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Prospects and Limitations of Predicting Fuel Ignition Properties from Low-Temperature Speciation Data

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Supplementary Material is available.

Abstract

Using chemical kinetics modeling and statistical analysis, we investigate the possibility of correlating key chemical "markers" – typically small molecules – formed during very lean ($\phi \sim 0.001$) oxidation experiments with near-stoichiometric ($\phi \sim 1$) fuel ignition properties. One goal of this work is to evaluate the feasibility of designing a fuel screening platform, based on small laboratory reactors that operate at low temperatures and use minimal fuel volume. Buras *et al.* [Combust. Flame, 216 (2020) 472-484] have shown that convolutional neural net (CNN) fitting can be used to correlate 1st-stage ignition delay times (IDTs) with OH/HO_2 measurements during very lean oxidation in low-T flow reactors with better than factor of two accuracy. In this work we test the limits of applying this correlation-based approach to predict the Low-Temperature Heat Release (LTHR) and total IDT, including the sensitivity of total IDT to equivalence ratio, ϕ. We demonstrate that 1st-stage IDT can be reliably correlated with very lean oxidation measurements using compressed sensing (CS), which is simpler to implement than CNN fitting. LTHR can also be predicted *via* CS analysis, although the correlation quality is somewhat lower than for 1st-stage IDT. In contrast, the accuracy of total IDT prediction at ϕ = 1 is significantly lower (within a factor of 4 or worse). These results can be rationalized by the fact that 1st-stage IDT and LTHR are primarily determined by low-temperature chemistry, whereas total IDT depends on low-, intermediate-, and high-temperature chemistry. Oxidation reactions are most important at low temperatures, and therefore measurements of universal molecular markers of oxidation do not capture the full chemical complexity required to accurately predict the total IDT even at a single equivalence ratio. As a result, we find that ϕ-sensitivity of ignition delay cannot be predicted at all using solely correlation with lean low-*T* chemical speciation measurements.

1. Introduction

Engine combustion is characterized by fuel-specific oxidation at temperatures below ~850 K and by rapid pyrolysis/small-molecule oxidation at $T > 1000$ K. At intermediate temperatures the formation (mainly *via* CH_2O) and the self-reaction of HO_2 lead to the accumulation of H_2O_2, which decomposes to two OH radicals and produces hot ignition as T further increases. Many new compression-ignition engine concepts control combustion phasing via low-T fuel-specific chemistry by optimizing intake conditions, charge stratification, and fuel molecular structure.[1-3] Consequently, engine/fuel co-design could strongly benefit from the ability to quickly assess the low-T combustion properties of potential new fuels, especially those with significant negative temperature coefficient behavior (NTC, meaning that ignition becomes slower with increasing T).

An ideal fuel screening platform should both be general (i.e., applicable to any proposed fuel candidate or blend) and require as little fuel as possible. Many tools for fuel screening have been described in the literature, e.g., those that measure ignition directly in chambers of various design.[4-6] While this approach is general, it typically requires numerous measurements in a broad range of pressures and temperatures, with 10s of milliliters of fuel used per each P and T point. Furthermore, direct measurements of specific ignition properties are often not easily extrapolated to different properties or different operating conditions. At the other possible extreme, one could learn the detailed chemistry of a potential fuel and then fully predict its behavior in any arbitrary environment. While this approach could be purely computational and therefore use no fuel at all, it requires enormous effort for each fuel, is clearly not general, and becomes impractical for realistic blends with many components.

As a way to overcome these limitations, we have previously proposed an intermediate approach: to correlate chemical speciation measurements during the oxidation of extremely lean ($\phi \sim 0.001$) fuel/air mixtures with ignition properties of interest.[7] To test this idea, we used chemical kinetics modeling to simulate 1) the production of OH, HO_2, and CH_2O (all universal molecular markers of oxidation) under very lean conditions and 2) ignition delays under stoichiometric conditions in air for a large pool of hypothetical fuels. We performed the simulations at P = 10 – 40 bar and T = 600 – 700 K because we expect fuel-specific differences in chemical reactivity to be most pronounced at these conditions. The chemical mechanisms of these hypothetical fuels were created *in silico* by small systematic perturbations of the rate coefficients of key reactions in existing, validated combustion mechanisms of 23 hydrocarbon and oxygenated compounds. The resulting 5296 perturbed mechanisms represented a wide range of hypothetical fuel reactivity, while retaining strong links to the structurally complete source mechanisms. A convolutional neural net (CNN) analysis of these simulations showed that the yield and appearance timescale of OH, HO_2, and CH_2O during very lean oxidation correlated within a factor of 2 or better with 1^{st}-stage IDT at stoichiometric conditions for all fuels, regardless of the source mechanism. These results imply that the reactions that control the efficiency of fuel oxidation also determine the overall 1^{st}-stage ignition timescale in the low-*T* autoignition regime, irrespective of the fuel molecular structure.

Furthermore, these results suggest a broader exploration of the influence primary oxidation reactions have at different stages of combustion. Specifically, by shaping the initial distribution of chemical intermediates and reactive radicals, primary oxidation may affect the heat release profile or even the total ignition time. In the present work, we ask the following questions: 1) Can very lean measurements of chemical markers of oxidation be used to predict near-stoichiometric combustion behavior of arbitrary fuels beyond the 1^{st}-stage ignition? and 2) can these predictions be extended above 700 K, which was our previous upper limit, to encompass the entire low-*T* combustion range?

This study builds on our initial findings by improving our statistical fit methods used to obtain correlations and by applying this approach to progressively more complex ignition properties. The CNN fitting that we relied on previously to predict 1^{st}-stage IDTs is costly, and we show here that a much simpler fit, based on compressed sensing (CS) suffices instead. We also extend our correlation-based approach to predict the Low-Temperature Heat Release (LTHR) and total IDT of arbitrary fuel at stoichiometric conditions. LTHR is an important parameter for HCCI engine performance[8] and was already shown to correlate with autoignition.[9, 10] Recent chemical analyses of LTHR and total IDT behavior suggest that a correlation between these ignition properties and small universal ignition markers may exist.[11, 12] However, total IDT may not correlate perfectly with oxidation chemistry because oxidation reactions are most important at low *T*, whereas total IDT is determined by low-, intermediate-, and high-*T* chemistry. Lastly, we explore whether our approach can predict ϕ-sensitivity (the dependence of total IDT on the equivalence ratio), which has become a fuel property of recent interest.[13, 14]

To achieve these objectives, we used automated chemical kinetics modeling with data augmentation to simulate the autoignition of hypothetical fuels, derived from 27 source mechanisms, under very fuel-lean as well as stoichiometric conditions at various pressures and temperatures. The source fuels represent a wide variety of functional groups and structural motifs, and the resulting extensive pool of hypothetical fuels covers a broad range of reactivity behaviors. We sought to correlate the properties of simulated chemical speciation data with the simulated ignition behavior using compressed sensing fits. The results confirm that a strong correlation of speciation measurement can be made with 1st-stage IDT over a broader *T* range than we surveyed previously. We also find a correlation with LTHR, which tends to be quite accurate for fuels with strong low-temperature chemistry but is somewhat less predictive for those with weak low-*T* chemistry. The predictive accuracy for total IDT is much lower than for 1st-stage IDT, although it can still be estimated within an order of magnitude or better. Furthermore, we find no useful correlation with ϕ-sensitivity, which requires simultaneous prediction of several total IDT values at varying ϕ and is thus the most complex of our target properties. We present an analysis based on known chemistry of ignition processes to explain these observations.

2. Methods

2.1. Generation of Dataset

Generating robust correlations *via* statistical fitting requires very large sample datasets. Unfortunately, there are not nearly enough detailed chemical speciation measurements in the combustion literature nor enough validated chemical mechanisms from which reliable simulated datasets can be produced. Because of this, we followed the chemical modeling/data augmentation approach that we developed previously[7] to generate thousands of hypothetical "clone" chemical mechanisms from a small number of well-established source mechanisms.

Briefly, for correlations of ignition delay times and LTHR, validated chemical mechanisms[15, 16] of 23 different fuels, including alkanes, alkenes, oxygenates, and reference blends, were used to simulate a homogeneous batch reactor containing mixtures of air and fuel at either stoichiometric (ϕ = 1.0) or very lean ($\phi \sim 0.001$) conditions in Chemkin Pro.[17] These source mechanisms were chosen to cover a broad range of structural motifs and functional groups, rather than to match the component profiles of any specific fuels, e.g. of conventional gasoline. For stoichiometric conditions, the simulations were run until fuel ignition occurred (typically up to a few ms); the time histories for temperature, pressure, and OH concentration were extracted. For very lean experiments the heat release was negligible, and the reactor pressure and temperature remained essentially constant. These simulations were propagated in time until significant fuel fraction was consumed (typically up to 100s of ms) and the time profiles of numerous chemical products and reaction intermediates were extracted.

To generate the “clone” chemical mechanisms, we identified the most sensitive reactions at both stoichiometric and very lean conditions (which were overwhelmingly fuel-specific oxidation reactions) in each source fuel simulation. We then systematically varied the rate coefficients of these reactions (individually or in random chosen pairs) by scaling their pre-exponential factors up and down by factors of two. Simulations with perturbed mechanisms were again run using automated scripts, until a dataset of ~27,000 pairs of stoichiometric/lean simulations was generated. The source mechanisms, *P*, and *T* of the simulations are listed in Table S1. Generally, the fuel-lean experiments were simulated over 600 – 850 K and 3 – 70 bar, depending on the range of conditions at which each source mechanism had been validated.

Figure 1 schematically shows representative simulation results: OH/HO_2 concentration vs. time for the lean case (on the left); reactor pressure and heat release profile vs. time for the stoichiometric mixture (on the right). At stoichiometric conditions the simulations produced clear ignition events, evident as a sudden rise in both *P* and *T*, which were sometimes preceded by a 1st-stage ignition, seen as an inflection in the *P*/*T* profiles. At very lean conditions the simulations typically produced clear maxima in the profiles of OH, HO_2 and other species. We define the characteristic timescale for spontaneous lean oxidation, τ_{SO}, as the time at which simulated OH maxima occurred.

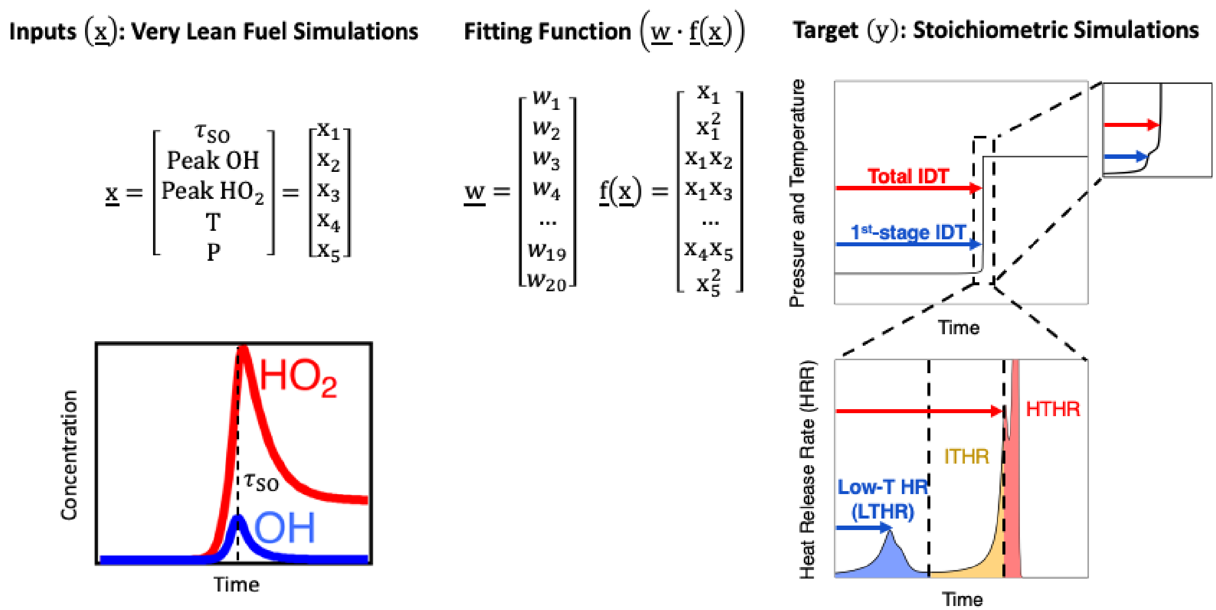

Figure 1: Schematic of overall approach to correlating dilute fuel simulations with fuel properties at stoichiometric conditions. Targets are bolded.

We extracted several features from both the lean and stoichiometric simulations for further analysis. The following features from lean oxidation were extracted for use as inputs for the correlation plots: T, P, the value of τ_{SO}, the peak values and maximum slopes in the concentration-time profiles of OH, HO_2, H, H_2O, H_2O_2, CO, CO_2, CH_2O, HCO, H_2, CH_3CHO, O, and CH_3. These molecules were chosen for two reasons. First, they are small species that are typically formed in the oxidation of nearly any fuel and are thus natural choices for "universal" markers of oxidation reactions. Second, they are routinely measured by optical spectroscopic methods or mass spectrometry and are therefore plausible targets of experimental rapid screening platforms. The main thrust of our analysis focused on OH and HO_2, and we found that including other molecules in the correlation had negligible impact on the results and conclusions (see Table S6 in SI).

In the stoichiometric case three features were extracted from each simulation to be used as targets for correlation: 1st-stage IDT (τ_1), defined similarly to Merchant *et al.*[18] as the time to maximum OH concentration, total IDT (τ_{total}), defined as the time to maximum slope in P, and Low-T Heat Release (LTHR), defined as the percentage of the total heat released during 1st-stage ignition.

We determined ϕ-sensitivity at near-stoichiometric conditions from simulated total IDT values at ϕ = 0.4 – 0.7, usng the "NREL" definition of ϕ-sensitivity,[13] which has the advantage of being largely ϕ-independent over this range of ϕ:

$$\Phi\text{-sensitivity} = -\frac{\phi}{\tau_{\mathrm{Total}}}\frac{\mathrm{d}\tau_{\mathrm{Total}}}{\mathrm{d}\phi}\bigg|_{\phi=0.4-0.7} \quad \text{(Eq. 1)}$$

Because ϕ-sensitivity is more computationally expensive to obtain than the other targets, a smaller simulation dataset was generated for this purpose specifically, using only the source fuel mechanisms (i.e., no perturbed "hypothetical" mechanism) at many *P* and *T* points. This dataset used the Co-Optima mechanism,[19] which includes detailed chemistry of many fuels. The 27 fuels that we simulated are listed in Table S2. In this manner, we generated a dataset with ~1,300 points without perturbing the original mechanisms.

2.2. Compressed Sensing (CS)

In this work, we used Compressed Sensing [20] to look for correlations between inputs derived from lean simulations, denoted $\underline{x}$, and the targets described above (τ_1, τ_{Total}, LTHR, and ϕ-sensitivity), denoted y. As shown in Fig. 1, CS, which is a variant of Polynomial Chaos Expansion (PCE) with regularization, consists simply of fitting a polynomial, $\underline{f}(\underline{x})$, of user-specified order, n. For example, if we used five inputs (P, *T*, τ_{SO}, peak OH, and peak HO_2) and a second-order polynomial, the fit function contained 20 terms, each with a fitting weight, w. These terms included five linear terms of the form $w_i \cdot x_j$ and fifteen second-order square and cross-terms of the form $w_i \cdot x_j \cdot x_k$ (i. e. j could be equal to k). The loss function, L, consists of two contributions: the error of the fit and a regularization term to prevent overfitting, as shown in Equation 2:

$$\mathrm{L} = |y - \underline{w} \cdot \underline{f}(\underline{x})| + \lambda|\underline{w}|_1 \quad \text{(Eq. 2)}$$

The regularization term in Eq. 2 is the L1 norm of the weight vector $\underline{w}$, multiplied by a tuned parameter, λ, which we optimized using sorted 10-fold cross-validation (CV) error, as in our previous work.[7] Briefly, for each target we attempted to fit, the simulation dataset was sorted in the order of increasing target value and divided into ten slices of equal size. Subsequently, independent CS fits were performed in which each of the ten slices was used for validation, while the remaining nine slices served as training data.

CS has three advantages over CNNs, which we used previously.[7] First, there are only two hyperparameters to tune, λ and n, compared to many for CNNs (e.g., number of filters, filter width, number of neural net layers and neurons). Second, there are also far fewer weights to fit (20 compared to 1000s potentially), which can be done deterministically. Finally, Sobol Sensitivities can be obtained to determine the relative importance of each input to the overall correlation.[21] CNN-based fits from our previous work establish a benchmark correlation accuracy of factor of two for τ_1, against which subsequent correlations can be compared. CNN fits are more flexible than CS because they use full species time profiles, rather than certain features of these profiles, selected *a priori*. However, by comparing different CNN fit inputs we concluded that τ_{SO} and maximum species concentrations enabled τ_1 predictions on par with those from the full time profiles. As a result, in the present work we focus on CS fits due to their simplicity.

We assessed the overall accuracy of the CS-based correlations using "Leave-One-Fuel-Out" (LOFO) tests, in which all simulations using perturbations of a single source mechanism comprise the validation set, and all remaining simulations are the training set. One exception to this approach was that reference fuel blends (PRFs, TRFs, TPRFs, EPRFs and ETPRFs) were lumped into a separate test set and were always left out of training set to avoid biasing the predictions in favor of the blend components (e.g., n-heptane and iso-octane). LOFO tests guard against overfitting by preventing simulations from closely related clone mechanisms from appearing in the training and validation datasets at the same time. In this manner, LOFO tests determine whether our discovered correlations are general and transferable to potential fuels with diverse molecular structure.

3. Results & Discussion

3.1. 1st-Stage IDT

In our previous work that introduced the idea of *in silico* automated hypothetical fuel generation, we correlated simulated lean oxidation measurements with τ_1 at stoichiometric conditions using CNNs, but only up to T = 700 K.[7] In the following, we employ CS to extend this correlation to 850 K, approaching the commonly accepted upper limit of the low-temperature oxidation regime.[22, 23] We developed the updated correlation using CS fitting to a second-order polynomial with only five scalar inputs, described in section 2.1: *P*, *T*, τ_{SO}, peak OH, and peak HO_2. The overall RMS error of the sorted 10-fold CV test and the LOFO tests of τ_1 predictions are 47% and 41%, respectively, as listed in Table S3.

According to the analysis of Sobol Sensitivities, three of the five scalar inputs are most important for the fit (see Figure S6): *T*, τ_{SO} and peak [OH]. We also investigated the effect of the polynomial order on the quality of the fit, as shown in Table S3. We found that a 3rd-order polynomial did not substantially improve either the 10-fold sorted CV or the LOFO test errors. Consequently, we consider a 2nd-order fit preferable because it uses many fewer coefficients.

Figure 2 shows the results of LOFO tests by plotting the errors of predicted 1st stage IDTs from simulated lean measurements relative to explicitly simulated τ_1 under stoichiometric conditions. To avoid skewing the analysis by a small number of strongly outlying simulations, we focus on the median rather than the mean errors in predicted τ_1; we also present the 25/75%, 10/90%, and min/max values of each error distribution. As Figure 2 shows, at least 75% of the predicted 1st stage IDTs fall within a factor of 2 of the explicitly simulated value for nearly all left-out fuels, which is the same level of accuracy achieved previously using CNNs.[7] The only exceptions are methyl cyclohexane (MCH), 2-hexene, and butylbenzene, for which slightly less than 75% of the error distribution are accurate to within a factor of 2. As in our earlier work,[7] we attribute the decrease in prediction quality for these fuels to likely imperfections in the source mechanisms.

Overall, these results are in excellent agreement with our previous findings over a more limited temperature range. However, we note that for many fuels the error distributions are more narrow than the factor-of-2 bounds, but not symmetric about zero. A more detailed look at this phenomenon is given in Figure 3, which shows parity plots of predicted vs. simulated τ_1 for hypothetical fuels spawned from select source mechanisms (Figure S1 shows parity plots for all 23 source mechanisms considered). Of particular interest are *n*-heptane and *i*-octane, which represent the conventional extremes of the octane number scale. For all hypothetical fuels from these two mechanisms, the predicted τ_1 values lie very close to the parity line, meaning that τ_1 is predicted better than a factor of two for all simulations over the entire *T* range, from 600 to 850 K. Above 850 K τ_1 is generally too short to be observable by realistic experiments, and at sufficiently high temperatures first-stage ignition ceases to be a meaningful concept.

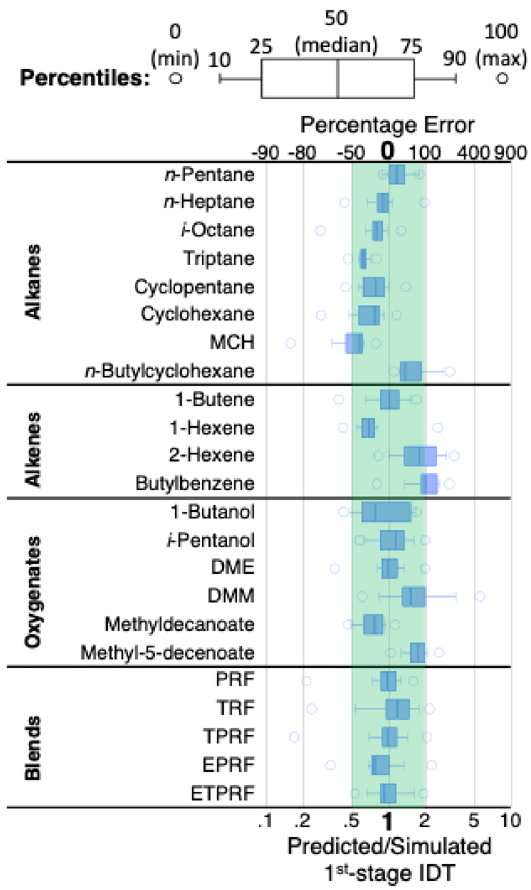

Figure 2: Summary of LOFO test results for predicting 1st-stage IDT. Green shading indicates factor of two accuracy.

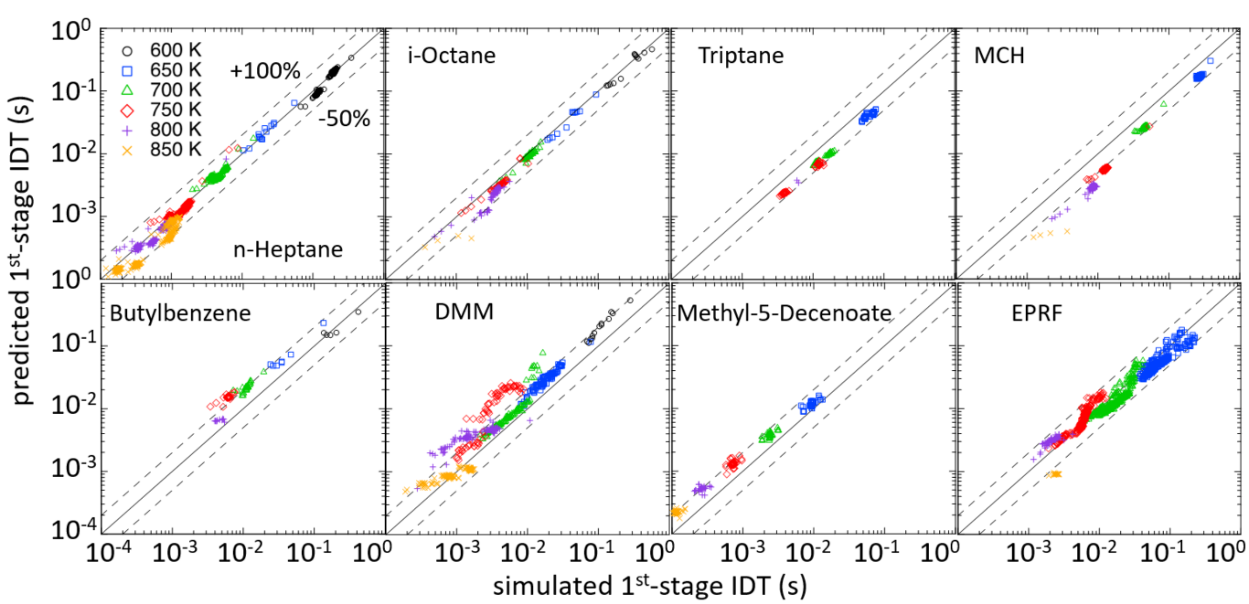

Figure 3: Parity plots of LOFO tests for predicting 1st-stage IDT for selected fuels. Dashed lines show factor of 2 error.

Interestingly, for several of the fuels in Figure 3 the predicted τ_1 values are offset from the parity line but have a slope close to the parity line, meaning that they differ from the explicitly simulated τ_1 by a constant factor. This behavior may be evidence of systematic errors in the source mechanisms, which are not fully captured by our correlation. If so, further improvements in the source mechanisms used for synthetic dataset generation as well as incorporation of experimental measurements to anchor training datasets may bring about even better accuracy in the prediction of 1st-stage IDT from extremely lean speciation experiments.

From the results above we conclude that it is possible to devise a procedure to predict 1st-stage IDT at *P* up to 10s of bar and *T* = 600 - 850 K for any arbitrary fuel or blend based on measurements under very lean conditions using small fuel quantities. The robustness of this correlation reflects the nature of OH as a universal chain carrier for 1st stage ignition and the close relationship between its production and the course of low-temperature chemistry.[24, 25] This observation is consistent with current chemical understanding that chain-branching reaction pathways at low temperatures can be written as R → RO_2 → QOOH → O_2QOOH → $OQ_{-H}O$ + 2 OH.

The fuel-structure dependence of this reaction sequence should be reflected in the timescale and intensity of various species formation, and therefore it is not surprising that speciation measurements can be correlated nearly quantitatively with τ_1. However, the quality of the correlation using only τ_{SO} and [OH], rather than full time profiles of multiple species, is a significant finding, which should facilitate the development of experimental measurements for fuel screening. In effect, our results suggest that such measurements need only determine τ_{SO} and peak [OH] accurately and that they may tolerate large uncertainty in [OH] at all other times. Numerous studies show that τ_1 is a key parameter to estimating total IDT at low and intermediate temperatures.[26-28] Integrating the inverse of the ignition time over full pressure-temperature trajectories, including the low-*T* regime, is a common tool for predicting engine performance at various operating conditions.[29] Thus, experimental probing of oxidation markers that we consider here can play a part in selecting fuel candidates for desired low-*T* combustion behavior.

3.2. LTHR

The correlation between autoignition and LTHR has long been noted.[9, 10] Specifically, Rapp *et al*. found that for many gasoline and reference fuel blends, earlier autoignition in an HCCI engine is also accompanied by more intense LTHR. This trend is replicated in our analysis, which provides additional evidence that the hypothetical fuels comprising our synthetic dataset maintain the physically correct ignition behavior of the source mechanisms. Figure 4 shows the inverse relationship between the simulated τ_1 and LTHR at any given temperature within our dataset of ~27,000 samples, in which points at different temperatures, 600 – 850 K, have been color-coded. The systematic *T*-dependent shift in the slopes of the data distributions in Fig. 4 suggests the possibility of developing a universal fuel-independent correlation between the lean oxidation measurements and LTHR.

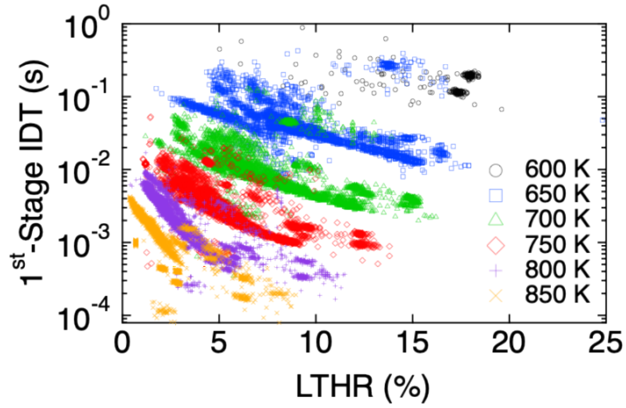

Figure 4: Explicitly simulated 1st-stage IDT vs. LTHR at T = 600 – 850 K.

Figure 5 presents the error distributions of the LOFO tests for LTHR correlation with lean speciation measurements, using 2nd-order polynomial fitting with *P*, *T*, τ_{SO}, peak OH, and peak HO_2 as inputs. Figure 6 shows detailed parity plots for select source mechanisms, and Fig. S3 shows all the parity plots. In all figures, LTHR is expressed as the percentage ot total heat released during ignition. These results demonstrate that although LTHR can be predicted from "lean" measurements, the accuracy of this prediction depends on how prominent LTHR is in the heat release profile. For all left-out fuels except triptane and cyclohexane 75% of the LTHR predictions fall within 4% of the explicitly simulated values; indeed, for many fuels they lie within ~2%. The overall absolute RMS errors of the sorted CV test and the LOFO test are 2.1 and 1.8%, respectively, as listed in Table S4. However, LTHR varies between 2 and 20% throughout the entire dataset, and therefore a typical absolute error of ±2% represents better relative accuracy for high-LTHR simulations than for low-LTHR cases.

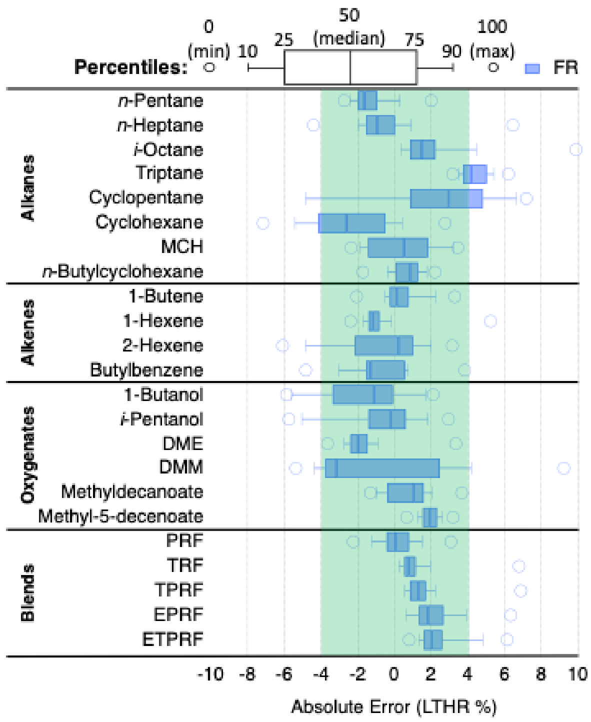

Figure 5: Summary of LOFO results for LTHR, with green shading indicating ±4% error.

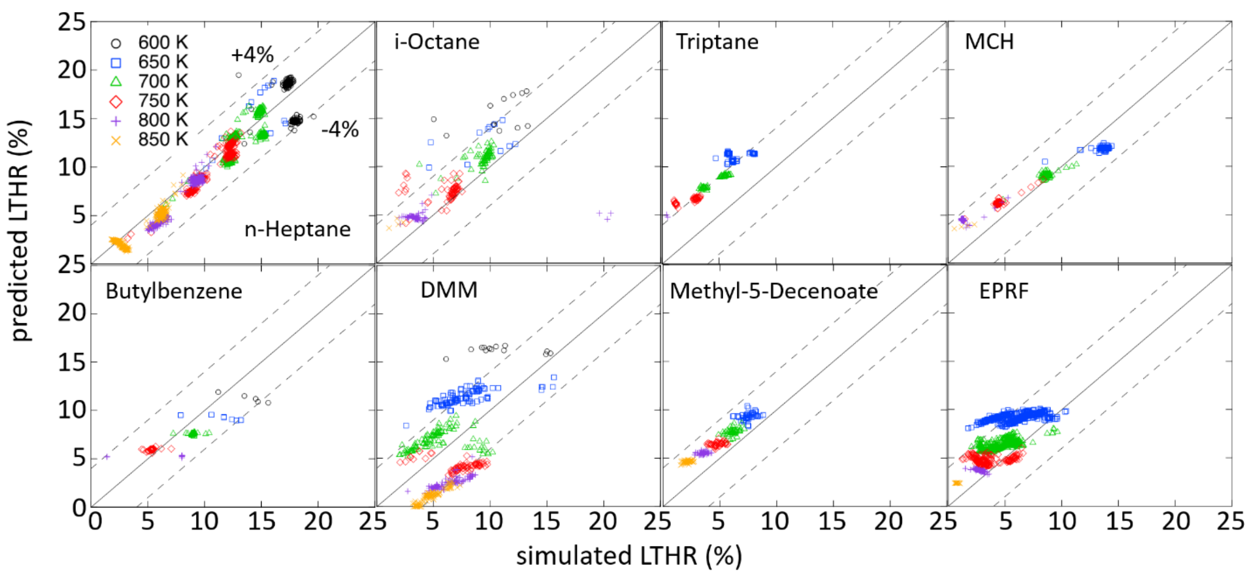

Figure 6: Parity plots of LOFO tests for predicting LTHR for selected fuels.

We found the same three scalar inputs to be important for the LTHR correlation as for the τ_1 correlation: T, τ_{SO}, and peak [OH] (see Figure S6). Increasing the polynomial fit order to 3 did not significantly improve the errors. In addition, we found that including species other than OH and HO_2 as inputs did not improve the prediction accuracy appreciably. These observations can be traced back to LTHR being not related closely to one or more radical species, but rather to specific chemical reaction classes and their fuel-specific equilibrium and exothermicity. Lokachari *et al*. point out that the low temperature exothermicity is dominated by the R + O_2 chemistry, with additional contributions from fuel + OH and HO_2 + HO_2 = H_2O_2 + O_2 reactions.[12] The main competitive endothermic reaction is the concerted elimination of HO_2 from RO_2. If the observed scatter in the LTHR predictions stems from a lack of knowledge of the relevant thermochemistry, then including more chemical species as inputs will not improve the correlation.

Even more so than τ_1, LTHR is a key indicator of low-*T* reactivity in engines[30, 31] and can be used to condition the P-T trajectory for optimal phasing and reduced knock propensity.[32-34] The correlation-based approach identified here can again be an important screening tool to estimate the engine performance of potential fuel candidates.

3.3. Total IDT and ϕ*-Sensitivity*

Compared to 1st-stage IDT, the processes underlying Total IDT are inherently more complex, fundamentally because chemistry in low, intermediate, and high-*T* regimes is involved.[18] Nonetheless, the low-temperature processes may condition the progress through subsequent stages of ignition, so we attempted to correlate the modeled fuel-lean oxidation experiments, which are most sensitive to low-*T* chemistry, with τ_{total}.

Figure 7 shows the relationship between τ_1 and τ_{total} in our dataset at various *T* from 600 to 850 K, each temperature coded by a specific color. Starting at 600 K the 1st-stage IDT is essentially identical to the total IDT, but as *T* increases, they increasingly diverge as has long been observed. At the highest temperatures we used, 850 K, τ_{total} is in some cases exceeds τ_1 by up to a factor of ~10. Our question then becomes: can information gained from probing oxidation reactions in fuel-lean experiments be correlated with the chemical evolution that takes place between the initial stages and bulk ignition (between τ_1 and τ_{total}) in a stoichiometric fuel/air mixture?

The results of the LOFO tests for τ_{Total} are presented in Fig. 8 for fits using the same five inputs as for τ_1 and LTHR. Comparing these results with those for 1st-stage IDT reveals a clear reduction in the correlation quality. The RMS errors of the 10-fold sorted CV and the LOFO tests (listed in Table S5), are 161% and 89%, respectively, which is significantly worse than for τ_1. It is noteworthy that the more rigorous of the two tests, LOFO, nominally produces smaller RMS errors than the CV test. This may be evidence that very poor predictions of total IDT for some hypothetical fuels contaminate the sorted CV test, in which all hypothetical fuel families are present in the training dataset.

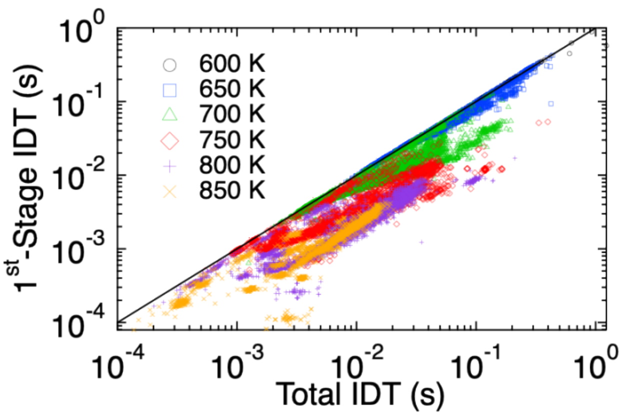

Figure 7: Simulated 1st-stage IDT vs. total IDT at temperatures 600 – 850 K. The solid black line indicates parity (y=x).

Indeed, the detailed parity plots of predicted vs. directly simulated τ_{total} in Figs. 9 and S2 show that the correlation is substantially worse than a factor of 2 for numerous left-out source mechanisms, including MCH, triptane, DMM, methyl-5-decenoate, and even some reference fuel blend simulations. Although DMM, which was also an outlier in the τ_1 correlation, might be similarly dismissed here as an aberration of a more general τ_{total} correlation, the same cannot be said of triptane, MCH and methyl-5-decenoate, all of which had good correlations for τ_1. In all the latter cases, it seems that the higher-*T* simulations are the problem and that predictions begin to fall outside the factor-of-2 bounds at ~750 K and above. This trend coincides with the onset of NTC behavior in all the problematic fuels and possibly stems from deficiencies in intermediate-*T* reactions in the source mechanisms. Notably, the well-studied fuels *n*-heptane, iso-octane, and EPRF blends perform well up to 850 K in our study. For methyl-5-decenoate in particular, whereas τ_1 was predicted uniformly well across all *T*, there is clearly a gradual worsening of prediction accuracy for τ_{total} with increasing *T*, which may be related to the divergence between τ_1 and τ_{total} with increasing *T*.

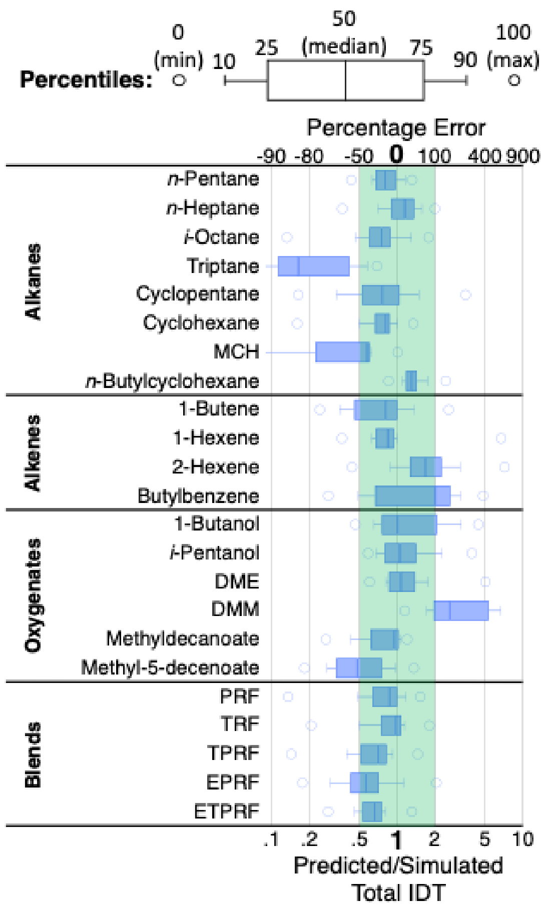

Figure 8: Summary of LOFO results for total IDT. Green shading indicates factor of two accuracy.

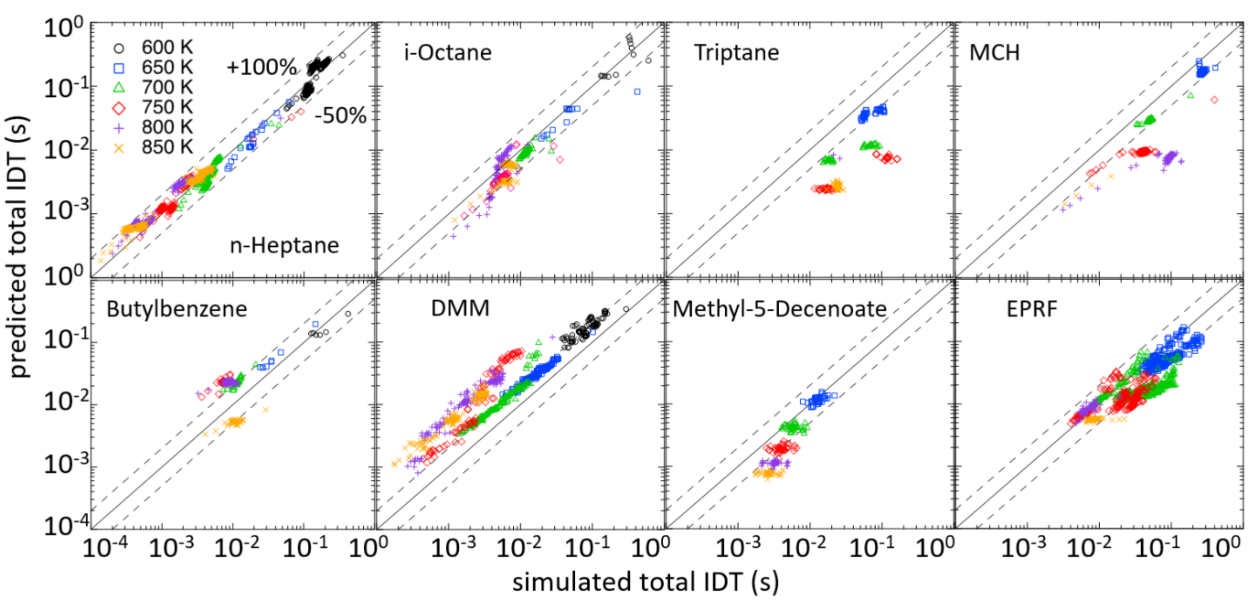

Figure 9: Parity plots of selected LOFO tests for total IDT. Dashed lines show factor of 2 error.

Our difficulty with predicting total IDT, especially at T = 750 – 850 K, stands in contrast to the successful modeling of high-temperature ignition delays and flame properties of hydrocarbon fuels by the HyChem approach.[35, 36] Because at T > 1200 K such fuels quickly decompose to a small set of fragments, HyChem proposed a simple "lumped" reaction mechanism that can be calibrated to experimental measurements of a few chemical markers of pyrolysis: CH_4, C_2H_4, C_3H_6, *n*- and *iso*-butene (C_4H_8), benzene (C_6H_6), and toluene (C_7H_8). Recently, Zhang *et al.* developed a fuel-structure based correlation to estimate the yields of these pyrolysis markers, potentially leading to a purely computational prediction of high-T combustion properties.[37] However, HyChem is by design intended for high-T applications; although Xu and Wang recently suggested that CO and CH_2O may serve as markers of NTC chemistry within HyChem,[38] HyChem is not used below 1000 K and its predictions deteriorate below ~1200 K. In this context, we see our poor prediction of total IDT at 750 – 850 K as evidence that the transition from a low-T, cool-flame regime to a high-T, hot-ignition regime is too complex to be accurately captured either by oxidation-only or pyrolysis-only markers.

Of all the fuel properties we targeted, ϕ-sensitivity is the most complex because it requires simultaneously predicting total IDTs at several equivalence ratios between ϕ=0.4 and ϕ=0.7. Figure 10 shows the error distributions of the LOFO tests of the predicted ϕ-sensitivity, and Figure S4 presents the parity plots from which the errors were determined. At first glance, the results in Fig. 10 seem to imply the presence of a coarse correlation between lean oxidation measurements and ϕ-sensitivity with absolute errors of ±0.5 for most of the left-out fuels. However, these errors are too large to be useful for fuel screening because, unlike ignition delay times, which can range over many orders of magnitude, typical ϕ-sensitivity values are between 0 and 2. Furthermore, as Figure S4 demonstrates, the plots of predicted vs. directly simulated ϕ-sensitivity exhibit unpredictable curved "horseshoe" shapes and in many cases are not single-valued. The direction and shape of these plots varies greatly from one left-out fuel (i.e., from one source mechanism) to the next. As a result, although a correlation between lean fuel measurements and ϕ-sensitivity may appear possible for any one left-out fuel, such a correlation is not universally applicable to all fuels.

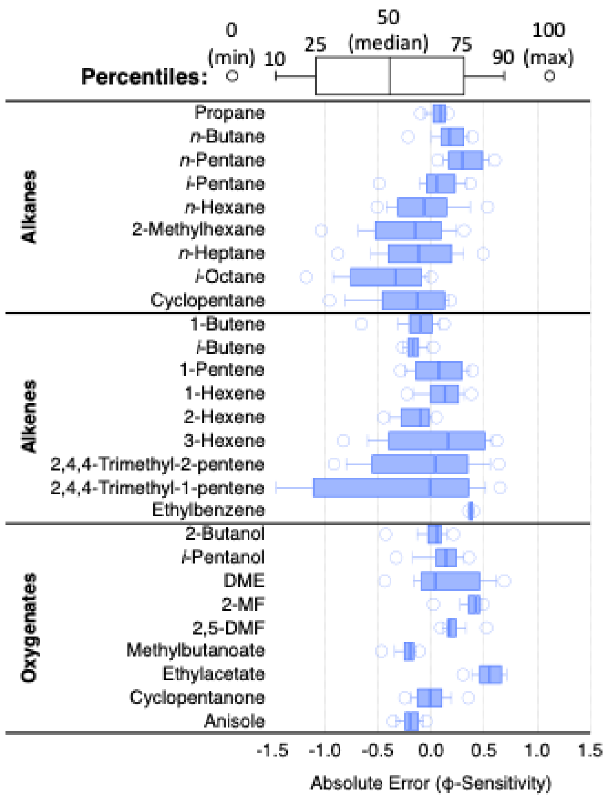

Figure 10: Summary of LOFO results for predicting ϕ-sensitivity.

Of course, the identified correlation for total IDT τ_{Total} is already weak for the reasons outlined above, so the same chemical arguments at least partially underlie the failure of the CS fit to predict ϕ-sensitivity. Analyses of the detailed chemistry behind ϕ-sensitivity have shown that fuel-structure sensitive low-*T* and intermediate-*T* reactions are operative, where the former generally involve peroxy radical chemistry on the backbone of the fuel molecule, and the latter involve the subsequent oxidation of smaller products such as formaldehyde (CH_2O) and hydrogen peroxide (H_2O_2).[13, 14]

However, we find that ϕ-sensitivity exhibits no robust correlation with profiles of small-molecule combustion intermediates. Table S6 details our attempts to improve this correlation by varying the polynomial fit order and including additional species and temporal features into the fit. Figure S5 shows the detailed parity plots resulting from these variations in the fit for a representative example of *i*-octane. The apparent structure of the parity plot changes dramatically from polynomial order n = 1 to n= 2, but never converges to a common "shape" with other fuels, indicating that a meaningful universal correlation likely does not exist.

Kukkadapu *et al*. noted that the rate constant for dissociation of hydrogen peroxide (H_2O_2) is quite important in determining the total ignition delay time, but not for the first stage ignition time.[11] Unfortunately, inclusion of H_2O_2 in our fits did not improve the results, possibly because OH concentrations in the fuel-lean oxidation simulations were too low to produce enough H_2O_2 populations from OH self-reaction. If true, then oxidation experiments with higher fuel levels may allow for better correlation, but such experiments would not meet the desired “minimal fuel” requirements of a practical rapid screening platform.

It might be worth testing whether including simulated profiles of alkylperoxy radicals (RO_2) and peroxyalkyhydroperoxide radicals (O_2QOOH) from lean simulations as inputs improves the correlation, because Kukkadapu *et al*. have also shown that the isomerization reactions of these intermediates control the total ignition delay time.[11] However, molecular structures of RO_2 and O_2QOOH are clearly fuel-dependent, and a universal experimental measurement of these radicals is likely to be practically impossible. Overall, it seems that a screening platform based on low-temperature chemical intermediates is unlikely to provide an accurate, fuel-agnostic prediction of total IDT or ϕ-sensitivity.

4. Conclusions

We used CS to look for correlations between OH and HO_2 production during simulated lean fuel oxidation ($\phi \sim 0.001$) and four fuel ignition properties at or near stoichiometric conditions: τ_1, LTHR, τ_{Total}, and ϕ-sensitivity. We found that CS fitting is simpler, less computationally costly, and more easily interpretable than the CNN fitting used by our group previously to discover a predictive correlation for τ_1.[7] In the present work, we demonstrated that τ_1 can be predicted from measurements of OH during lean fuel oxidation within a factor of two or better, which is similar accuracy to the earlier CNN-based prediction. Additionally, we have shown here that such a correlation exists over the extended temperature range of 600 – 850 K, and that only two features (τ_{SO} and peak [OH]) are adequate to achieve a strong correlation.

We found that the correlation with LTHR is weaker than with 1st-stage IDT but may still be useful for coarse screening (~4% absolute accuracy). It is notable that the LTHR, which is generally thought to be the most fuel-specific part of ignition, is susceptible to such a simple and universal correlation. Finally, the poor Leave-One-Fuel-Out tests for τ_{Total} and ϕ-sensitivity suggest that the course of the intermediate- and higher temperature ignition is not sufficiently conditioned on low-temperature chemistry for a correlation with ultra-dilute measurements to succeed. Overall, these results suggest that measurements of chemical speciation in lean oxidation below 850 K will be most useful for predicting low-T behavior, specifically τ_1 and LTHR.

Current engine models are tasked with predicting performance over an enormous range of operating conditions, including variable engine load, intake temperature, boost, amount of end-gas recirculation, and fuel injection mode. We propose that our findings can be translated into practice as a rapid screening method of potential fuels and blends for desirable low-*T* combustion properties, especially for compression-ignition and multi-mode engines that rely at least to an extent on low-*T* chemistry to optimize performance. Importantly, measurements of oxidation markers using minute fuel quantities can be done in flexible laboratory reactors over much wider ranges of conditions that are achievable in research engines without expensive modifications. The resulting predictions of 1st-stage ignition, total ignition (at T < 750 K) and LTHR can then be directly used in engine models to select promising fuel candidates for further study.

Supporting Material. List of source chemical mechanisms, detailed results of CS fitting.

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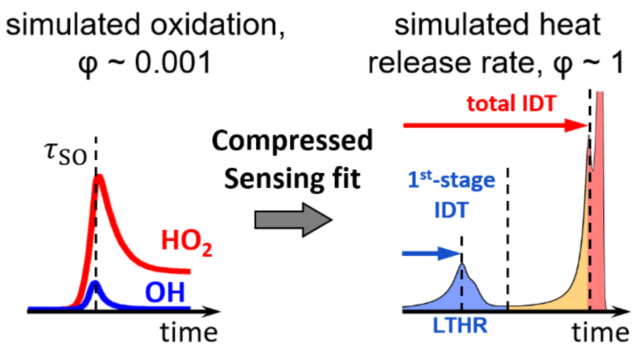
TOC graphic



simulated oxidation,
φ ~ 0.001
τ_{SO}
HO_2
OH
time
Compressed
Sensing fit
simulated heat
release rate, φ ~ 1
total IDT
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IDT
LTHR
time