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Disclaimer

An approach for formulating surrogates for gasoline with application towards a reduced surrogate mechanism for CFD engine modeling

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Abstract

The numerical study of engine combustion requires the coupling of advanced computational fluid dynamics and accurate chemical kinetic models. This task becomes extremely challenging for real fuels. Gasoline is a mixture of hundreds of different hydrocarbons. Detailed modeling of its chemistry requires huge numbers of species and reactions, and exceeds present numerical capabilities. Consequently, simpler surrogate mixtures are adopted to approximate the behavior of the real fuels. Large kinetic models for surrogates are developed to characterize their chemistry, but these models still contain thousands of species and reactions and can usually only be used for simulating simple homogeneous systems. For multidimensional engine applications, they must be reduced.

In this work, we propose a methodology for the formulation of gasoline surrogates. Using the proposed procedure, a candidate surrogate containing four components has been identified to match a real non-oxygenated gasoline. Starting from this formulation, the LLNL detailed kinetic mechanism has been reduced while maintaining its ability to reproduce targets of ignition delay times and flame speeds over a wide range of operating conditions. The reduction was carried by construction of a preliminary version of skeletal mechanism using the Computer Assisted Reduction Mechanism (CARM) code under a set of targeted conditions.

Further reduction is made with a search algorithm that sequentially tests the importance of each species leading to a much smaller mechanism. Finally, the resulting reduced mechanism has been validated against the detailed mechanism and available experimental data.

1. Introduction

Computational fluid dynamic (CFD) calculations for internal combustion (IC) engines are widely used by engine designers and automotive researchers to optimize IC engine designs for performance, efficiency and low pollutant emissions [1]. The introduction of reformulated fuels, Fischer-Tropsch fuels, biofuels and others, has made assessing the effect of fuel composition on engine performance and emissions increasingly important. Chemical kinetic models for real fuels need to be developed and coupled with CFD engine codes to assess fuel effects and to advance new engine design technologies. Chemical kinetic models for the thousands of individual constituents in real gasoline fuels would make CFD modeling computationally unfeasible, so surrogate fuels, which are mixtures of a small number of compounds to represent real fuels, are often developed to limit the size of the chemical kinetic model. Also the approximate description of the surrogate fuel is reflective of the limited knowledge usually available about the exact composition of the real fuel. However, even detailed chemical kinetic models of surrogate fuels are often too large for inclusion in a CFD code. This is because the number of species in the detailed chemical kinetic model determines how many equations have to be solved in each computational cell of the CFD mesh of combustion chamber (a 3D mesh easily include 10^5-10^7 cells). To limit the number of equations that have to be solved, the number of species in the chemical kinetic model must be restricted to tens or a few hundred species so that the execution times of the CFD code are not excessive.

The present study addresses two major challenges in CFD modeling of gasoline fuels, specifically, the methodology for formulating a surrogate fuel and the reduction of its detailed chemical kinetic model for use in practical CFD simulations. A detailed chemical kinetic

model for gasoline surrogate fuels has been previously developed and widely tested against experimental data [2]. Using that mechanism a four component surrogate has been identified to match the reactivity of a real non-oxygenated gasoline fuel based on a new procedure involving kinetic calculations. Starting from this formulation, the detailed kinetic mechanism is reduced while maintaining its ability to reproduce targets of ignition delay times and flame speeds in a wide range of operating conditions. The resulting model is finally validated against the parent detailed mechanism and experimental data. This reduced mechanism represents a useful chemical kinetic model for gasoline for use in CFD applications for IC engines.

2. Background

2.1 Surrogate fuel formulation background

CFD simulation of conventional gasoline combustion requires the identification of a surrogate fuel that reproduces the physical and chemical properties of the real fuel. A common approach to the formulation of surrogates is to match the reactivity of the fuel in a set of well-controlled conditions. For a long time, the engine community relied on ignition data collected in Cooperative Fuel Research (CFR) engines used to evaluate octane numbers (e.g., research octane number (RON, ASTM D2699 - 11) and motor octane number (MON, ASTM D2700 - 11)). The knock propensity of the fuel of interest is determined under standardized conditions and compared with the combustion behavior of n-heptane/iso-octane mixtures, the primary reference fuels (PRFs). For a long time these mixtures were supposed to be representative of the combustion behavior of the gasoline at idle and high load operating conditions. This approach was adequate in the past, when the technology of commercial engines was still relatively similar to the dated 1929 Waukesha engine and the octane performances of industrial gasoline were much different from current ones. However, the evolution of engine technology and the development of new combustion strategies necessitate a more careful characterization of the fuel reactivity including operating conditions far away from the one realized in the CFR research engine [3-4].

Today, combustion researchers rely on ignition delay times measured in shock tube (ST) and rapid compression machine (RCM) facilities to investigate temperature and pressure conditions found in engines [5]. These devices allow to investigate the fundamental chemistry leading to autoignition and can be used to characterize the combustion behavior of fuels across a wide range of conditions. Moreover, there is also a strong interest in matching not only the ignition properties, but also other relevant aspects such as the distillation curve, sooting tendency, and flame propagation. Finally, a "trial and error" procedure in a selected engine device is often considered necessary to blend an adequate surrogate mixture for specific engine applications [6]. Unfortunately these new methods require a broad set of experiments that are generally time consuming and costly to obtain.

Therefore, the present work proposes an alternate method for the formulation of surrogate mixture based on limited composition information and chemical kinetic modeling calculations.

2.2 Mechanism reduction background

The application of detailed kinetic mechanisms to the study of complex reacting flows (i.e. in engine combustion) is limited by the computational cost of integrating the chemical evolution of a complex mixture in each computational cell of the domain. From a numerical standpoint, the time advancement of the species composition in each control volume corresponds to the solution of a system of N_{spec} ordinary differential equations. The different characteristic timescales of the chemical species in the mechanism (e.g. fast reacting radicals vs. slow reacting molecules) introduce a strong numerical stiffness which requires robust numerical methods to be treated. As a matter of fact for a restricted regime of interest, many intermediate species can be removed from the ODE system without losing accuracy in the solution. As a result, the computation load can be reduced as the number of ODEs is decreased by removing certain intermediate species from the detailed mechanism. The computational time saving results directly from the reduction of the system size as well as the reduction in stiffness. A numerically efficient skeletal mechanism for the practical combustion regime of interest is therefore obtained by judicially removing unimportant species and reactions.

Many methods for constructing skeletal mechanisms have been developed including rate analysis [7], sensitivity analysis [8], and Computer Singular Perturbation (CSP) [9], generic algorithms [10], Directed Relation Graph (DRG) [11], and simulation error minimization [12]. Some recent developments have been summarized by a recent review [13]. As chemical kinetics is highly nonlinear and dependent on the regimes of interest, each approach has its own advantages and shortcomings. When a large detailed mechanism is considered, the computational effort to generate the numerical data for the targeted regimes becomes an influencing factor in choosing the method for developing skeletal mechanisms. Both sensitivity analysis and CSP require information on the Jacobian matrix, say $\partial T / \partial k_i$, where k_i is the reaction rate of *i-th* step. Such information is expensive to generate when the detailed mechanism contains a large number of species and reaction steps. In order to construct skeletal mechanisms rapidly, it becomes necessary to use methods with the least computer time in generating numerical data. In this work a mixed strategy has been used, including automated flux analysis, Quasi Steady State approximation (QSS) and targeted search algorithms.

In the next section we will discuss in detail the methodologies used in our paper, starting with the methodology for formulating the surrogate fuel and ending with the methodology for mechanism reduction.

3. Methodologies

3.1 *Surrogate fuel formulation methodology*

The current study proposes an alternate method for the formulation of surrogate mixture based on limited composition information and chemical kinetic modeling calculations. The main advantage of this technique is that it requires a limited set of information about the targeted fuel, and it can be applied by modelers without the support of a specific set of experiments on the ignition properties of the fuel.

The most relevant aspect in reproducing the combustion behavior of a real gasoline is to match its reactivity in terms of ignition propensity and its composition in terms of the

carbon/hydrogen (C/H) ratio, which depends on the composition of the fuel. The C/H ratio influences the flame speed, flame temperature, and heat of combustion of the surrogate. [14]. The ignition propensity of the fuel is evaluated using its RON and MON values. These are measured using ASTM standard procedures based on the reactivity of the primary reference fuels (PRFs) mixtures of *iso*-octane and *n*-heptane. The overall ignition propensity, also known as octane index (OI), of the fuel is determined by the average of the RON and the MON (e.g., OI=87). The difference between RON and MON is the octane sensitivity (e.g., SEN=8), and this parameter is related to how the reactivity of the fuel changes with pressure and temperature conditions. Together with the octane rating, the qualitative composition of the fuel is also determined by a simple analytical analysis providing an estimate of the alkane, olefin, and aromatic content. These measurements are routinely done on blended refinery streams and results can be easily obtained from refinery data. Our objective is to use this limited set of information to propose a surrogate formulation suitable for a particular gasoline and for engine simulations.

The first step of the proposed procedure is the numerical analysis of a representative set of reference fuels covering a wide range of octane indexes and sensitivities. As a result, the octane rating can be mathematically correlated to other key indexes derived from the calculated ignition behavior of the fuels over a range of conditions of interest. Using the obtained transfer function, the Octane Index and the sensitivity can be translated in two new parameters that can be easily evaluated by autoignition calculations.

To assess the effectiveness of the method, a real fuel has been selected and a surrogate has been formulated on the basis of the two proposed key indexes.

3.1.1 Defining of a database of reference fuels and key indexes

Although the qualitative effect of certain components on the octane rating of the fuel is well known, a quantitative correlation between octane rating and ignition time of different blends of hydrocarbons has been infrequently reported [15]. From a recent paper by Morgan et al. [16] and through personal communications, we obtained RON and MON data for a wide

range of *iso*-octane/*n*-heptane/toluene/1-hexene surrogate mixtures, and used them to build a database of octane numbers for various of surrogate fuel mixtures. This experimental database was then analyzed using ignition delay simulations (i.e., zero-dimensional constant volume homogeneous reactor simulations) with a well validated kinetic mechanism for *iso*-octane/*n*-heptane/toluene/1-hexene mixtures [2] to estimate the ignition behavior of the different mixtures at various temperatures and pressures.

The two key ignition parameters used in the procedure are obtained from the ignition delay time curves resulting from kinetic calculations. For many hydrocarbons this curve shows a typical S shape which can be divided in three parts; the first is the low temperature region where the slope is positive on a plot of ignition delay versus inverse temperature. The second part of the curve is the negative temperature coefficient (NTC) region where the slope is negative, and the third part is the high temperature region where the slope of the curve is again positive. The first key parameter we identified in the S-shaped ignition curve is the slope of the NTC region, and the second key parameter is the ignition delay time in the middle of the NTC region. A previous study by Mehl et al. [17] showed that these key parameters are related to the OI and sensitivity of the fuel. In order to study how these variables are correlated with the measured RON and MON values by Morgan et al. [16], ignition delay curves were calculated for each surrogate mixture at 25 and 50 atm for stoichiometric fuel/air mixtures. Figure 1 shows the curves for all surrogate mixtures examined.

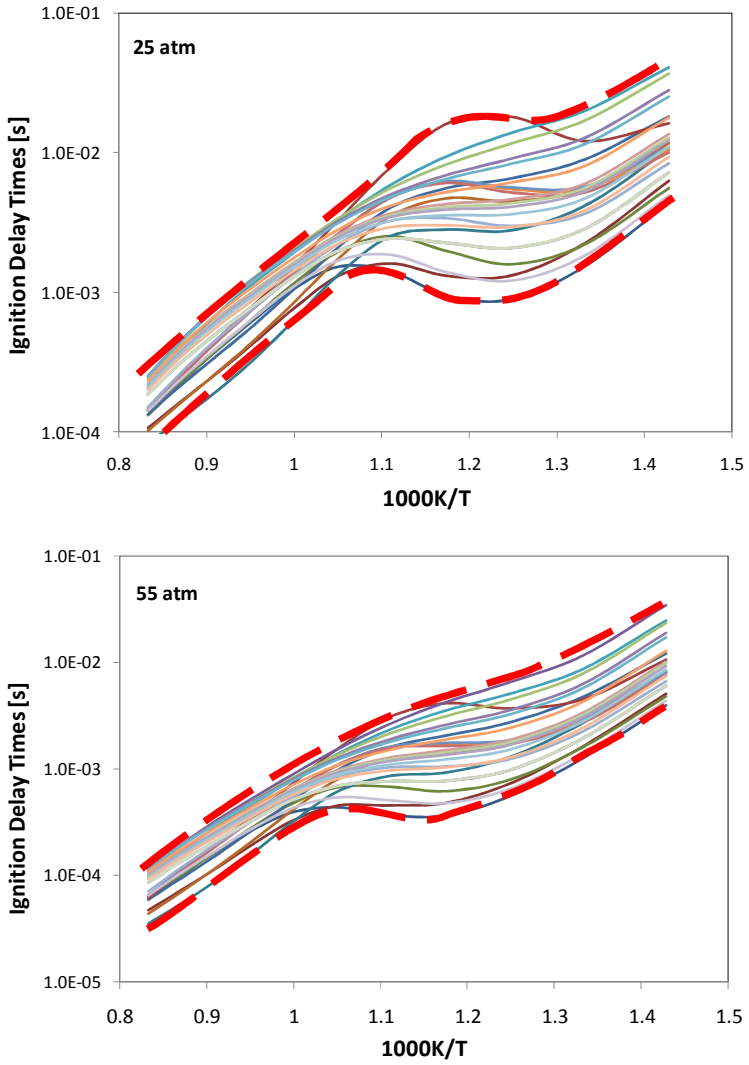

Figure 1: Simulated ignition delay times of the surrogate fuels included in the experimental database by Morgan et al. [16]. Simulations were conducted at 25 atm and 55 atm for stoichiometric fuel/air mixtures. The dashed lines delimit the space of the ignition delays covered by the experimental database.

The logarithm of the ignition delay times were used to calculate the slope of the ignition delay curve in the NTC region and these values were correlated with the measured sensitivity of the mixture, as shown in Figure 2a. Some scatter is present in the correlation between the slope of the NTC region and the sensitivity, but a definite trend can be observed. For the correlations, we used the results at 25 atm, since at these conditions the NTC behavior is easier to characterize. The second parameter, the logarithm of the ignition delay time in the NTC region at 825 K, was correlated with the measured OI. The correlation for the second

parameter is given in Figure 2b where OI is plotted as a function of the ignition time at 825 K, and the correlation appears very strong.

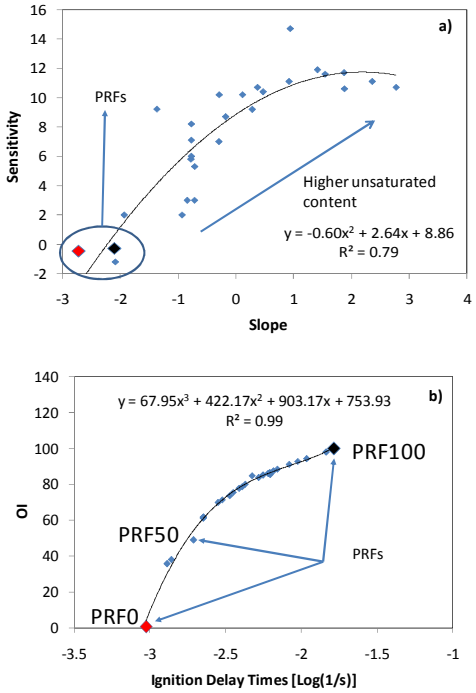

Figure 2: a) Calculated correlation between sensitivity and slope of the NTC, b) Calculated correlation between Octane Index (OI) and Ignition delay times at 825K. These correlations performed at 25 atm.

Figures 2a and 2b also highlights where three PRFs lie on these plots (*n*-heptane in red, *iso*-octane in black, and the PFR50 mixture fall in this picture. It is interesting to note that fuels having a different octane number, such as pure *n*-heptane and *iso*-octane, have a similar negative slope, which is consistent with their zero sensitivity (note that the measured values highlighted in Figure 2b, where the small deviation from the zero are associated with the experimental uncertainty). This behavior is somewhat surprising since engine studies have shown that *iso*-octane lacks the low temperature heat release typical of fuels with a lower octane index (e.g., PRF mixtures with significant amounts of *n*-heptane) at most of the operating conditions [18] and therefore a much different reactivity would be expected. However, chemical kinetic modeling studies [19] have shown that *iso*-octane has some low temperature chemistry leading to NTC behavior due to same classes of reactions observed for

n-heptane. This analogy explains why the NTC region of iso-octane is comparable to the one of more reactive PRFs despite the significant slower reactivity,as highlighted by figure 2b, where the two PRFs fall far apart

3.1.2 Defining the target fuel

The target fuel used for implementing the methodology is the research gasoline provided used by Dec and Yang in [20]. Table 1 provides the main characteristics of this specific gasoline fuel.

	Gasoline
Alkanes	73.1 %Vol
Aromatics	22.7 %Vol
Olefins	4.2 %Vol
A/F Ratio	14.79
H/C	1.946022
RON	83.2
MON	90.8

Table 1: Composition and ignition properties of the gasoline targeted

The octane index of this gasoline is in line with the one of a common commercial gasoline (OI=87) and the sensitivity is about 8 points. The alkane fraction in the gasoline is mostly composed of a variety of *iso*-alkanes with a distribution of molecular weights centered around 100-110 g/mole. The aromatic fraction of gasoline fuels is mainly comprised of mono- and di-alkyl-substituted benzenes such as toluene, ethylbenzene and xylenes, while olefins are mostly short chains in the molecular weight range of 70-85 g/mol derived from the cracking of C_8-C_{10} alkanes [21].

For alkane fuels and their mixtures, a PRF blend matched to the octane index is a good surrogate over a wide range of conditions. On the other hand, when aromatics and olefins are present in the fuel, PRF mixtures are unable to reproduce the ignition characteristics of the fuel

over a broad range of conditions since these unsaturated components have a larger impact on the sensitivity of gasoline fuels. Aromatics have been used for a long time as octane improvers [21] and have shown to suppress the low temperature heat release typical of alkanes. A similar effect is found when olefins are blended in gasoline. These components play also an important role in determining the sensitivity of the fuel [17]. These features of the target fuel suggest that the gasoline surrogate must be more complex than a simple PRF mixture, in order to adequately capture the real fuel's reactivity over a range of operating conditions.

3.1.2 Formulating the surrogate fuel

Four components have been selected to represent the four classes of compounds measured in the real gasoline: *iso*-octane, *n*-heptane, toluene and *2*-pentene. The choice of *iso*-octane, *n*-heptane and toluene is based on historical reasons; these three components fit well the molecular weight range of interest, and they have been widely used by the combustion community to represent the chemistry of *iso*-alkanes, *n*-alkanes and aromatics. Toluene and xylenes can be present in US gasolines up to 35% by volume [21]. *2*-Pentene has been selected because it matches the typical molecular weight of olefins found in gasolines and it has a higher sensitivity than *1*-pentene, its straight chain isomer. These components have been blended to match the broad molecular composition of the target gasoline in Table 1, as well as its H/C ratio and stoichiometric air/fuel ratio. This matching of the molecular composition fixes the concentrations of toluene and *2*-pentene to capture the aromatic and olefin content of the target fuel. These concentrations also correctly reproduce the desired slope in the ignition delay profile (and so the sensitivity of the gasoline) and therefore are not changed. If an adjustment in the slope of the NTC region is needed, then different aromatics or olefins can be blended in the mixture to better match the target (e.g. 1-pentene or 1-hexene to make it steeper, 2-methylbut-2-ene, to make it flatter). The ratio of *iso*-octane/*n*-heptane is finally varied to match the overall reactivity of the target fuel (OI=87), based on the correlations established in the previous section. Table 2 summarizes the surrogate composition identified:

	Surrogate
iso-Alkanes	57%Vol
n- Alkanes	16%Vol
Aromatics	23%Vol
Olefins	4%Vol
A/F Ratio (mass)	14.60832
H/C	1.924567

Table 2: Composition of the surrogate formulated according the proposed methodology.

3.2 Mechanism reduction

The reduced mechanism is developed in two stages. First, the detailed mechanism is reduced to an intermediate skeletal mechanism with 862 species using the Computer Assisted Reduction Mechanism (CARM) [22] algorithm, where unimportant species and reactions are eliminated according to their importance on the basis of rate production and species magnitude [23]. Other methods, such as DRG [24] or its derivatives [12], can be used for construction of this intermediate skeletal mechanism. Past experiences have shown that the skeletal mechanism may not be optimal [25]. Therefore the second step involves reducing the skeletal mechanism to fewer species and reaction steps using the Targeted Search Algorithm (TSA) [25]. The species kept in the current skeletal mechanism are ranked according to their maximum concentrations under all targeted conditions in ascending order, as intermediate species with low concentrations may be good candidates for removal. The resulting error by removing one immediate species is evaluated by constructing a skeletal mechanism with one less species and running the targeted conditions. If the results errors exceed an upper limit (10% in the current study), the immediate species is kept in the skeletal mechanism. The above evaluation process is repeated for all immediate species. For a large detailed mechanism, the associated computational cost with TSA can be high. Fortunately, TSA is well suited for

parallel computing and the current results were obtained by running four CPU processors. At the end of TSA, a skeletal mechanism with 256 species was constructed.

The Targeted Search Algorithm (TSA) developed by Tham et al. [25] is extended for construction of a skeletal mechanism for predicting autoignition delays with reasonable accuracy. TSA was developed for construction of reduced chemistry with the Quasi-Steady State (QSS) assumption. The strong nonlinear coupling among species motivates the development of TSA; however when a group of species is approximated by QSS, the instantaneous errors become more difficult to assess. The overall impact of a group of QSS species on the accuracy of predicted global combustion behaviors by the reduced system, such as autoignition delay or flame speed, often cannot be quantified until the reduced system is used for such predictions. Under certain conditions, the low temperature ignition can greatly influence the second ignition at high temperatures in a nonlinear fashion. For the first objective of predicting autoignition delays, a set of conditions were selected for the intended HCCI operations listed in Table 3. Ignition delays were computed with the detailed surrogate mechanism to established references.

Equivalence Ratio (ϕ)	T (K)	P (atm)
1.0	800	10
1.0	750	60
0.6	1200	60
0.6	1100	10
0.6	1000	60
0.6	800	10
0.6	750	10
0.6	750	60
0.2	800	60
0.2	700	20
0.2	700	20

Table 3: Conditions used in development of an accurate skeletal mechanism using targeted search algorithm (TSA)

The 256 species skeletal mechanism optimized for the autoignition did not give accurate predictions for flame speeds. Since the reduction of the mechanism was based on the autoignition, some relevant reactions for flame conditions were excluded from the skeletal mechanism. In fact, the autoignition chemistry is mostly affected by fuel specific reactions that influence the initial stages of the formation of the radical pool while flame speeds depend more on the core chemistry. The ignition delay times are therefore an inadequate target for the definition of a comprehensive high temperature mechanism suitable for flame simulations. The detailed surrogate mechanism was at first manually reduced by eliminating the reactions relevant to the low temperature mechanism and a skeletal mechanism was developed in a similar fashion as the previous one targeting flame conditions. This second skeletal mechanism contained a subset of reaction (relevant only at high temperature conditions) that was missing from the ignition mechanism. To build a more general kinetic mechanism, the 256 species mechanism has been manually integrated with this new group of reactions, reaching the final size of 312 species.

In the following paragraphs the proposed surrogate model and the relating kinetic models will be validated against ignition, flame and engine data.

4. Results and Discussion

The validity of the proposed surrogate and the kinetic models here proposed have been validated against shock tube ignition delay times, premixed laminar flame speeds, and engine experimental data for a real non-oxygenated gasoline fuels. A first set of comparisons were performed using the detailed kinetic model, finally, the reduced kinetic model containing 312 species has been tested at the same conditions, to verify its ability to mimic the full model.

Gautier et al. [26] collected shock tube ignition data for a blended gasoline surrogate, the General Motor RD 387, at pressures of 25 atm and 55 atm and stoichiometric conditions. This research gasoline was blended to represent a “customer average” with no oxygenates and an octane index of 87 (no sensitivity information was available). Figure 3 presents the

experimental data and ignition delay times calculated using the detailed surrogate model, as well as the ignition curve of a PRF87 (87%vol iso-octane, 13%vol n-heptane). It should be noted how the PRF87 shows a very similar reactivity compared to the proposed surrogate fuel, but the slope at the inflection point is distinctly different. Both the mixtures well reproduce the experimentally measured data, but it must be highlighted how the shock tube experiments start only above 900K, where the NTC behavior is absent; therefore this comparison is not capable of discriminating the validity of the chosen surrogate with the desired level of confidence.

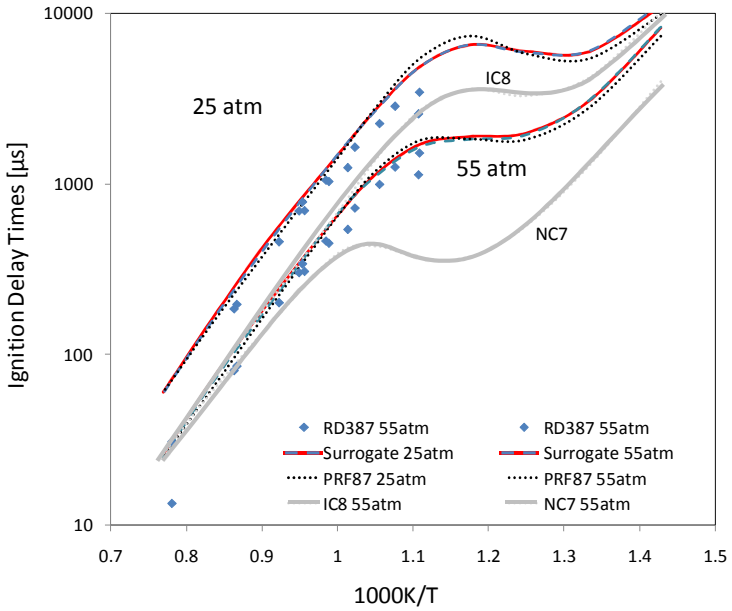

Figure 3: Direct comparison of the calculated ignition delay times of the proposed surrogate vs. the selected ternary reference fuel, PRF 87 and the ignition experiments of the RD387 gasoline [26].

The detailed surrogate model was also tested against premixed laminar flame speed data measurements on a non-oxygenated gasoline by Tian et al. [27]. They used a constant volume vessel, schileren imaging and flame stretch corrections to obtain laminar flame speeds in air. The exact specifications of the gasoline were not reported; however, the uncertainty in the composition and in the octane rating is less relevant for this type of comparisons because the flame speed is primarily determined by high temperature chemistry (i.e., above 1000K)

and the small molecule chemistry (i.e., the core chemistry) shared by all the fuel components. In addition, comparisons are made with high-pressure laminar flame speed data by Jerzembeck and Peters [28], who investigated gasoline in air and a corresponding PRF87 over a range of pressures (e.g. 10 - 25atm) and at 100°C.

Figure 4a compares model predictions against Tian's experimental data. The measurements cover a wide range of unburned gas temperatures spanning from 50°C to 100°C. The calculated flame speeds show reasonable agreement with the experimental values. The maximum measured flame speed at the highest temperature (i.e., 100°C) appears anomalous, since the measurement reported at Φ=1.1 and 100°C is not consistent with the other measurements. Figure 4b compares the model against data by Jerzembeck and Peters. The model well reproduces the flame speed at the lowest pressures, but the burning velocity at the highest pressures is underestimated. The experimentally observed trend of decreasing flame speed with increasing pressure is well reproduced, and the agreement on the lean side is generally satisfactory. At richer conditions, the model predictions under predict the experimental data. Further investigation is necessary to clarify whether these discrepancies are due to uncertainty in the surrogate formulation, the validity of the chemical kinetic model, or the accuracy of the experimental data.

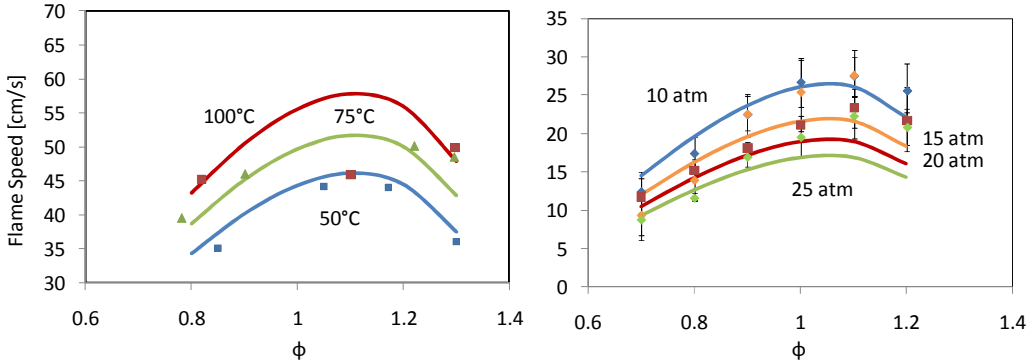

Figure 4: Laminar flame speed calculations obtained using the detailed kinetic model and the proposed surrogate compared with experimental data from Tian et al [27] (left) at 1 atm and Jerzembeck and Peters *[28] at 100°C (right). One the right, the orange curve and symbols (diamonds) correspond to 15 atm.*

The surrogate model was also compared with homogeneous charge compression ignition engine (HCCI) data collected at Sandia National Laboratory by Dec and coworkers [20] using the target gasoline fuel defined previously. The experimental data presents the engine crank angle degree (CAD) at which 10% of the total heat release is achieved (CA10) as the intake pressure (P_{in}) is varied. The single zone HCCI engine model implemented in ChemkinPro was used to compare model predictions with the experimental data. In order to account for inhomogeneity in the experimental engine that are not captured in the modeling simulations, we follow the work of Sjoberg et al [29] and compare the CA50 from the single zone simulations to the CA10 from the experiments. In these simulations, the same ignition phasing targeted by the experiments was reproduced varying the intake temperature while the boost conditions and the amount of exhaust gas recirculation (EGR) used at high loads were imposed to match the conditions operated in the engine. The bottom dead temperature necessary to achieve the desired phasing were then compared with the engine ones. Figure 5 shows a good agreement with the experiments, wherein the four component surrogate model well reproduces the reactivity observed in the experiments under similar engine settings. These comparisons support the validity of the surrogate not only in the high temperature region, but also at conditions where the low temperature chemistry and the NTC play an important role. A deeper discussion on these set of simulation will be included in a future paper to be presented at the next SAE world congress in 2012.

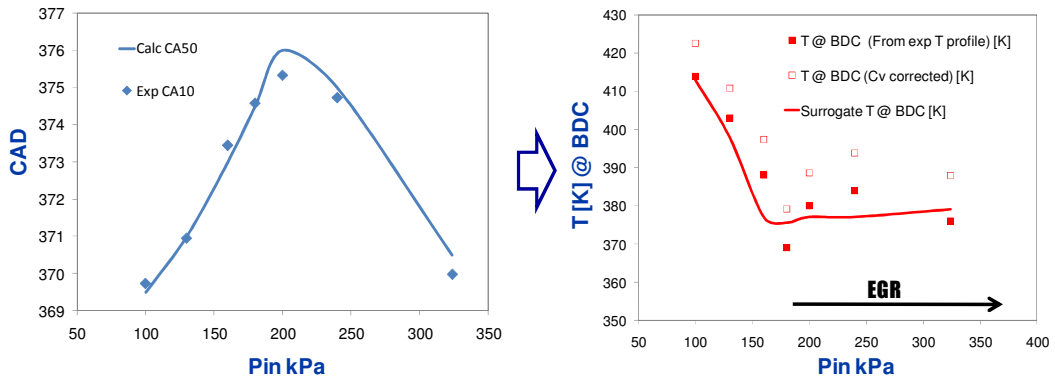

Figure 5: HCCI Engine comparisons using the selected surrogate mixture a) targeted ignition timing, b) intake conditions. Symbols: experiments [20], Lines: calculations. 360 Crank angle degrees (CAD) corresponds to top-dead-center. Exhaust gas recirculation is added from intake pressures (Pin) above 175 kPa.

5. Reduced Mechanism

The overall good agreement with the experiments shown by the detailed kinetic model of the surrogate fuel supports its validity for a broad range of applications. For this reason, the surrogate composition and detailed kinetic model were used as a starting point for the reduction of the detailed kinetic model, in order to create a skeletal model that is suitable for the CFD simulation of gasoline fuels.

The skeletal mechanism was developed with the aim at predicting autoignition and flame speeds with reasonable accuracy. The development was carried out in two stages: first, a preliminary skeletal mechanism using the Computer Assisted Reduction Mechanism (CARM) code was used under a set of selected conditions; second, further reduction was made with a search algorithm that sequentially tests the importance of each species, which leads to a much smaller mechanism.

5.1 Stage 1: autoignition delays

Figure 6 presents comparisons of predicted autoignition delays with the detailed mechanisms and the 2 skeletal mechanisms previously discussed showing good agreement at phi=1 and 0.3. The good agreement between the two mechanisms is also apparent at all the pressures studied. These results indicate that the skeletal mechanism is suitable for predicting autoignition delay times in real systems.

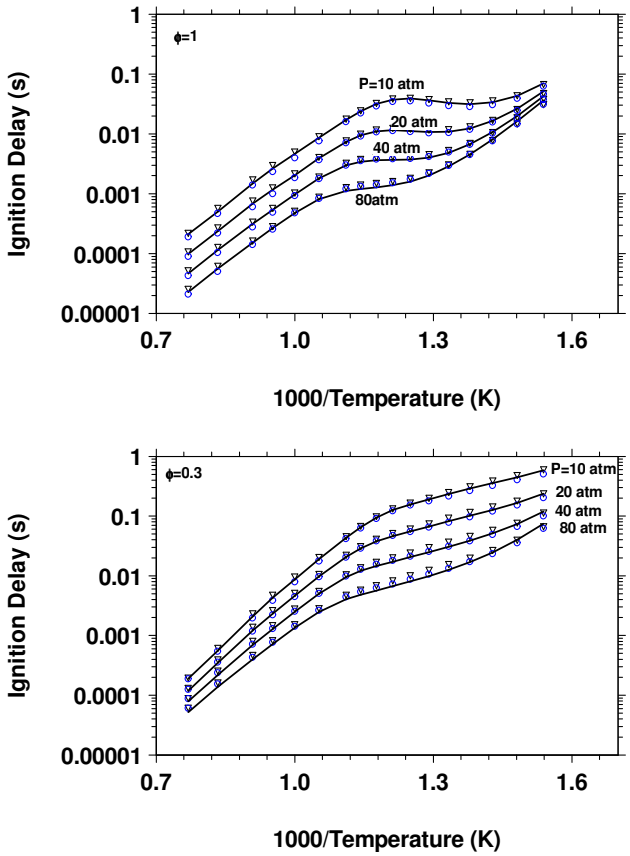

Figure 6: Comparisons of predicted autoignition delays with the detailed mechanisms (lines) and the 256 species skeletal mechanism (O) and the combined 312 species skeletal mechanism (∇) showing good agreement at ϕ=1 (top) and 0.3 (bottom).

5.2 Stage 2: Flame speed

The skeleton mechanism containing 312 species successfully reproduces not only the detailed ignition calculation, but also the two sets of flame experiments we considered (Figure 7).

The flame speed predictions provided by the reduced mechanism are slightly faster than the ones previously shown for the detailed mechanism. The discrepancy is most likely due to the fact that only a limited number of alternative pathways are still in the mechanism and can interfere with the main oxidation process. However, this difference in behavior between the two models is beneficial to the agreement with the data: a slightly higher predicted flame speed provides values that are closer to the experimental ones

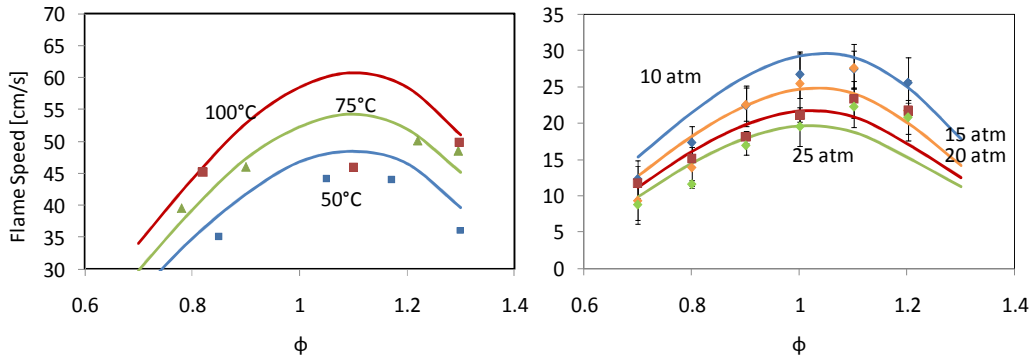

Figure 7: Flame speed calculations obtained using the reduced 312 species kinetic model with the surrogate here proposed. They are compared to available experimental data for gasoline in air. Symbols: data [27-28], Lines: calculations

Conclusions

A procedure for the formulation of gasoline surrogates for modeling purposes has been proposed. The numerical analysis of the octane numbers of a wide range of surrogate fuels allowed the definition of a well defined method for the definition of gasoline surrogates on the basis of a limited set of information on the real fuel and the use of a kinetic model. The procedure has been applied to one practical case and the resulting mixture has been applied to the simulation of engine data, shock tube data and flame speed data. The good agreement with the experiments suggested that the mixture represented by the model has a broad general validity. Therefore, the kinetic model has been reduced targeting the detailed simulations to a skeleton mechanism containing about 300 species. The skeleton mechanism has been successfully validated on the basis of 0 and 1-D simulations. The derived model is small enough to be practically applied to high level CFD simulation. Both the mechanisms are available for download from the LLNL combustion website [30].

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