Simplifying Ignition Delay Prediction of Chemical Kinetic Models by Means of Ignition Correlations

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1 Abstract

Sustained research activities in combustion chemistry have yielded multi-component chemical kinetic models for various combustion simulations. These models are often very large, with over a thousand chemical species and thousands of elementary chemical kinetic reactions. Although model reduction can be used to obtain smaller versions to lower the computational cost, the resulting skeletal schemes are still too large to permit direct implementation in some transport-dominated combustion simulations.

For predictions of ignition delay times, it would be useful to develop analytic expressions which summarize the performance of given detailed chemical kinetic models. In this work, an approach is demonstrated for ignition delay correlation developments from chemical kinetic models. Ignition delay times are simulated using literature models over a range of temperatures and pressures. The data set is used to develop ignition delay time correlations which enable the prediction of simulated ignition delay times at a wide range of conditions. The correlation consists of three sub correlations covering the low-temperature, high-temperature, and Negative Temperature Coefficient (NTC) regions, with switch functions which capture the pressure-temperature dependence of the boundaries of the NTC region. This approach can also be applied to experimental data, providing a means of rigorously constraining and comparing the performance of kinetic models with respect to experimental observations.

2 Introduction

Auto ignition is the transition of combustible mixtures from a stable unburned state to a burned state after subjection to a temperature increase. Because of the non-equilibrium nature of the phenomenon, its incorporation in combustion simulations requires detailed chemical kinetic models. There has been substantial progress in the development of these models for transportation fuels. However, combustion in engines occurs in turbulent compressible flows, so that combustion models have to contend with challenges related to turbulent flows and those associated with coupled multi-step chemical reactions. There seem to be two paths taken in combustion research, with chemical kinetic modeling favoring chemically consistent and comprehensive models while the practical needs of the combustion analyst requires simpler models which incorporate chemical kinetic effects to a satisfactory degree.

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A number of approaches are used in the literature to address this problem. These include the development of skeletal models, highly-reduced models, global reaction models, reactor networks, and empirical correlations. Skeletal models are derived from detailed models by identifying and eliminating chemical species and reactions which are inconsequential to the prediction of combustion properties, such as flame propagation characteristics and ignition delay times. Highly-reduced models are often derived from skeletal chemical kinetic models and include parameters different from those in the original model. A global reaction model is often employed with the aim of capturing steady combustion behavior that is less kinetically dependent, such as total heat release. Several sensitivity and graphical methods are currently used to obtain skeletal mechanisms for fuel surrogates [1]. For heavy hydrocarbons, such as n-heptane and larger, it is observed that skeletal models which retain the predictive capability of detailed models generally have about a hundred species or more. Further reduction to obtain even smaller models requires a combination of lumping, steady-state assumptions and modification of reaction rate parameters or introduction of other model constants.

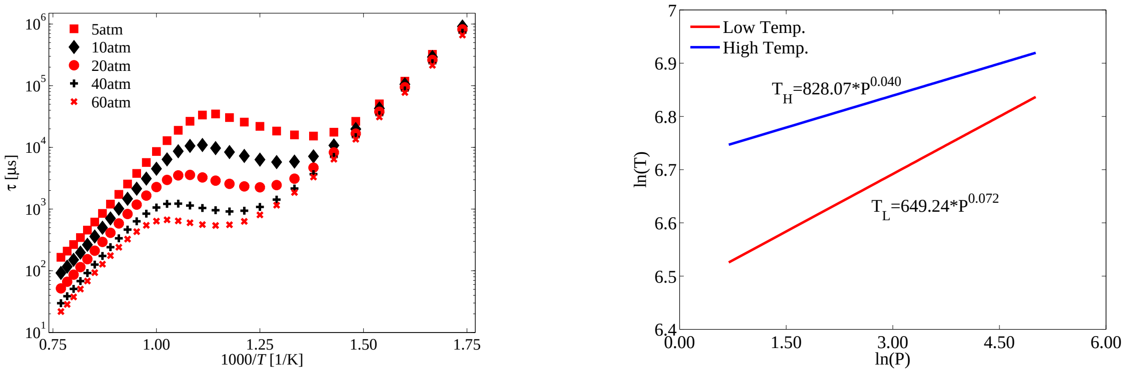
With regards to simplifying the ignition delay prediction using correlation methods, some work based on chemical kinetic models has been presented in the literature. While most focus on empirical Arrhenius-type expressions, there has been sustained effort by researchers to develop highly reduced chemical kinetic models based on analysis of detailed and skeletal chemical kinetic models. A detailed analysis of temperature cross-over effects in n-heptane ignition was presented by Peters et al. [2]. Following in this direction, Saxena et al. [3] developed a generalized expression for the prediction of high-temperature ignition delay times of n-alkanes, starting from a highly reduced skeletal mechanism. A recent extension of this analytic approximation of ignition delay times has been presented by Beeckmann et al. [4], focusing on both the low- and high-temperature ignition of dimethyl ether.

The other approach to simplifying prediction is empirical correlation development [5]. An empirical ignition correlation capable of capturing the complex temperature and pressure dependence of ignition delay times for long-chain hydrocarbons has been proposed by Vandersickel et al. [6], comprising separate correlations for the low-, high-, and intermediate-temperature or NTC regions. This approach has recently been used by Gowdagiri and Oehlschlaeger [7] to obtain generalized ignition correlations for alternative jet fuel and diesel. The main ignition correlation is obtained from sub correlations using the relation $\frac{1}{\tau} = \frac{1}{\tau_{low}+\tau_{mid}} + \frac{1}{\tau_{high}}$, which could be written as $\tau = \frac{\tau_{high}(\tau_{low}+\tau_{mid})}{\tau_{low}+\tau_{mid}+\tau_{high}}$. It can be shown that in the region where a change in temperature sensitivity is experienced, some deviations would be observed between the correlations and the original data on which it is based. Such a correlation method can also be applied to detailed chemical kinetic model simulations to obtain simplified ignition models. It would be useful if other chemical kinetic relevant features such as cross over temperatures could be explicitly accounted for in the ignition model to provide further insight on the chemical kinetic effects.

In this work, two detailed chemical kinetic models for combustion modeling of jet fuel surrogates are used to obtain generalized ignition correlations for stoichiometric fuel/air mixtures. The correlation is intended to reproduce ignition delay time predictions over a wide range of pressures and temperatures, including the pressure-dependent Negative Temperature Coefficient region. An explicit relation between cross-over temperatures and pressures is first sought. The performance of the correlations is then assessed and the correlation approach is also applied to a selected dataset on shock tube ignition of a jet fuel surrogate. This work is based on chemical kinetic models for jet fuel surrogates by Dooley et al. [8] and Honnet et al. [9] .

3 Ignition delay correlation development

Ignition delay times are calculated with CHEMKIN for stoichiometric fuel/air ratios over a range of temperatures and pressures. The model by Dooley et al. [8] consists of 1599 species and 6633 reac-



(a) Ignition delay simulation ($\phi = 1$) (b) Cross-over temperatures dependence on pressures

Figure 1: Representative ignition simulation for correlation development based on the jet fuel model by Dooley et al. [8] and dependence of cross-over temperatures on reactor pressures.

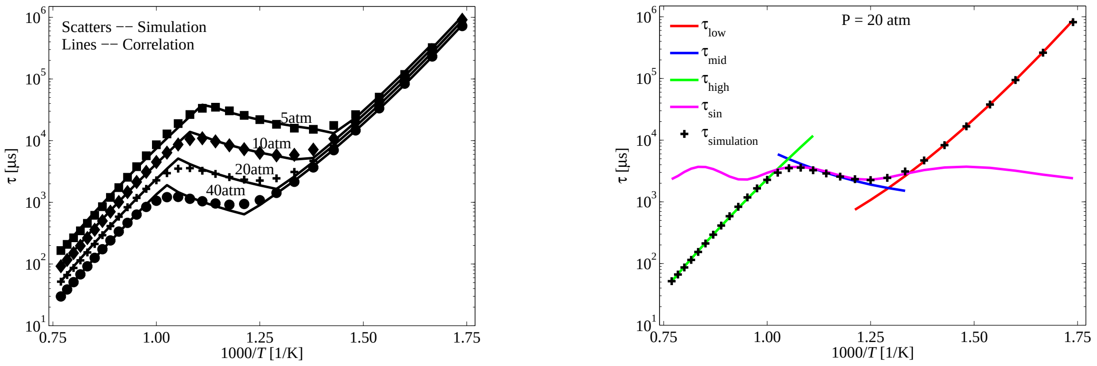
tions. A smaller model for kerosene by Honnet et al. [9] comprises 119 species and 527 reactions. The surrogate composition used for the Dooley et al. [8] is n-decane, iso-octane, and toluene in the ratio 42.67/33.02/24.31, referred to as the Princeton Surrogate. The Aachen surrogate composition, 80% n-decane and 20 % trimethylbenzene, is used to develop the correlation of the Aachen model. The ignition delay time is defined as the time from reaction onset to the time when the maximum OH concentration is observed, with the verification that it is indeed the main ignition.

Figure 1a shows the simulations of the Princeton Surrogate at various pressures. The NTC behavior is observed at all pressures considered. It is seen that the pressure dependence of the low-temperature region is weaker than that observed for high-temperature and NTC. The NTC behavior is such that its onset and end temperatures shift to higher temperatures as the pressure increases. In the current correlation approach, a relation is sought between the cross-over temperature and the pressure of the reactor. A relation is postulated as shown in Figure 1b of the form $T \propto p^m$, where the pressure, p, is in atm and m is an exponent.The proportionality constant and the exponent are obtained through linear regression of a set of turning points at various pressures obtained from simulations.

By linearly regressing the data using a postulated ignition dependence, three separate correlations are obtained. Parameters for correlations of each region of the form $\tau = cp^{\alpha}\left(\frac{T}{T_{ref}}\right)^{\beta}\exp\left(\frac{\theta_a}{T}\right)$ are obtained by inverse matrix division using the MATLAB software package, here T_{ref} = 298 K. The format is motivated by the the Arrhenius rate constant, since we can interpret ignition time scale as reciprocal of a first order global reaction. For the constants to be physically meaningful, the presumed rate constant should be regressed in the format: $\tau \propto \exp\left(\frac{E_a}{RT}\right)$. For the For a pressure of 20 atm, these correlations are plotted alongside the original data in Fig. 2b. It is observed that the correlations accurately reproduce the simulations in each region, while deviations are shown around the cross-over temperatures as expected.

In the current approach, we combine the sub-correlations by introducing the hyperbolic tangent as a switch function with parameters consisting of cross-over temperatures and a temperature difference over which the function transitions. With two switches at the cross-over temperatures, we evaluate the performance of the correlation with respect to reproducing the original simulation data. The switches have the form $\eta_1 = \frac{1}{2}(1 - \tanh[\frac{T-(T_L-10)}{10}]$, $\eta_2 = \frac{1}{2}(1 - \tanh[\frac{T-(T_H+10)}{10}]$ and the correlation has the form $\tau = \tau_{low}\eta_1 + \tau_{mid}(1-\eta_1)\eta_2 + \tau_{high}(1-\eta_2)$, capturing the whole temperature region. However, deviations are observed at the cross-over points as shown in Fig. 2a.

To further improve the agreement between correlation and detailed model simulations in the vicinity of the cross-over temperatures, a sine function is introduced around the transition points as shown in Fig.



(a) Comparison of the correlation with two switches

(b) Three sub-regions correlations

Figure 2: Comparision with two switches at cross-over temperatures and representative behavior of the sub-correlations (the high-temperature, NTC, and low-temperature regions).

2b and four switches are effectively used to control the smooth change around the transition points. The cross-over temperatures can be used to center the sine wave around the point of interest but an amplitude function is necessary to capture the departure of the ignition dependence at various pressures. For the Dooley model, these amplitudes, t_L and t_H, are found by further regression analysis of the form $t \propto p^k$. The final sine function, τ_{sin}, takes the form as shown in the eqn. 1.

$$T_{cross} = ap^m \quad t_{cross} = bp^n \quad \tau_{sin} = \frac{t_H - t_L}{2}\sin\left(\frac{\pi}{T_H - T_L}\left(T - \frac{T_H + T_L}{2}\right)\right) + \frac{t_H + t_L}{2} \tag{1}$$

The switch functions have the form $\eta = \frac{1}{2}(1 - \tanh(\frac{T-(T_{cross}+k)}{5})$, where T$_{cross}$ corresponds to T$_L$ and T$_H$ for the first two and last two switches, k equals to -50, 25, -25, and 50 for η_1 to η_4 respectively.

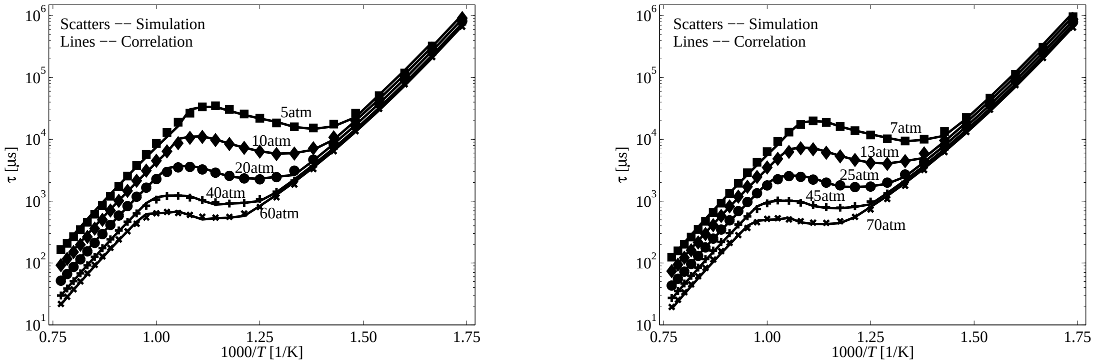
The igntion correlation is now:

$$\tau = \tau_{low}\eta_1 + \tau_{sin}(1-\eta_1)\eta_2 + \tau_{mid}(1-\eta_2)\eta_3 + \tau_{sin}(1-\eta_3)\eta_4 + \tau_{high}(1-\eta_4) \tag{2}$$

With the sine wave modification, parameters for the generalized correlation form in the eqn. 2 are shown in Tab. 1. The correlation shown in Fig. 3a is now in better agreement with the original simulation data over the whole temperature and pressure ranges. To further test performance of the correlations, simulations are carried out at various pressures different from those previously used. Fig. 3b confirm that the correlations accurately predict model simulations over a wide range of pressure conditions.

A similar correlation is developed for the Aachen surrogate using the model by Honnet et al. [9]. The resulting generalized correlation is also shown to be able to accurately predict ignition delay times that would be obtained using the original detailed chemical kinetic model.

The correlation approach can be applied to simulation data as well as ignition delay times with a well resolved temperature range. The delineation of the three ignition regions also makes it possible to compare the cross-over temperatures predicted by detailed models and their temperature dependence. In Fig. 4, ignition delay times of a jet fuel surrogate are compared to predictions of the chemical kinetic model by Dooley et al. [8]. It is observed that the temperature sensitivities of the experimental data set



(a) Comparison with the orignal simulation data

(b) Comparison at new conditions

Figure 3: Comparison of the correlation with four switches with original simulation data and new conditions at various pressures.

and the model prediction are similar, while the model shows longer ignition delay times and predicts higher cross-over temperatures. Taking these into account, constants of the generalized correlation developed in this work are modified in accordance with the quantitative differences between the model correlation and using the experimentally observed cross-over temperatures. The model predicts longer ignition delay times than experimentally observed by a factor of approximately 2.0 for the low- and

Table 1: Parameters for ignition correlation with four switches based on model by Dooley et al. [8].

	c	α	β	θ_a	
τ_{low}	7.93×10^{-29}	-0.23	30.16	34070	
τ_{mid}	4.68×10^{-11}	-1.76	20.53	13070	
τ_{high}	6.95×10^{7}	-0.82	-10.37	4740	
	a	m		b	n
T_L	649.24	0.072	t_L	1.26×10^5	-1.34
T_H	828.07	0.040	t_H	4.35×10^5	-1.59

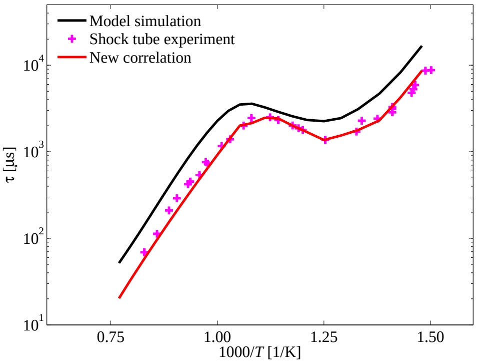


Figure 4: By modifying correlation parameters, the model-based correlation is can be brought to better agreement with experimental data. Experimental data taken from Dooley et al. [8].

high-temperature regions and a factor of 1.3 for the NTC region (within experimental uncertainties). The cross-over temperature between the NTC and high-temperature region at 20 atm is predicted by the model to be 933.5 K whereas the experiment suggests that it is 886.8 K which needed to bring the correlation in better agreement with the experiment. For the NTC and low-temperature regions, the model predicts that the cross-over occurs at 805.5 K which is in close agreement with the experimental value of 797 K. These changes applied to the model correlation are sufficient to yield a new representation of the data by a correlation as shown in Fig. 4.

4 Conclusion

This work demonstrates the simplification of detailed chemical kinetic models for ignition delay times of stoichiometric mixtures of fuel and air in the form of generalized correlations. An ignition correlation consists of three correlations for the NTC, low- and high-temperature regions as well as switch functions based on the relation between cross-over temperature and reactor pressure. A more accurate generalized correlation further incorporates a sine-function to account for deviations from model predictions at the cross-over temperatures. It is found that the much simplified correlations accurately predict the ignition delay times simulated by the original models with over thousands of reactions. It is further shown that these correlations facilitate the comparison of models and measured delay times. This work contributes to simplifying the incorporation of chemical kinetic effects in combustion modeling of practical systems.

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