes from treating each rate parameter value as an experiment in its own right, with uncertainty σ_n equal to

1/2, i.e., by assuming that x_n is normally distributed. As discussed in [23], the covariance matrix $\Sigma^* = \boldsymbol{\alpha}^* \boldsymbol{\alpha}^{*T}$ can be approximated by linearizing the response surfaces in the vicinity of $\mathbf{x}^{(0)*}$, which gives

$$\Sigma^* = \left[\sum_{r=1}^{N_e} \frac{\mathbf{J}_r^* \mathbf{J}_r^{*T}}{(\sigma_r^{obs})^2} + 4\mathbf{I} \right]^{-1}. \quad (8)$$

In the above equation, $\mathbf{J}_r^*$ is the gradient of the r^{th} model response with respect to the factorial variables, evaluated at $\mathbf{x}^{(0)*}$ and $\mathbf{I}$ is the identity matrix, following which $\boldsymbol{\alpha}^*$ is calculated from the Cholesky factorization of Σ^* .

It is worthwhile to have a brief discussion about the degree of freedom of the system. Because the S_u° target data are not entirely independent of each other and considering the large number of rate parameters that may impact the flame speed prediction, the mathematical system remains under-defined. This is unfortunately a general feature of reaction model development. It is precisely for this reason that the above covariance matrix technique was introduced: although it is impossible to constrain the model parameters to a unique set, the joint probability distribution function provides coupled ranges of uncertainty of the rate parameters within which the target data can be reconciled.

Consideration will now be given to the circumstance whereby a constrained S_u° prediction, $S_{u,r}^\circ(\mathbf{x}^{(0)*})$, do not agree with the corresponding experimental observation, $S_{u,r}^{\circ,obs}$. The disagreement could be caused by a number of factors including, but not limited to, under-statement of experimental uncertainty, under-estimation of rate parameter uncertainty, and missing reaction pathways within the model. Towards addressing these issues, a data-consistency analysis algorithm [23] was proposed. Constraining the uncertainty of a kinetic model is a two-stage process. Firstly, the model is constrained by minimizing the least-squares difference between the model prediction and experimental measurements, weighted by σ_r^{obs} . MUM-PCE will then check for inconsistencies in the experimental target dataset by calculating the contribution of the r^{th} experiment to the objective function, F_r [23]:

$$F_r = \frac{S_{u,r}^{\circ, \text{obs}} - S_u^{\circ}(x_0^*)}{2\sigma_r^{\text{obs}}}. \quad (9)$$

If, the r^{th} experiment is deemed inconsistent with the initially constrained model if the model prediction falls outside the r^{th} experimental target's uncertainty bounds. The effect of a particular target on the constrained model is measured by the normalized scalar product S_r between the response surface gradient $\nabla S_{u,r}^{\circ}(x^*)$ and the constrained factorial vector or the change in the response caused by model constraint [23],

$$S_r = \frac{[\nabla S_{u,r}^{\circ}(x^*)] \cdot [x^*]}{\|\nabla S_{u,r}^{\circ}(x^*)\| \cdot \|x^*\|}. \quad (10)$$

The target with the greatest effect on the posterior model will have the largest value of S_r .

If only one target satisfies the criteria, $|F_r| > 1$, it will be removed from the optimization data target set and the model is then re-constrained. However, when multiple targets satisfy $|F_r| > 1$, MUM-PCE first calculates the weighted scalar product W_r :

$$W_r = S_r F_r. \quad (11)$$

The single target that has the greatest $|W_r|$ is removed and the model is then re-constrained. This procedure was repeated until an $\mathbf{x}^*$ is calculated such that all F_r are smaller than unity. These tests are referred to as F and W tests, respectively. If the standard deviation of the target experiment (σ_r^{obs}) was small, it will tend to have a greater impact on the posterior model so it would have a large contribution to the optimized value, and hence have larger S_r value.

5. Results and Discussion

5.1. Experimental data

Figure 1 summarizes the experimental S_u° 's for mixtures of C₃₋₄ hydrocarbons with air at $T_u = 298$ K and $p = 1$ atm. The variations of S_u° with respect to ϕ and the fuel structure are well

within our understanding: alkenes have higher S_u° 's than comparable alkanes largely because of differences in the adiabatic flame temperature; branched chain alkane and alkenes have lower S_u° 's than comparable straight-chain compounds, because of fuel structure influence on the formation of intermediates and their resulting radical production and destruction.

Measurements made in the current work and from prior studies of the USC group [24, 25] all tend to result in somewhat lower S_u° values than other studies especially under fuel rich conditions. For example, values reported for CH₄/air flames by Bosschaart and de Goey [27] are larger than those of the present authors' values by about 6 cm/s at $\phi \leq 1.3$. The discrepancy just discussed is a cause for concern, and for this reason experimental S_u° values for all C₁-C₄ hydrocarbons considered here are compared in Figs. S3-S5 of SPM. The data are plotted as a function of the equivalence ratio, and following Law et al. [59], also the normalized equivalence ratio $\bar{\phi} = \phi/(1 + \phi)$. The data shown were determined using a number of techniques, including counterflow flames [2, 3, 24, 25, 31], stagnation flames [26], spherically expanding flames [4, 28-30, 32], and the heat flux [27] methods. With the exception of acetylene for which the measurements were made in N₂-diluted air, all others are fuel/air mixtures with the unburned gas temperature $T_u = 298$ K and pressure $p = 1$ atm and over a range of ϕ 's.

In general, the reproducibility of S_u° values is reported to be ± 2 cm/s or better within each laboratory. Yet from laboratory to laboratory the data scatter is larger. In almost all cases, the nominal S_u° values and their uncertainties, when provided, do not overlap; and the data discrepancy remains too large to draw a consensus about the S_u° value for any fuel to within ± 2 cm/s. The left panel of Fig. 2 shows the results of rational function analysis [59] of the data uncertainty for C₃H₆/air and 1-C₄H₈/air mixtures. A similar result is shown for CH₄/air mixtures in Fig. 3, and additional results are presented in Figs. S3-S5 of SPM for fuels where statistically significant numbers of measurements are available. The width of the 2σ -uncertainty band of the data varies typically from roughly ± 5 cm/s to ± 7.5 cm/s for all fuels analyzed. These uncertainty band sizes are substantially larger than the uncertainty reported in individual studies. Clearly, the

uncertainty values as reported in the individual studies should be considered as the reproducibility of the data for a given method in a given facility.

At least some of the data scatter is the result of systematic error that is known to have occurred in data interpretation. For example, the S_u° values reported by Davis and Law [3] and Kumar et al. [31] are impacted by the assumption of linear dependency of the reference velocity with respect to flow stretch. The assumption produces systematically larger S_u° values for the fuels considered. For 1-C₄H₈ and maybe some other fuels, the method of extrapolation is perhaps insufficient to explain the discrepancy of the S_u° 's values between Davis and Law [3] and those determined here, as discussed in section S1 of SPM.

How to treat the interlaboratory uncertainty is an as-yet unresolved question [22], as discussed in a recent review. There are three schools of thought on this issue. In the MUM-PCE algorithm used here and in related works [22, 23], a model is generated that agrees with as many measurements as possible, each of which has its own uncertainty. In the Bayesian algorithm used by Raman and coworkers [60], every measurement has the same uncertainty which is solved for as part of the optimization problem. Finally, Turanyi and coworkers [61] present a hybrid approach, wherein there is a component of the uncertainty for each measurement reported by the investigators and a component coming from the scatter in the measurements that is evaluated as part of the optimization problem.

Each method has its advantages and disadvantages, which can be seen most clearly in the case of a single spurious measurement with an unreasonably small uncertainty that does not agree with the other measurements of its type. In the case of MUM-PCE, this experiment might end up being labeled as inconsistent and as such removed, or it might end up overwhelming all the other measurements and generating a model that is consistent with neither the actual physics nor the actual precision of that physics; that is, the physics will be wrong and it will be overconfidently wrong. In methods of [60] or [61], this single measurement would instead introduce a large uncertainty into the posterior model. Turányi and coworkers [62] have also implemented an approach to handling inconsistent data whereby data not reproduced within 4

sigma are excluded from the final optimization. Thus, the resulting physics will not be wrong, but it will also not be reflective of the precision present in the other, non-spurious, measurements.

This argument is further complicated by the fact that a measurement that appears spurious may in fact be accurate, and it may be the other measurements that are truly spurious. It is impossible to know in fact who is right and who is wrong especially when the measurement is insufficiently repeated. The only way to examine this question is to consider the consequences of the alleged outlier, as will be discussed later.

For the above reasons, we use as-reported nominal values and uncertainties of S_u° for model optimization in the current work, despite the fact that such an approach is equivalent to adopting the reported data at their face values. Nonetheless, we expect that a careful data consistency analysis (integrated in the MUM-PCE algorithm) and a sensitivity analysis to data sets considered in optimization would yield useful information regarding the data and model uncertainty.

5.2. Comparisons among models and experimental data

Prediction uncertainties of USC Mech II remain large. The right panel of Fig. 2 depicts the probability density functions and the 2σ uncertainty bands of the model, calculated for C_3H_6 and 1- C_4H_8 flames using eq (4). In these figures, the dashed lines correspond to predictions at $\pm 2\sigma$ uncertainty or 95% confidence interval. The intensity of the grey level represents the normalized probability density function. For comparison, the 2σ uncertainty values computed for S_u° 's of C_3H_6 flames are ± 7.5 and ± 5 cm/s for $\phi = 1.0$ and $\phi = 1.2$, respectively. These values are ± 10 and ± 8.5 cm/s for 1- C_4H_8 at $\phi = 1.0$ and $\phi = 1.4$, respectively. The somewhat larger uncertainty values of 1- C_4H_8 are the result of a larger number of fuel-specific reactions that impact S_u° of 1- C_4H_8 flames. Yet, the S_u° model prediction uncertainty of C_3H_6 and 1- C_4H_8 is not substantially larger than that of CH_4 . As shown in the right panel of Fig. 3, CH_4 has a prediction uncertainty of ± 7 cm/s at $\phi = 1.0$, and ± 8 cm/s at $\phi = 1.3$, similar to the values computed by Zádor et al. [63].

This comparison is consistent with our understanding that S_u° is influenced by a set of common reactions that govern the radical processes in flames regardless which hydrocarbon fuel it is.

While we have a poor convergence of the experimental data, there is some convergence in the predictions by the reaction models. As shown in Fig. 2, the prediction of the original Galway model (model g) lies outside the 2σ uncertainty bands of USC Mech II for some fuel-rich C_3H_6 and 1- C_4H_8 flames, suggesting fundamental kinetic differences between the models. The more recent models, Aramco Mech 1.3 (model a-1) and Aramco Mech- C_3H_6 (model a-2), on the other hand, show notable improvements over the original Galway model. More importantly, if the rate parameter uncertainties assigned in USC Mech II are realistic, the predictions by USC Mech II and the two versions of the Aramco models all fall within the expected uncertainties of the rate parameters for at least C_3H_6 .

For CH_4 flames, discrepancies are still significant among model predictions, as shown in Fig. 3, despite the fact that the Galway, Aramco, and San Diego models all predict S_u° values well within the 2σ -uncertainty band of USC Mech II. Thus, fundamental differences among these reaction models, if any, are not manifested as far as S_u° prediction here. Rather, the discrepancies in model prediction are the most likely the result of choices of rate parameters.

5.3. Model optimization and uncertainty minimization

As we discussed earlier, it is not our purpose to explore the sources of discrepancy among S_u° data, nor is it our intention to explore differences in the kinetic assumptions of the different models and their resulting impacts on S_u° prediction. Our purpose is to explore the question of, given the current state of knowledge in the S_u° 's of almost every relevant C₁₋₄ hydrocarbon compounds, what we can learn from the data as far as model accuracy is concerned. In particular, how small can the prediction uncertainty of the model become for S_u° predictions, based on experimental knowledge? For this purpose, multiple sets of experimental data of C₁₋₄ S_u° 's were tested as optimization targets. Sources of target data and the corresponding labels for the posterior models are listed in Table 2. Table 3 lists the target values and their 2σ uncertainty values. For those data values where an uncertainty estimate is reported, that estimate was used as is. Otherwise, the uncertainty was assumed to be ± 2 cm/s. Excluding the data of Davis and Law [3] and Kumar et al. [31] (see Section 5.1), the spread in experimental S_u° values is generally smaller than the prediction uncertainty of the prior model. Therefore a model jointly constrained by all relevant C₁₋₄ S_u° targets is expected to yield useful information about the impact of the current S_u° database on reaction model development.

To test the impact of the data scatter on model uncertainty minimization, three computational tests were made with increasingly larger target sets. First, only experimental data sets of [24, 25] and from the present work were considered as the optimization targets and the corresponding optimized model (posterior model) is referred to as OM I. The OM II and OM III target sets include those of OM I plus literature data values [3, 4, 26, 27, 31]. While the OM III set includes data considered, OM II considers all but those of Ref. [3, 31].

Active rate parameters were chosen for the optimization by considering jointly the sensitivity and uncertainty of a rate constant. For this purpose, an impact factor u is introduced here:

$$u = 2 \left(\frac{\partial \ln S_u^\circ}{\partial \ln A} \right) \ln f, \quad (12)$$

where $\partial \ln S_u^\circ / \partial \ln A$ is the logarithmic sensitivity coefficient. Figure 4 depicts the ranked impact factor u and the corresponding sensitivity coefficient for CH_4 and $1\text{-C}_4\text{H}_8$ as examples. Similar results can be seen for all other hydrocarbons in Figs. S6-S17 of SPM. As can be seen in these figures, reaction processes that impact flame propagation are typically those of H, CO, HCO and small HC species, yet owing to their larger uncertainty factors, the rate coefficients of some fuel specific reactions can impact the S_u° prediction notably. For example, the prediction of the S_u° of $1\text{-C}_4\text{H}_8$ is influenced by the uncertainty of the rate coefficient of reaction ($f_{\text{R556}} \sim 5$)

despite the fact that the sensitivity coefficient of reaction R556 is substantially smaller than that of the key chain branching reaction R1 ($f_{\text{R1}} = 1.2$)

Reaction (R1) has a large u factor for nearly all fuels even though its uncertainty is about only 20%. Other high-impact factor reactions that are common to all fuels include

and

MUM-PCE results for the 12 fuels are shown in Figs. 5 through 10, in which we compare the probability density functions and 2σ uncertainties of S_u° predicted using the prior model and the three optimized models. Several immediate observations can be made: (1) the MUM-PCE analysis reduces the prediction uncertainties of the reaction model notably when compared to those of the prior model; (2) with the exception of $1\text{-C}_4\text{H}_8$ and $2\text{-C}_4\text{H}_8$ (Fig. 9), USC Mech II is able to reconcile all data sets taken from Ref [24, 25] and the present work, as seen in the OM I plots; (3) the effect of adding literature data beyond those of Ref [24, 25] is a somewhat increased S_u° value (as predicted by OM II and OM III compared to OM I); (4) the uncertainty band size decreases somewhat from OM I to OM II, suggesting the data beyond those from Ref [24, 25] and the present work help to constrain the model uncertainty to an extent. The fact that

USC Mech II exhibits difficulties reconciling with the 1-C₄H₈ and 2-C₄H₈ S_u° data suggests that the reaction model may have missing reaction pathways relevant to their oxidation. Indeed the chemistry specific to C₄H₈ oxidation is known to be rather weak in USC Mech II. The elementary reaction kinetics of the C₄H₁₀ isomers are not as well understood as other fuels.

Most of the optimized rate parameters of H₂/CO/HCO reactions are centered around their nominal values, as shown in Table 4, in which the ratios of optimized-to-nominal rate coefficients of selected reactions are compared between OM I and OM II. The results show that the inclusion of additional targets from OM I to OM II did not lead to significant changes in individual, active rate parameters. Except for R95, the difference between OM I and OM II is rather small. The large change in the rate coefficient of R95 from OM I to OM II indicates that the current S_u° dataset yields little insight into k_{95} . Suffice it to note that many of the rate parameters in USC Mech II are outdated. Jasper et al. [65] carried out a careful analysis of k_{95} as a part of study of the CH₃ + OH and methanol decomposition. At 1 atm pressure, they calculated k_{95} to be around 4×10^{12} cm³/mol-s from 1500 to 2000 K. The nominal value of k_{95} in USC Mech II is 2.5×10^{13} cm³/mol-s. Thus, the ratio values of Table 4 gives $k_{95} = 3.8 \times 10^{13}$ and 1.2×10^{13} cm³/mol-s for OM I and II, respectively. Clearly, the OM I value diverges from the theoretical result of [65], while OM II yields the k_{95} value closer to the theoretical result. Interestingly, the k_{95} value optimized in OM II is quite close to Baulch's compilation [43], which gives k_{95} to be 1.2×10^{13} cm³/mol-s at 1500 K, decreasing to 9.3×10^{12} cm³/mol-s at 2000 K.

The covariance matrix, Σ , indicates how the rate coefficients are constrained by experimental targets (see, Fig. S18 of SPM). The diagonal elements of Σ are relatively large, indicating that the uncertainty of any single rate coefficient is not effectively constrained by S_u° measurements. Instead, as indicated by the off-diagonal elements of Σ , the constraint on the model uncertainty comes mostly in the form of interparameter coupling. The covariance matrix is relatively sparse, but there are several groups of reactions whose rate coefficients are prominently coupled. For instance, the uncertainty in k_{95} is constrained relatively quite tightly, but k_{95} is also strongly coupled to the rate coefficient of reaction R99:

Interestingly, OM II yields an optimized k_{99} to be $0.7 \times 1.34 \times 10^{13} = 9.4 \times 10^{12} \text{ cm}^3/\text{mol-s}$, which is in better agreement with the more recent measurement of Hong et al. [66], $6.8 \times 10^{12} \text{ cm}^3/\text{mol-s}$ with an uncertainty factor of 1.4. Additionally, OM II also gives a more reasonable R108 than OM I. Nonetheless, the coupling just discussed underscores the limitation of MUM-PCE, given the currently available data. The MUM-PCE method can be used to calculate the uncertainty of a simulation result and this can be compared directly with the corresponding experimental uncertainty. The results obtained from this method also indicated that the rate parameters are highly correlated and therefore assignment of an individual uncertainty limit to each parameter is not possible, such uncertainty limits have no physical meaning. However, the correlation matrix of the rate parameters can be used to characterize the joint uncertainty of the rate parameters, which is the only meaningful uncertainty measure for the rate parameters [23].

5.4. Data consistency

During the optimization process, a target may be removed either because multiple measurements for a particular experimental condition do not agree with each other or the experimental measurement cannot be reconciled with the other targets within the uncertainty bounds of the prior model. A comprehensive tabulation of the included and excluded datasets as a result of the F/W test is provided in Table S2 of SMP. For the case of OM I, none of the target experimental data was removed as optimization targets. Therefore, it can be concluded that, the OM I dataset forms a self-consistent target set within the framework of USC Mech II. The rejection of a target during optimization does not imply that the particular measurement was incorrect. It merely suggests that the data may need further evaluation. Many of experimental targets in OM III were deemed inconsistent. These are mostly for fuel-rich C_4 -hydrocarbon flames. The large spread of experimental target sets under those conditions clearly indicates that the relevant data should be carefully re-evaluated.

5.5. Data subset tests

Given our understanding of the hierarchical nature of chemical kinetic reaction models, it is natural to ask, what is the impact of a particular set of data on constraining overall model predictions and their uncertainties? We explore this question here within the framework of MUM-PCE. When reducing the uncertainty of model predictions for S_u° the question arises as to which subset of S_u° targets impacts this uncertainty reduction to the largest extent. For example, in order to reduce the 2σ uncertainty band for $n\text{-C}_4\text{H}_{10}$ flame predictions, will it be necessary to include all experimental targets of flames of C_{1-4} hydrocarbons or is there an optimal subset which will have the largest impact? A natural follow-on question is, what precision is needed in experimental measurements of S_u° to sufficiently constrain the uncertainty in predictions of laminar flame speed.

Table 5 lists a selection of case studies, ranging in target data size. Only the OM I data set was considered in the series of tests. While Test Ia contained only the S_u° 's of CH_4 flames as targets, Ib considered CH_4 and C_2 hydrocarbons; Id used C_{1-3} hydrocarbons. In contrast, Ic* used only the dataset of the target fuel alone. That is, there is a Test Ic* for each fuel and the purpose of this model is to compare the uncertainty in S_u° predictions for a given fuel constrained by only its own measurements. OM I* used the data of C_4H_{10} isomers [19, 67] in addition to the OM I data set.

We illustrate the principal findings of the aforementioned tests using C_3H_8 and C_3H_6 flames as examples. Figure 11 shows 1σ uncertainty predicted for S_u° 's of (a) $\text{C}_3\text{H}_8/\text{air}$ and (b) $\text{C}_3\text{H}_6/\text{air}$ mixtures over a range of ϕ 's at $T_u = 298\text{ K}$ and $p = 1\text{ atm}$. It can be seen that qualitatively the model prediction uncertainty responds to dataset expansion in an expected manner: an increase in the datasets considered reduces the prediction uncertainty. At the quantitative level C_3H_6 responds to dataset expansion somewhat differently from C_3H_8 . The prediction uncertainty for C_3H_6 flames decreased marginally from the prior model to Ia and Ib. Only when the data of C_3H_6 are introduced as targets (test Id) does the prediction uncertainty reduce to below 1 cm/s . On the other hand, the use of C_{1-2} hydrocarbon S_u° 's alone can reduce the prediction uncertainty for

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5 C₃H₈ efficiently. Clearly, the difference arises from the fact that the S_u° of C₃H₆ is more sensitive
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7 to fuel-specific reaction rates than that of C₃H₈ (*cf.* Figs. S10 and S11). The above observation
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9 can be made equally for C₄ fuels, as shown in Fig. 12. Overall, our ability to predict the S_u° of
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11 saturated hydrocarbons is impacted mostly by the S_u° data of C₁₋₂ hydrocarbon fuels, whereas for
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13 unsaturated C₃₋₄ hydrocarbons fuel specific chemistry are more relevant and as such a more
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15 precise prediction of their S_u° 's relies on the availability of the data for these fuels.
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18 Figure 11 also shows that the prediction uncertainties of Test Ic* are comparable to those of
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20 Id. That is, precise predictions for S_u° 's of a particular fuel can be attained by using the data of
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22 that fuel alone, but the approach inevitably leads to the “many model” problem. Although a
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24 model optimized with the data of a particular fuel may achieve good predictions for that fuel,
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26 there is no reason to expect that such a model can make precise predictions for other fuels.
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29 The impact of experimental uncertainty on the degree with which the measurement
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31 constrains the reaction model was examined next. The 2σ uncertainty of C₃H₈/air S_u° determined
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33 in the present study was estimated to be 1.0 to 1.2 cm/s from the current study. Assuming that
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35 the uncertainty value includes a consideration of the systematic error of the experiment, reducing
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37 this uncertainty would, of course, improve the model precision. Table 6 illustrates the variation
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39 of the prediction uncertainty of OM I as a function of the measurement uncertainty. An
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41 improvement of the experimental accuracy clearly tightens posterior model uncertainty, but we
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43 see diminishing return when the 2σ uncertainty of the experimental S_u° value decreases to
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45 between ± 2 and ± 1 cm/s. This result suggests that it would be beneficial to see convergence of
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47 measurements of the S_u° values to within around ± 2 cm or smaller across different laboratories,
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49 facilities and methods.
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52 The final component of our tests illustrates the importance of foundation fuel chemistry on
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54 making accurate predictions for the flame properties of alcohols. For this purpose, USC Mech II
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56 was combined with the butanol submodel of Moss et al. [17]. A conservative uncertainty span of
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58 2.5 was assigned to all butanol related reactions although the true uncertainty for some of these
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60 rate parameters could be larger. The prediction uncertainty values are shown in Fig. 13 for S_u° 's
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of *normal*-butanol ($n\text{-C}_4\text{H}_9\text{OH}$), *iso*-butanol ($i\text{-C}_4\text{H}_9\text{OH}$) and *tert*--butanol ($t\text{-C}_4\text{H}_9\text{OH}$) isomers in air. The prior model has a 1σ prediction uncertainty of 3-5 cm/s for $n\text{-C}_4\text{H}_9\text{OH}$ and $i\text{-C}_4\text{H}_9\text{OH}$, depending on ϕ , whereas this uncertainty is somewhat smaller for $t\text{-C}_4\text{H}_9\text{OH}$. The uncertainty was constrained quite efficiently by Test Ia, and is reduced further in cases Ib and Ic as $\text{C}_{2-3} S_u^\circ$ data are added. The full OM I dataset is sufficient for constraining the prediction of butanol S_u° 's. The inclusion of the butanol S_u° data (Test I*), in fact, adds little to model improvements. The exercise just discussed illustrates an important point. Because of the hierarchical nature of reaction kinetics, what really matter is the availability of accurate combustion data for foundation, small hydrocarbon fuels if our interest is to make accurate predictions for the combustion properties of larger hydrocarbon fuels, including oxygenates. Wang and Sheen [22] have also demonstrated that H_2/CO and C_2H_4 experimental dataset significantly reduces uncertainty in the predicted n -octane flame speeds using JetSurF 1.0 [68], in which USC Mech II is the foundational fuel chemistry model of JetSurF.

5.5. Impact of model optimization on prediction of other combustion properties

Perfectly stirred reactor (PSR) simulations are carried out here to demonstrate how the S_u° data can constrain model uncertainty and achieve more precise predictions for a different combustion phenomenon. The PSR simulates an idealized combustion problem in which fuel and oxidizer enter a reactor and the products leave the reactor in a steady state. The reactor is assumed to be spatially uniform. The rate of conversion of reactants to products is controlled by chemistry, not mixing.

Figure 14 shows OH mole fractions with respect to residence time in a PSR for the oxidation of an $n\text{-C}_4\text{H}_9\text{OH}/\text{air}$ mixture at the constant temperature of 1500 K, constant pressure of 1 atm, and $\phi = 1.0$ along with associated uncertainties predicted by the prior model, the optimized OM II and OM II*. Two distinct branches are observed. At the short residence times, we have a weakly reactive state (lower branch) where chemistry is largely frozen. As the resident time is

increased, a critical point is reached where the OH concentration or reactivity increases suddenly. The upper branch represents the strong or vigorously reacting state.

As expected, the largest uncertainty in the OH concentration occurs in the hysteresis region, whereas for long residence times, the prediction uncertainty decreases because of chemical equilibrium. There is a significant reduction in the prediction uncertainty near extinction from the prior model to the optimized OM II and II* models, as seen in Fig. 14. On the other hand, adding constraints from experimental S_u^o 's of *n*-C₄H₉OH/air flames to the OM II set does not have a notable effect on reducing the model prediction uncertainty further in the hysteresis region.

6. Concluding remarks

Laminar flame speeds were measured in the counterflow flame configuration for mixtures of air with propene, propane, 1,3-butadiene, 1-butene, 2-butene, iso-butene, *n*-butane, and *iso*-butane at 298 K temperature and 1 atm pressure and over a range of equivalence ratios. This dataset supplements recently reported results [24, 25] and presents a self-consistent set of laminar flame speed data of 12 C₁₋₄ hydrocarbons of direct relevance to the development of foundation fuel chemistry models. Utilizing this and other data sets in the literature, a reaction model of foundation fuel chemistry (USC Mech II) was analyzed by the Method of Uncertainty Minimization using Polynomial Chaos Expansion (MUM-PCE) along with the experimental data. Key conclusions may be summarized as follows:

- (1) Although the reported uncertainties of the flame speed data are relatively small within each laboratory, interlaboratory data scatter remains too large to reach consensus about the flame speed value of a particular fuel under a certain condition to within ± 2 cm/s;
- (2) Nonetheless, laminar flame speed data are useful to constraining reaction model accuracy and precision if they are used jointly across a range of fuel sizes and structure, and equivalence ratio;
- (3) Among the C₁₋₄ foundational hydrocarbons, the model accuracy and precision of C₃₋₄ alkanes can be constrained efficiently by only the C₁₋₂ flame speed data; whereas model accuracy and

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5 precision of unsaturated alkenes should require the data of the fuels themselves owing to a
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7 greater number of fuel specific reactions that can play a role in the overall oxidation process;
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10 (4) Beyond the C₁₋₄ foundational hydrocarbons, the model accuracy and precision for predictions
11 of the laminar flame speeds of higher hydrocarbons and alcohols is expected to be constrained
12 quite efficiently by the flame speeds of C₁₋₄ foundation hydrocarbons, to an extent that there is
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14 little to no benefits to collect the flame speed values for these higher hydrocarbons other than a
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16 quick test of the accuracy of the nominal prediction by a model.
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20 (5) The application of uncertainty minimization to a reaction model within a narrow range of
21 constraints can lead to improvements of the precision of the model, both within and outside the
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23 conditions against which the model is constrained.
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Table 1. Summary of reaction models tested

Model name/group	Abbreviated name ^a	Year	Source
USC-Mech II	--	2007	[33]
Nancy	Model n	2008	[17]
San Diego Mech	Model s	2009	[44]
Galway	Model g	2010	[5, 45]
Aramco Mech1.3	Model a-1	2013	[46]
Aramco Mech - Propene	Model a-2	2015	[47, 48]
Orléans	Model o	2015	[49]

^a The manuscript text will refer a particular model by its abbreviated name.

Table 2. List of datasets tested for model optimization.

Mixture	Data set ^a		
	OM I	OM II	OM III
CH ₄ /air	[25]	[25-28]	[25-28]
C ₂ H ₂ /O ₂ /N ₂ ^b	[24]	[2, 24]	[2, 24]
C ₂ H ₄ /air	[24]	[4, 24, 29, 30]	[4, 24, 29-31]
C ₂ H ₆ /air	[24]	[4, 24, 26, 27]	[4, 24, 26, 27]
C ₃ H ₈ /air	c	c, [4, 26, 27]	c, [4, 26, 27]
C ₃ H ₆ /air	c	c, [4]	c, [3, 4]
<i>n</i> -C ₄ H ₁₀ /air	c	c, [27]	c, [3, 27]
<i>i</i> -C ₄ H ₁₀ /air	c	c, [27]	c, [3, 27]
1-C ₄ H ₈ /air	c	c	c, [3]
2-C ₄ H ₈ /air	c	c	c
<i>i</i> -C ₄ H ₈ /air	c	c	c, [3]
1,3-C ₄ H ₆ /air	c	c	c, [3]

^a OM I: data from refs. [24, 25] and this work; OM II: all literature data except for those of [3]; OM III : all data. ^b 13% O₂ + 87% N₂ (mol). ^c this work.

Table 3. Experimental S_u^o (cm/s) target values and their associated 2σ uncertainties.

Fuel ^a	ϕ						Fuel ^a	ϕ			
CH ₄		[25]	[27]	[26]	[28]		<i>n</i> -C ₄ H ₁₀		b	[27]	[3]
	0.7	18.2±1.3	15.1±1	15.8±2	17.2±2			0.7	21.1±1.1	19.08±1	20.2±2
	0.8	25.4±1.5	23.7±1	24.1±2	24.9±2			0.8	28.2±1.0	26.84±1	26.8±2
	1.0	35.9±1.0		36.5±2	34.7±2			1.0	36.9±1.0	37.11±1	38.0±2
	1.2	31.2±1.3	33.8±1	31.8±2	31.2±2			1.2	34.3±1.1	36.71±1	37.9±2
	1.3	20.8±1.4	26.5±1	20.8±2	21.2±2			1.4	18.5±1.5	23.68±1	24.8±2
C ₂ H ₂		[24]	[2]				<i>i</i> -C ₄ H ₁₀		b	[27]	[3]
	0.7	19.7±1.0	19.1±2					0.7	19.7±1.1	16.5±1	18.6±2
	0.8	29.3±1.0	30.1±2					0.8	25.8±1.0	23.3±1	24.9±2
	1.0	44.4±1.3	45.9±2					1.0	33.4±1.0	33.4±1	35.4±2
	1.2	50.3±1.6	51.7±2					1.2	30.3±1.0	33.4±1	34.9±2
	1.4	39.8±1.3	40.1±2					1.4	16.8±1.3	20.4±1	22.9±2
	1.6	23.0±0.8	23.2±2								
C ₂ H ₄		[24]	[4]	[29]	[30]	[31]	1,3-C ₄ H ₆		b	[3]	
	0.7	36.9±1.5	35.1±2			43.2±2		0.7	28.5±1.0	27.4±2	
	0.8	47.0±1.2	48.8±2		49.3±2	53.7±2		0.8	39.5±1.0	37.5±2	
	1.0	64.6±1.2	62.3±2	64.7±2	65.7±2	68.5±2		1.0	51.0±1.1	51.5±2	
	1.2	66.5±1.4	63.4±2	64.4±2	66.0±2	70.6±2		1.2	52.0±1.5	55.7±2	
	1.4	51.6±1.7	52.0±2	57.9±2		58.8±2		1.4	38.0±1.5	45.1±2	
C ₂ H ₆		[24]	[4]	[27]	[26]		1-C ₄ H ₈		b	[3]	
	0.7	20.0±1.6						0.7	25.2±1.2	22.8±2	
	0.8	29.1±1.2	28.4±2	29.7±1				0.8	31.8±1.3	31.9±2	
	1.0	39.1±1.2	38.1±2	40.8±1	40.2±2			1.0	41.5±1.2	43.9±2	
	1.2	37.5±1.9	38.5±2	40.5±1	40.9±2			1.2	40.0±1.5	45.8±2	
	1.4	22.8±1.5	26.3±2	26.7±1	26.2±2			1.4	25.5±1.5	34.7±2	
C ₃ H ₈		b	[4]	[27]	[26]		<i>i</i> -C ₄ H ₈		b	[3]	
	0.7	22.5±1.0	21.7±2	20.2±1	20.3±2			0.7	17.3±1.0	20.1±2	
	0.8	30.0±1.0	29.9±2	28.5±1	30.0±2			0.8	25.8±1.0	25.9±2	
	1.0	38.3±1.0	41.4±2	39.4±1	39.0±2			1.0	35.0±1.6	37.8±2	
	1.2	36.0±1.2	39.5±2	38.4±1	38.8±2			1.2	32.5±1.1	39.1±2	
	1.4	18.7±1.2	26.7±2	23.8±1	24.5±2			1.3	17.8±1.5	35.6±2	
C ₃ H ₆		b	[4]	[3]			2-C ₄ H ₈		b		
	0.7	24.4±0.8	20.1±2	20.6±2				0.7	22.2±1.3		
	0.8	32.5±0.8	28.7±2	29.9±2				0.8	30.7±1.3		
	1.0	42.0±1.0	40.3±2	41.5±2				1.0	39.5±1.6		
	1.2	40.5±1.2	40.7±2	43.9±2				1.2	36.1±1.5		
	1.4	25.5±1.3	27.4±2	33.1±2				1.4	21.2±1.5		

^a Fuels in air except acetylene (C₂H₂) with dilute air: 13% O₂ + 87% N₂ (mol). ^b This work.

Table 4. Uncertainty spans and ratios of optimized-to-nominal rate coefficients for selected reactions of OM I and OM II.

	Reactions	Span, f^a	OM I	OM II
1	$\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$	1.2	0.94	1.02
12	$\text{H} + \text{O}_2 + \text{M} \leftrightarrow \text{HO}_2 + \text{M}$	1.2	1.05	1.06
17	$\text{H} + \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{HO}_2 + \text{H}_2\text{O}$	2.5	1.03	1.04
34	$\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$ (high T)	1.2	0.92	0.94
35	$\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$ (low T)	1.2	0.96	0.95
38	$\text{HCO} + \text{H} \leftrightarrow \text{CO} + \text{H}_2$	2	0.94	0.71
41	$\text{HCO} + \text{OH} \leftrightarrow \text{CO} + \text{H}_2\text{O}$	3	0.82	0.88
42	$\text{HCO} + \text{M} \leftrightarrow \text{CO} + \text{H} + \text{M}$	4	1.42	1.54
43	$\text{HCO} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H} + \text{H}_2\text{O}$	2	1.21	1.07
53	$\text{CH} + \text{O}_2 \leftrightarrow \text{HCO} + \text{O}$	10	3.75	2.26
91	$\text{CH}_3 + \text{H} + \text{M} \leftrightarrow \text{CH}_4 + \text{M}$	2	1.11	0.93
92	$\text{CH}_3 + \text{O} \leftrightarrow \text{CH}_2\text{O} + \text{H}$	2	0.71	1.18
93	$\text{CH}_3 + \text{OH} + \text{M} \leftrightarrow \text{CH}_3\text{OH} + \text{M}$	5	0.76	0.92
95	$\text{CH}_3 + \text{OH} \leftrightarrow \text{CH}_2(\text{s}) + \text{H}_2\text{O}$	5	1.50	0.47
99	$\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{OH}$	3	1.07	0.70
108	$\text{CH}_3 + \text{CH}_3 \leftrightarrow \text{C}_2\text{H}_5 + \text{H}$	5	2.44	1.24
152	$\text{HCCO} + \text{O}_2 \leftrightarrow \text{OH} + 2\text{CO}$	5	0.35	0.29
197	$\text{C}_2\text{H}_3 + \text{O}_2 \leftrightarrow \text{CH}_2\text{CHO} + \text{O}$	4	1.56	1.32
198	$\text{C}_2\text{H}_3 + \text{O}_2 \leftrightarrow \text{HCO} + \text{CH}_2\text{O}$	4	0.69	0.63
252	$\text{C}_2\text{H}_4 + \text{H} + \text{M} \leftrightarrow \text{C}_2\text{H}_5 + \text{M}$	3	0.47	0.34
268	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3 \leftrightarrow \text{C}_4\text{H}_7$	2	0.69	0.79
328	$a\text{-C}_3\text{H}_5 + \text{H} + \text{M} \leftrightarrow \text{C}_3\text{H}_6 + \text{M}$	3	0.66	0.59
337	$a\text{-C}_3\text{H}_5 + \text{HO}_2 \leftrightarrow \text{OH} + \text{C}_2\text{H}_3 + \text{CH}_2\text{O}$	3	1.48	1.28
442	$i\text{-C}_4\text{H}_3 + \text{H} \leftrightarrow \text{C}_4\text{H}_2 + \text{H}_2$	10	1.42	1.80
483	$\text{C}_4\text{H}_6 + \text{H} \leftrightarrow i\text{-C}_4\text{H}_5 + \text{H}_2$	5	5.0	4.07
484	$\text{C}_4\text{H}_6 + \text{H} \leftrightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_3$	2	0.80	0.83
490	$\text{C}_4\text{H}_6 + \text{O} \leftrightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_3$	3	0.72	0.81
491	$\text{C}_4\text{H}_6 + \text{OH} \leftrightarrow n\text{-C}_4\text{H}_5 + \text{H}_2\text{O}$	3	1.59	1.53
492	$\text{C}_4\text{H}_6 + \text{OH} \leftrightarrow i\text{-C}_4\text{H}_5 + \text{H}_2\text{O}$	5	0.46	0.45
549	$i\text{-C}_4\text{H}_7 + \text{H} + \text{M} \leftrightarrow i\text{-C}_4\text{H}_8 + \text{M}$	2	0.81	0.73
565	$2\text{-C}_4\text{H}_8 + \text{H} + \text{M} \leftrightarrow s\text{-C}_4\text{H}_9 + \text{M}$	3	1.73	1.05
566	$2\text{-C}_4\text{H}_8 + \text{H} \leftrightarrow \text{C}_4\text{H}_7 + \text{H}_2$	3	0.33	0.45
567	$2\text{-C}_4\text{H}_8 + \text{O} \leftrightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{CHO}$	3	3.0	2.86
573	$i\text{-C}_4\text{H}_8 + \text{H} \leftrightarrow i\text{-C}_4\text{H}_7 + \text{H}_2$	3	0.76	0.73
578	$i\text{-C}_4\text{H}_8 + \text{OH} \leftrightarrow i\text{-C}_4\text{H}_7 + \text{H}_2\text{O}$	3	0.83	0.75
592	$\text{C}_3\text{H}_6 + \text{CH}_3 + \text{M} \leftrightarrow s\text{-C}_4\text{H}_9 + \text{M}$	2	1.30	1.37
634	$\text{C}_4\text{H}_{10} + \text{H} + \text{M} \leftrightarrow s\text{-C}_4\text{H}_9 + \text{H}_2$	3	1.30	1.61

Table 5. Summary of test cases.

No.	Target data
Ia	CH ₄
Ib	All C ₁₋₂ hydrocarbons
Ic*	Single, target fuel (see text)
Id	All C ₁₋₃ hydrocarbons
I	All C ₁₋₄ hydrocarbons ^a
I* (or II*)	OM I (or II) + three butanol isomers ^b

^a identical to the OM I dataset. ^b S_u° data of *n*-butanol is taken from [67] and those of *i*- and *t*-butanol from [19].

Table 6. Relationship between measurement and model uncertainties of the C₃H₈/air mixture at $\phi=1.2$. Values listed are 2σ uncertainty.

Experimental	Model
∞	7.4
5.0	3.1
4.0	2.6
2.0	1.7
1.0	1.2

Figure 1. S_u^o 's of C_{3-4} hydrocarbons/air mixtures determined in the current study at $T_u = 298$ K and $p = 1$ atm. The error bars represent 2σ uncertainty. The data are provided in SPM.

Figure 2. Left panel: selected experimental data (symbols) and results of uncertainty analysis (solid lines, nominal fits to data; dashed lines: 2σ uncertainty) of S_u° of C_3H_6 /air and $1-C_4H_8$ /air mixtures at $p = 1$ atm and $T_u = 298$ K. Right panel: Selected experimental (symbols) and computed (lines) S_u° also at $p = 1$ atm and $T_u = 298$ K. The error bars represent 2σ uncertainty of the data. The grey level indicates the normalized probability density function of S_u° predicted by USC Mech II. See Table 1 for the labels of the models used for predictions. Symbols: ● present data; ■ Davis and Law, 1998 [3]; ▲ Jomaas et al., 2005 [4]; ▽, □, ◆ Burke et al., 2015 [48]; ▲ Kelley, 2011 [32]; ◇ Fenard et al., 2015 [49]; ▽ Zhao et al., 2015 [64].

Figure 3. Left panel: selected experimental data (symbols) and results of uncertainty analysis (solid lines, nominal fits to data; dashed lines: 2σ uncertainty) of S_u^o of CH_4/air mixtures at $p = 1$ atm and $T_u = 298$ K. Right panel: Selected experimental (symbols) and computed (lines) S_u^o also at $p = 1$ atm and $T_u = 298$ K. The error bars represent 2σ uncertainty of the data. The grey level indicates the normalized probability density function of S_u^o predicted by USC Mech II. See Table 1 for the labels of the models used for predictions. Symbols: ● Park et al., 2011 [25]; ▲ Vagelopoulos & Egolfopoulos, 1998 [26]; ■ Bosschaart & de Goeij, 2004 [27]; ▼ Halt et al., 2010 [28].

Figure 4. The ranked impact factor u and logarithmic sensitivity coefficient $\partial \ln S_u^\circ / \partial \ln k$ computed for stoichiometric (a) CH₄/air and (b) 1-C₄H₈/air flames at $\phi = 1.0$, $T_u = 298$ K, and $p = 1$ atm using USC Mech II.

Figure 5. Experimental ($\circ$ [24, 25], $\square$ [27], $\blacktriangle$ [4], $\blacklozenge$ [29]) and computed (lines) S_u^o of CH_4/air (left panel) and $\text{C}_2\text{H}_4/\text{air}$ (right panel) at $p = 1$ atm and $T_u = 298$ K as a function of ϕ . The grey level indicates the probability density function of the uncertainty of flame speed predicted by the prior and optimized models; the dashed lines correspond to $\pm 2\sigma$ uncertainty of the respective models.

Figure 6. Experimental ($\circ$ [24], $\square$ [27]) and computed (lines) S_u^o of ethane in air (left panel) and $C_2H_2/O_2/N_2$ mixtures (right panel) at $p = 1$ atm and $T_u = 298$ K as a function ϕ . The grey level indicates the probability density function of the uncertainty of flame speed predicted by the prior and optimized models; the dashed lines correspond to $\pm 2\sigma$ uncertainty of the respective models.

Figure 7. Experimental ($\circ$ this work, $\square$ [27], $\blacktriangledown$ [4], $\blacktriangle$ [3]) and computed (lines) S_u^o of C_3H_8 /air (left panel) and C_3H_6 /air (right panel) at $p = 1$ atm and $T_u = 298$ K as a function of ϕ . The grey level indicates the probability density function of the uncertainty of flame speed predicted by the prior and optimized models; the dashed lines correspond to $\pm 2\sigma$ uncertainty of the respective models.

Figure 8. Experimental ($\circ$ this work, $\square$ [27], $\triangle$ [3]) and computed (lines) S_u^o of n -C₄H₁₀/air (left panel) and i -C₄H₁₀/air (right panel) at $p = 1$ atm and $T_u = 298$ K as a function of ϕ . The grey level indicates the probability density function of the uncertainty of flame speed predicted by the prior and optimized models; the dashed lines correspond to $\pm 2\sigma$ uncertainty of the respective models.

Figure 9. Experimental ($\circ$ this work; $\triangle$ [3]) and computed (lines) S_u^o of 1-C₄H₈/air (left panel) and 2-C₄H₈/air (right panel) at $p = 1$ atm and $T_u = 298$ K as a function of ϕ . The grey level indicates the probability density function of the uncertainty of flame speed predicted by the prior and optimized models; the dashed lines correspond to $\pm 2\sigma$ uncertainty of the respective models.

Figure 10. Experimental ($\circ$ this work; $\triangle$ [3]) and computed (lines) S_u^o of $i\text{-C}_4\text{H}_8/\text{air}$ (left panel) and $1,3\text{-C}_4\text{H}_6/\text{air}$ (right panel) at $p = 1$ atm and $T_u = 298$ K as a function of ϕ . The grey level indicates the probability density function of the uncertainty of flame speed predicted by the prior and optimized models; the dashed lines correspond to $\pm 2\sigma$ uncertainty of the respective models.

Figure 11. 1σ uncertainty predicted for S_u° 's of (a) C_3H_8 /air and (b) C_3H_6 /air mixtures at $T_u = 298$ K and $p = 1$ atm.

(a) $n\text{-C}_4\text{H}_{10}/\text{air}$

(b) $i\text{-C}_4\text{H}_{10}/\text{air}$

(c) $1\text{-C}_4\text{H}_8/\text{air}$

(d) $1,3\text{-C}_4\text{H}_6/\text{air}$

Figure 12. 1σ uncertainty predicted for S_u° 's of (a) $n\text{-C}_4\text{H}_{10}/\text{air}$, (b) $i\text{-C}_4\text{H}_{10}/\text{air}$, (c) $1\text{-C}_4\text{H}_8/\text{air}$, and (d) $1,3\text{-C}_4\text{H}_6/\text{air}$ mixtures at $T_u = 298$ K and $p = 1$ atm.

Figure 13. 1σ uncertainty predicted for S_u° of (a) $n\text{-C}_4\text{H}_9\text{OH}/\text{air}$, (b) $i\text{-C}_4\text{H}_9\text{OH}/\text{air}$, and (c) $t\text{-C}_4\text{H}_9\text{OH}$ mixtures at $T_u = 298$ K and $p = 1$ atm.

Figure 14. Variations of OH mole fraction with mean residence time in a simulated PSR in which n -C₄H₉OH is oxidized in stoichiometric air at a constant temperature of 1500 K and 1 atm pressure. (a) The prior model; (b) OM II; (c) OM II*. Lines are results of nominal predictions, and symbols are Monte Carlo sampling of the respective uncertainty spaces.