A Surrogate Mixture and Kinetic Mechanism for Emulating the Evaporation and Autoignition Characteristics of Gasoline Fuel

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Gasoline direct-injection spark-ignition engines and gasoline direct-injection compression-ignition engines have received attention due to their higher fuel economy with respect to conventional port fuel injected internal combustion spark-ignition engines. Combustion modeling of these types of engines requires a fuel surrogate that mimics both physical (e.g., evaporation) and chemical (e.g., combustion) characteristics of the gasoline fuel. In this work, we propose a novel methodology for the formulation of a gasoline surrogate based on the essential physical and chemical properties of the target gasoline fuel. Using the proposed procedure, a surrogate with seven components has been identified to emulate the physical and chemical characteristics of a real non-oxygenated gasoline fuel, RD387. A surrogate kinetic mechanism was developed by combining available detailed kinetic mechanisms from the Lawrence Livermore National Laboratory library. The modeling results for distillation curve, ignition delay and laminar flame speed were validated against available experimental data in the literature. The surrogate and gasoline fuels display similar physical/chemical properties, including distillation curve, H/C ratio, density, heating value, and ignition behavior and flame propagation over a wide range of pressures, temperatures, and equivalence ratios.

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1. Introduction

Gasoline direct-injection (GDI) [1] and GDI compression-ignition (GDCI) engines [2,3] have received attention due to their higher fuel economy with respect to conventional port fuel injected internal combustion spark-ignition engines. Spray characteristics including evaporation history and penetration have great importance in the design and development of these engines; since spray physical phenomena play such an important role in the formation of the air/fuel mixture in the combustion chamber.

Gasoline, diesel, and jet fuels are mixtures of many structural classes of molecules such as paraffins, aromatics, olefins, and naphthenes. For the purposes of formulating surrogate mixtures to represent the combustion behavior of oxygenated gasoline, some of the hydrocarbon group representatives used in surrogate mixtures in prior studies are n-heptane for n-paraffins, iso-octane for iso-paraffins, toluene for aromatics, pentene for olefins, and ethanol for oxygenated groups [4-7]. Mixtures of these components can be formulated to mimic the ignition delays and laminar flame speeds of gasoline but cannot emulate the spray behavior of gasoline as the distillation curves and evaporation behaviors of these components and their mixtures are different from gasoline as discussed later. On the other hand, suggested representatives for modeling gasoline distillation or evaporation behavior are n-pentane, n-heptane, and n-decane (e.g., [8]). However, mixtures of these components cannot emulate the ignition delays and laminar flame speeds of gasoline adequately. The question of the present work is: can a single mixture be formulated that will mimic both the evaporation and combustion characteristics of the target gasoline? Towards that goal, a surrogate that includes most of the hydrocarbon group representatives found in a non-oxygenated gasoline is developed here to emulate the combustion and evaporation behaviors of this target gasoline. The surrogate contains n-alkane, iso-alkane, aromatic, and olefin representatives and a detailed kinetic mechanism is built from literature mechanisms for each of the species. The surrogate components and mixture composition are defined via a methodology that seeks a surrogate formulated

from a minimum number of species that have relatively well defined kinetic mechanisms and provides adequate emulation of real gasoline evaporation and ignition behaviors.

2. Background

Surrogate mixtures are formulated for the purpose of numerical simulation of complex real fuel mixtures using a small number of components. Design of surrogate mixtures is usually focused on the emulation of a particular property of the target real fuel such as evaporation (e.g., [9]), thermodynamic properties (e.g., [10]), or combustion (e.g., [7,11]). The behaviors of multicomponent fuels are more complicated than single component fuels because species produced from one component can react with species from another component. These interactions often manifest themselves in the observed ignition delay times, laminar flame speeds, and other macroscopic combustion characteristics of surrogate mixtures [4]. Ethanol-gasoline fuels includes n-alkanes, iso-alkanes, naphthenes, olefins, aromatics, and oxygenated groups with different distributions depending on the season, market place, crude source, and refinery processes. The naphthenes present in gasoline blends mostly represent "leftover" material from other refinery processes and most of naphthenes will be converted to aromatics in refinery processes [4,12]. United States gasoline (e.g., non-oxygenated RD387) can contain up to 16% by volume of naphthenes [13] and European gasoline (e.g., Exxon 708629-60) can contain around 9% by weight of naphthenes [14]. It is common practice to include all of these hydrocarbon groups in gasoline blend surrogates for emulating ignition delay, laminar flame speed, and species consumption. However, it is a challenge to generate a predictive kinetic mechanism for each individual species/group while maintaining suitable mechanism size, in terms of the numbers of species and reactions, for computational fluid dynamics (CFD) applications such as combustion engine modeling. The process for developing and validating chemical kinetic models has been described by Frenklach et al. [15] and Simmie [16]. The physical properties and availability of kinetic mechanisms for several components (relating to gasoline surrogate) are presented in Table 1.

Table 1. Ethanol-gasoline fuel component representatives. (Adapted from [4])

	Group name	Boiling temp. (°C)	Understanding of the mechanism ^{1*}	
			Low and intermediate temperature	High temperature
CH ₄ to nC ₄ H ₁₀ ^{2*} , nC ₈ H ₁₈ to nC ₁₆ H ₃₄ ^{3*} , nC ₇ H ₁₆ ^{4*} iso-octane ^{4*}	n-alkane	-164 to 287	A	A
2-methylbutane (iC ₅ H ₁₂) ^{6*}	iso-alkane	99	A	A
2-methylpentane (iC ₆ H ₁₄) ^{6*}	iso-alkane	28	A	A
toluene ^{5*}	aromatics	61	A	A
ethanol ^{6*}	oxygenate	110	B	B
1-pentene and 2-pentene ^{5*}	olefin	78	B ^{8*}	A ^{6*} and 8*
2-hexene ^{5*, 7*}	olefin	30	B	B
		63	B	B

A: Detailed mechanism that has been validated over wide range

B: Mechanism reported, but with major discrepancies or limitations

^{1*}Pitz et al. [4], ^{2*}Marinov et al. [17], ^{3*}Westbrook [18], ^{4*}Curran et al. [19], ^{5*}Mehl et al. [6],

^{6*}Marinov [20], ^{7*}Mehl et al. [21], ^{8*}Sarathy et al. [22]

Pitz et al. [4] reviewed the development of fuel surrogate mixtures that represent gasoline combustion behavior. Their work involved separating all of the components into five distinct groups (A to D and F) from very important (group A) to no-relevance (group F). The chemical mechanisms and thermophysical properties of the components in group A are well understood and defined. iso-Octane, n-heptane, and toluene are among group A components and they are typically used in a gasoline surrogate models. The second important group (group B) includes ethanol, xylene, 1-pentene, and di-isobutylene. Most of the oxygenated gasoline fuels contain a considerable amount of ethanol in the mixture. Mehl et al. [6] developed a four-component gasoline fuel surrogate and mechanism which contains TRF (Toluene Reference Fuel, comprised of iso-octane, n-heptane, and toluene) and 2-pentene. Their mechanism was made from assembly of existing Lawrence Livermore National Laboratory (LLNL) detailed mechanisms. Kukkadapu et al. [13] showed that this gasoline surrogate mechanism can emulate the ignition delay characteristics of the target gasoline (RD387) by comparison with available rapid compression machine (RCM) and shock tube data. Samimi Abianeh [7] studied and developed a skeletal combustion

mechanism for ethanol reference fuel, which includes TRF and ethanol. This mechanism has 62 species and 194 reactions, of suitable size for engine modeling. However none of these studies addressed gasoline or ethanol-gasoline blend evaporation characteristics.

The distillation curve of the surrogate should be the same as the target real fuel in order to mimic the fuel spray evaporation behavior and fuel-air mixture preparation prior to combustion [23,24]. For example, a fuel surrogate with lower boiling temperature will have lower spray penetration [23]. All of the utilized surrogates/components in gasoline combustion mechanisms, discussed before, have the same range of boiling temperature (iso-octane: 99°C, n-heptane: 98°C, and toluene: 110°C) and, therefore, cannot emulate the evaporation behavior of gasoline fuel. The distillation curve of gasoline covers a temperature range between 20°C to 200°C. Samimi Abianeh et al. [8] studied and developed a three component surrogate (nC_5H_{12} , nC_7H_{16} , and $nC_{10}H_{22}$) that does emulate the distillation curve of gasoline fuel. Ra and Reitz [24] developed seven component surrogates (iC_5H_{12} , iC_6H_{14} , iC_7H_{16} , iC_8H_{18} , nC_9H_{20} , $nC_{10}H_{22}$, and $nC_{12}H_{26}$) to address the distillation curve of gasoline fuel. They also utilized components like n-heptane and iso-octane in their surrogate palette which are important for combustion prediction. Ahmed et al. [25] studied surrogate development for Fuel for Advanced Combustion Engine (FACE) gasolines by using an optimization algorithm. They targeted RON, distillation curve, density, carbon type, and H/C ratio to develop five different surrogates for FACE A and C gasolines. It is noted that in Ahmed et al. [25] the distillation curves of the surrogates were poorly matched with those of the FACE gasolines, and while their validation was performed by analyzing the carbon monoxide concentration of the exhaust gas from an internal combustion engine, the measured carbon monoxide amount of the FACE gasoline exhaust gas was not well correlated with that obtained in surrogate experiments. However, none of these studies address the combustion characteristics of gasoline fuel such as ignition delay or laminar flame speed. There are some studies which address the evaporation and combustion of diesel and JP-8 fuels (e.g., [26-27]); however, there is no comprehensive gasoline surrogate that can mimic both of the evaporation and combustion of the target gasoline simultaneously with a limited number of components.

In subsequent sections, the methodology for developing a new surrogate is discussed, followed by results and discussions.

3. Methodologies

It is common practice to include most of the available hydrocarbon groups in gasoline surrogates to emulate gasoline fuels. Two variables (component choice and component mass fractions) should be described to fulfill all of the desired fuel property targets. Here surrogate components are selected to emulate hydrogen-to-carbon ratio (H/C), hydrocarbon class distribution, heating value, research and motor octane numbers (RON and MON), density, and distillation curve and are constrained by the availability of kinetic mechanisms. As an example, RD387 gasoline has a boiling temperature at 90% evaporated mass in batch distillation around 147 °C; hence, a surrogate component should be chosen with boiling temperature higher than or around 147 °C to emulate the distillation curve [8]. Surrogate component mass fractions are then optimized by using a genetic algorithm or other mathematical methods [e.g., 8] to match the real fuel property targets. Surrogate ignition delay times are then computed using the developed surrogate mixtures and provide further refinement of surrogate distribution and a reduction of the number of surrogate species (if possible). Finally, a skeletal mechanism is developed for calculation of laminar flame speeds for comparison with experiments (if available); however, these comparisons only serve as validation and are not used as an input/output to the genetic algorithm, as mechanism reduction and laminar flame speed calculations are too computationally expensive to be part of the surrogate formulation process.

The present methodology is as follows:

- 1) Surrogate database. A surrogate component database is formulated. For non-oxygenated gasoline, this includes relevant species with reliable kinetic mechanisms found in the literature including n-alkanes from C₅ to C₁₂, iso-alkanes from C₄ to C₈, cyclo-hexane and methyl-cyclo-hexane, toluene, 1- and 2-pentene, and 1- and 2-hexene. The term “relevant species” infers that the selected component properties

should be close to gasoline fuel properties. All of the mentioned components were added to the palette for surrogate mixture optimization.

2) Primary targets. The primary targets for surrogate formulation are distillation curve, H/C, octane numbers (RON and MON), heating value, and density of the gasoline fuel. Modeling of primary targets is computationally inexpensive and can allow for a preliminary determination of a suitable surrogate mixture composition. The properties modeling methodology are addressed in Section 4.

3) Surrogate blend optimization. Surrogate mixture composition is first defined by seeking a best fit to the primary targets by defining weight (or importance) factor for each primary target utilizing a genetic algorithm and Powell minimization. All of the primary targets have the same weight/importance with respect to each other initially. Objective functions describing the differences between computed and specified values of properties (called function values) are employed. The method samples all regions of the mole fraction space and gradually settles towards lower function values. If the optimum surrogate properties are not close enough to the experiments, the weight factors and/or mixture composition will be modified and the optimization process will be re-executed. The optimization or objective function (OF) in this work is:

$$OF = W_{dis} \sum_{i=1}^n D_i^2 + \sum_{j=1}^m W_j D_j^2 < \theta, \quad (1)$$

where θ is the total error/difference of objective function, W_{dis} is the distillation curve whitening factor, D_i is the difference between surrogate and real fuel distilled temperatures at each cut, n is the number of cuts in the distillation curve, m is the number of the primary targets (except the distillation curve target), W_j is the whitening factor for each primary target other than the distillation curve, D_j is the difference between surrogate predicted and real fuel experimental values. Another constraint of the objective function is:

$$D_k^2 < \varepsilon_k \quad (k=1 \dots p), \quad (2)$$

where ε_k is the error for each of the primary targets including each cut of the distillation curve. The last constraint in the optimization algorithm is the hydrocarbon group mixture composition in surrogate. The

constraint for mixture composition is to have representative components from each fuel hydrocarbon group with almost the same mixture composition as the target real fuel, e.g. having around 40% ($\pm 5\%$) iso-octane component in surrogate mixture since the target real fuel contains 40% iso-alkane. The question is: does this problem have at least one solution for all of the conditions? For example, if the surrogate has five components and the targets are fuel density and thermal conductivity, then three equations should be solved to satisfy 5 constraints. Three equations are mixture density, mixture thermal conductivity and total component mass fraction (which should be one) and the 5 constraints are that each component mass fraction should be between zero and 1 (or some number less than 1 which represent the hydrocarbon group mass fraction in real fuel mixture). Since numerous solutions (component mass fractions) may satisfy this problem conditions with various error margins, Eq. 2 was introduced to guide the optimization function (e.g., *OF*, Eq.1) to the area of interest within the solution map with acceptable error margin. The solution may not converge for certain condition, if the error margin is too small. The error margin may need to be relaxed to first provide a converged solution. Then sensitivity analysis can be performed on each component mass fractions to further understand the influence of surrogate composition on primary targets. The solution of this kind of problem was explained briefly in [8] and [10] and has been shown that this problem has always an answer, depending on error margin. The WORKBENCH software [28] was utilized for optimization within this work.

4) Secondary target – ignition delay. Ignition delay is defined as a secondary target since it requires calculation performed with a kinetic mechanism and is, hence, more computationally expensive to compute. The kinetic mechanism of the surrogate is first developed by combining reliable and state-of-the-art pure component combustion mechanisms from the literature. The ignition delay of the surrogate is then computed using the zero dimensional constant volume chamber model (CV model) and a rapid compression machine model (RCM model) accounting for RCM finite compression time and heat loss characteristics. The ignition delay times are carried out over a relatively wide range of pressures, temperatures, and equivalence ratios and are compared to measurements for gasoline fuel (e.g., RD387) ignition delay times made in shock tubes and RCMs. If the ignition delay of the surrogate is not within

the acceptable tolerance real fuel ignition delay measurements, the component and/or mixture composition and/or weight factors of primary targets are modified. This mixture composition sensitivity analysis can be performed by varying each component mass fraction slightly (e.g. 10%) to optimize the mixture composition. As an example, if the slope of the ignition delay curve in the negative-temperature-coefficient (NTC) regime on Arrhenius axes is not adequately captured by a surrogate containing 1-pentene, a different olefin representative could be required; e.g., 1-hexene will make increase the NTC slope magnitude and 2-methylbut-2-ene will decrease the slope magnitude [6]. The acceptable tolerance could be as small as zero mathematically; however, it is limited by the reliability/certainty of available component kinetic models. For example, there may be a need for a surrogate component from the cyclo-alkane group, based on real fuel composition, but the only two components for cyclo-alkanes with reliable known kinetic models are cyclo-hexane and methyl-cyclo-hexane which may or may not be appropriate to represent the whole cyclo-alkane group, especially when they should also satisfy gasoline physical properties such as distillation curve.

5) Reducing surrogate size. The size of the surrogate is next reduced by removing components with small concentrations (e.g., component mass fraction less than 3%). Steps 3 and 4 can then be repeated until the fulfillment of the desired sized surrogate.

6) Final target – laminar flame speed. The final surrogate kinetic mechanism is reduced for wide range of pressures, temperatures, and equivalence ratios and laminar flame speeds are calculated and compared with experimental data, if available.

With an adequately-reduced chemistry that matches well with the detailed mechanism, the discrepancy between computed and experimental laminar flame speeds, if exists, could be due to several reasons such as uncertainties in the high temperature reaction kinetics [6], surrogate formulation, or experimental uncertainties as discussed by [29]. In this paper, the laminar flame speed will not be investigated in detail since there is no reliable database for RD387 to develop and verify the current methodology further. Instead, computed laminar flame speeds of RD387 surrogates will be compared

with the experimental results of EN 228 gasoline [30,31] in Section 4.4 and we will further investigate this flame target when reliable experimental datasets for RD387 become available.

Developing a surrogate needs huge amount of labor work regarding the number of targets that should be satisfied. The first step, as explained, is optimization which is very fast, about couple of minutes, which can reduce the labor work cost. But regarding the weight/importance of each target, different surrogates can be generated. All of these different surrogates need to be check for ignition delays and then the sensitivity analysis should be performed on some of them to find the optimum surrogates. The flow chart of the current methodology is shown in Figure 1.

The methodology described above has been implemented for formulating a surrogate for RD387 as described in Section 4.

Figure 1. The optimization methodology flow chart, where ε is the acceptable error tolerance, e.g., 3% for RON, 10% for distillation curve, 5% ignition delay, etc. and n^* is the maximum acceptable iteration number, e.g., 20. ε , θ , and β are acceptable errors, see Equations 1–2 and step 4 in section 3.

4. Results and Discussions

4.1. Research grade gasoline (RD387)

A fully characterized research grade non-oxygenated gasoline, RD387, is considered. Tables 2 and 3 show the key properties of RD387.

Table 2. RD387 physical and chemical properties.

	RD387 [13]	RD387 [32]
Saturates (liq. volume %) n-/iso-/cyclo-alkanes	67.8 (9.5/42.3/16)	-
Alkenes (liq. volume %)	4.7	-
Aromatics (liq. volume %)	26.4	-
H/C ratio	1.869	1.85
RON/MON	91/82.7	-
Specific gravity @15.56 °C (gr/cm ³)	0.7456	-
Net heating value (MJ/kg)	43.152	-

Table 3. RD387 distillation curve determined by ASTM D86 method.

Evaporated volume (v/v %)	Temperature, °C
10	63
20	71
30	78
40	87
50	96
60	105
70	114
80	125
90	147

4.2. Surrogate Formulation

Figure 2 shows a comparison of simulated ignition delay curves for pure surrogate components, carried out using the LLNL suite of kinetic mechanisms [33] under an adiabatic constant volume constraint, and measured ignition delay times for RD387 [13]. As illustrated in Figure 2 the measured

ignition delays of RD387 are somewhere between the ignition delays of the pure components. Therefore, it may be possible to formulate a surrogate made up of a distribution of the pure components yielding ignition delays that are similar to RD387. We used “may be possible” in the previous statement since species produced from one component can react with species from another and, hence, there is no linear combination of pure component ignition delay to generate ignition delay for a mixture, especially in the NTC regime (if exists).

Figure 2. Simulated ignition delay times for the pure components in air at a pressure of 40 bar and equivalence ratios of $\phi=0.3$ and 1.0. Simulations were carried out using the LLNL suite of kinetic mechanisms [33] and an adiabatic constant volume model. RD387 ignition delay experimental results were taken from Kukkadapu et al. [13].

The fuel surrogate given in Table 4 was developed by the methodology described in Section 3. Simulated distillation curves for the present surrogate and the gasoline surrogate of Mehl et al. [6] and measured distillation curve for RD387 fuel are also shown and compared in Figure 3. The simulated distillation curves are based on the staged equilibrium distillation model. At each equilibrium stage, the saturated vapor pressure of each pure component was evaluated based on the Design Institute for Physical Properties (DIPPR) correlation [34] and the activity coefficient was calculated based on Universal

Functional-group Activity Coefficients (UNIFAC) correlation [35]. The simulated distillation curves of Figure 3 account for mixture non-ideality and interaction between different hydrocarbon groups.

Table 4. Composition and properties of RD387, current surrogate, and Mehl et al. surrogate [6].

	RD387	Current surrogate	Mehl et al. surrogate [6]
iso-alkanes (v/v, %)	42.3	47.67	57.0
iC ₅ H ₁₂		8.98	0
iC ₆ H ₁₄		8.98	0
iC ₈ H ₁₈		29.71	57.0
n-alkanes (v/v, %)	9.5	14.47	16.0
nC ₅ H ₁₂		6.47	0.0
nC ₇ H ₁₆		0.0	16.0
nC ₁₂ H ₂₆		9.0	0.0
cyclo-alkanes (v/v, %)	16	0.0	0.0
Aromatics (v/v, %)	26.40	29.0	23.0
C ₆ H ₅ CH ₃		29.0	23.0
Olefins (v/v, %)	4.70	7.87	4.0
2-C ₅ H ₁₀		7.87	4.0
H/C ratio	1.869	1.849	1.926
RON/MON	91/82.7	88.8/84.5	89.5/85.7
Specific gravity @15.56°C (gr/cm ³)	0.7456	0.7275	0.7272
Net heating value (MJ/kg)	43.152	43.40	43.57

Figure 3. Distillation curves for RD387 fuel and Mehl et al. [6] and current surrogates.

As shown in Table 4, the current surrogate properties are close to RD387 properties with H/C within 1%, RON and MON within 2.2 units, specific gravity within 2.5%, and net heating value within 0.6%.

Linear correlations were adopted for mixture density and heating value computation. Noticeably, the Mehl et al. [6] surrogate does not predict the gasoline distillation curve (Figure 3). With the accurate representation of H/C, the combustion products (CO, CO₂, and H₂O), flame temperature and speed (primarily dependent on flame temperature), and thermal NO_x formation (dependent on flame temperature) of the current surrogate should be close to that of RD387. Furthermore, H/C is fundamental in determining the air/fuel ratio of the charge. The accurate representation of H/C is important for modeling the exhaust gas emissions of an internal combustion engine since the combustion products CO + CO₂ and H₂O will be produced in near identical quantities for a real fuel and surrogate with the same H/C. The RON and MON of Table 4 were calculated using the nonlinear correlation of Ghosh et al. [36]. RON and MON of Table 4 are different from what Mehl et al. [6] reported since they utilized different correlation. Noticeably, while both the current and Mehl et al. surrogates reasonably emulate RD387 RON and MON (within 2.2 units), neither capture the RD387 sensitivity (Sensitivity = RON – MON; RD387 = 8.3, current surrogate = 4.3, Mehl et al. surrogate = 3.8). The emulation of sensitivity is something that should be improved upon in future surrogates. Since different literature correlations lead to different values of RON, MON, and Sensitivity, the current approach of matching the simulated ignition delays of surrogate with the experimental data of RD387 over a wide range of temperatures (including NTC regime) is expected to provide a much better representation of octane characteristics.

In comparison to historical gasoline surrogates (e.g., [4]), four new components were introduced to the gasoline palette in the present study: iC₅H₁₂ (2-methylbutane or iso-pentane), iC₆H₁₄ (2-methylpentane or iso-hexane), nC₅H₁₂, and nC₁₂H₂₆ (Table 4). nC₅H₁₂ was added to help match the boiling temperature at 10% (v/v) cut; the temperature of 10% cut is around 63 °C and the boiling temperature of nC₅H₁₂ is 35.8 °C. Subsequently, iC₅H₁₂ and iC₆H₁₄ were added to adjust the ignition delay behavior. Although the compositional breakdown of RD387 shows that the high boiling point of gasoline appears to be caused mostly by C₉ aromatics, the reaction mechanisms of these C₉ aromatic components are still under development and are unavailable at present. As such, n-dodecane with a boiling temperature of 216 °C was included in the surrogate palette in order to match the gasoline boiling temperature at 90% and higher

cuts. See Table 4 for the final surrogate composition determined via genetic algorithm optimization. As stated in the methodology section, these surrogate components were considered and their concentrations were determined by minimizing objective functions defined as the difference between RD387 and surrogate properties. The first round of optimization was carried out using the WORKBENCH software [28] for the primary targets (H/C, RON, MON, heating value, density, and distillation curve). Then surrogate ignition delays were calculated and compared with experimental data. The kinetic mechanism library of LLNL [33] was used to develop a surrogate mechanism and ignition delay calculations were carried out using CHEMKIN-PRO [37]. The present kinetic mechanism was developed by combining the gasoline surrogate mechanism of [38] as a master mechanism and the n-alkane mechanism of [39] as a donor mechanism in a hierarchical manner. The master mechanism has n-heptane/iso-octane to smaller species and the donor mechanism includes n-hexadecane to n-octane. These master and donor mechanisms are connected to each other through the core of the merged mechanism which includes smaller hydrocarbons. While it may be important to model the potential co-oxidation reactions when merging different mechanisms, such efforts were not carried out herein. During the merging of the master and donor mechanisms, there were cases where the two mechanisms had differences in rate coefficients for the same reaction. In these cases, rate coefficients were taken from the more recently developed master mechanism [38]. Ignition delay predictions of the current mechanism were compared with those of other detailed mechanisms for different surrogates and are provided as supplementary material to this paper.

Recognizing that the mechanism development is an evolving process and that the current LLNL kinetics library will be updated with more accurate reaction coefficients in the future, sensitivity analyses have been performed in Section 4.3 to show how significantly the changes of reaction coefficients and surrogate component composition can affect surrogate ignition delay times. Based on comparison of surrogate simulated and RD387 measured ignition delay times, surrogate composition was slightly adjusted, by increasing/decreasing each species mass fraction by e.g., 10%, for a best agreement between ignition delay simulations and experiments, as will be discussed in Section 4.3.

4.3. Ignition delay simulations and comparison with experiments

Ignition delay measurements for RD387 were performed by Kukkadapu et al. [13] using a rapid compression machine and by Gauthier et al. [29] using a shock tube. Here we have utilized these experiments as targets for the current gasoline surrogate mixture. The uncertainty in the reported RCM ignition delay data is about $\pm 10\%$ [13], while that reported in the shock tube ignition delay time measurements is about $\pm 15\%$ [32].

The shock tube environment was simulated using an adiabatic constant volume constraint and the onset of ignition was defined as the time when the OH mole fraction reaches its maximum value. Our experience shows that this ignition delay definition is equivalent to definitions based on pressure or pressure rise rate. The ignition delay was also computed using these methodologies to check for consistency. The difference between these definitions is negligible for all cases of the present study.

The RCM data were simulated using a zero-dimensional model that accounts for the finite compression time and heat loss to the walls. The calculations start at the initial conditions of the experiment and the mixture is compressed at the same rate as occurs in the RCM experiment, determined by the measured pressure. The heat loss characteristics are determined and modeled by interrogation of non-reacting experiments in which the oxygen in the fuel-air mixture was replaced by nitrogen [13]. In the RCM simulations the ignition delay time is defined as the time when OH mole fraction reaches its maximum value and compared with pressure rise rate as mentioned before.

A comparison of total ignition delays obtained from RCM experiments, shock tube experiments, and simulations, at varying equivalence ratios and compressed pressures of 20 and 40 bar, are shown in Figure 4. P_C (or P) and T_C (or T) symbols in figures are the gas and fuel mixture final compression pressure and temperature at RCM condition and mixture shock pressure and shock temperature at shock tube condition. It is noted that there are potential differences between RCM and CV modeling results due to chemical reaction during the compression stroke [13,40] and heat losses to the walls. The surrogate and gasoline fuels display similar ignition behavior for wide range of pressures and temperatures at lean

conditions, but differences are observed at low temperatures for stoichiometric mixtures. This difference could be due to fidelity of the mechanism as shown in RCM experimental studies of gasoline and its surrogate by Kukkadapu et al. [41] or current surrogate formulation. The current surrogate formulation may be improved in the future by substituting or adding components (e.g., cyclo-alkane constituent) to the surrogate palette; however, the present surrogate is the optimum obtained within the constraint of the availability of kinetic models from the LLNL database using the present methodology.

The surrogate model reproduces the temperatures for the entrance to and exit from the NTC regime for all the conditions investigated. The Mehl et al. [6] surrogate underpredicts ignition delay at low temperatures for an equivalence ratio of 0.5 and overpredicts ignition delay at low temperatures for an equivalence ratio of 0.3 and pressure of 20 bar.

Figure 5 plots time variations of pressure and percent fuel conversion for current surrogate using rapid compression machine simulation with equivalence ratio of 0.3 and the end-of-compression conditions corresponding to 731 K and 20 bar. It is shown that at the end of first stage ignition, the 2-pentene and n-dodecane are approximately 90% consumed, while comparatively lower fractions of other components have been consumed.

Figure 6 illustrates the performance of the current and Mehl et al. [6] surrogate models in predicting the first stage ignition using the RCM model. It is shown in Figure 6 that the current and Mehl et al. [6] models overpredict the first stage ignition delay at stoichiometric conditions but the current surrogate reproduces the ignition delay at lean conditions adequately.

Figure 7 compares the experimental data and simulated pressure trace for $\phi=1$ at an end-of-compression pressure of $P_C=20$ bar and several compression temperatures (T_C). At $T_C = 731$ and 780 K, current surrogate predicts the pressure trace adequately but Mehl et al. [6] surrogate overpredicts the ignition delay. Both surrogates underpredict the ignition delay at $T_C = 879$ K but accurately predict the pressure trace at 930 K.

The effect of compositional changes in the surrogate mixture is shown in Figure 8. Two RCM compressed temperatures of 731 K and 850 K at compressed pressure of 20 bar and equivalence ratio of

0.3 were considered and studied. These two temperatures represent the low temperature (731 K) and NTC (850 K) regions. Note, the current surrogate ignition delay is very close to RD387 at those two temperatures. The base surrogate composition has been varied by doping the surrogate with an additional 10% liquid volume fraction of each of the seven surrogate components. While such compositional variations affect the base physical properties, such as distillation curve, H/C ratio, density, heating value, and RON/MON, insignificantly (less than 2%), they affect simulated ignition delay more significantly. Adding 10% more n-pentane, n-dodecane, iso-hexane and/or iso-pentane to the surrogate mixture decreases the ignition delays at both temperatures. This effect could be explained by considering Figure 2. The ignition delays of all of these components except iso-pentane are shorter than the ignition delay of RD387 as shown in Figure 2 and, hence, adding more of these components to the surrogate mixture causes a shorter surrogate ignition delay. Adding iso-pentane has the opposite effect; despite the fact that iso-pentane has a longer ignition delay than base surrogate, as shown in Figure 2, the simulated mixture ignition delay is reduced by increasing the concentration of iso-pentane in the surrogate. This could be due to chemical interactions of iso-pentane with other components which need further investigation in future work. Increasing the concentrations of toluene and 2-pentene increases the surrogate first-stage and total ignition delays as shown in Figure 8, a pattern consistent with the pure component ignition delays shown in Figure 2 (both components have a higher ignition delay than RD387). The total surrogate ignition delay increases with increased iso-octane concentration but the surrogate first-stage ignition delays in the NTC region decrease. Hence, a combination of the iso-octane and toluene or iso-octane and 2-pentene concentrations can be used as optimization parameters to control the first-stage ignition delay or the induction period between the first-stage and total ignition delays.

Sensitivity analysis has been conducted in order to identify the reactions within the current mechanism for the current RD387 surrogate that influence ignition delay time under constant-volume conditions at an initial temperature of 731 K, initial pressure of 20 bar, and fuel-air equivalence ratio of 0.3, conditions of relevance to RCM data found in the literature and advanced compression ignition engines. A linear sensitivity analysis was carried out by doubling the pre-exponential factor, A , for each

reaction rate coefficient in the kinetic mechanism. The sensitivity, defined as $S = \frac{\tau(2A) - \tau(A)}{\tau(A)} \times 100 \%$, was used to evaluate the influence of a particular rate constant on the total and first-stage ignition delays. Negative sensitivity implies that shorter ignition delays results from a doubling of the pre-exponential factor and that the reaction of interest promotes or accelerates the overall reaction rate. The linear sensitivity analysis was performed on all of the reactions; the most sensitive reactions resulting in a least a 5% change in first-stage or total ignition delay are shown in Figure 9. Species and reactions names in Figure 9 follow Refs. [38, 39].

The important reactions responsible for first-stage ignition are different from total ignition delay because of the gas temperature and radical pool temporal development. As shown in Figure 10, the gas temperature at the strong second-stage ignition is 200 K higher than that at first-stage ignition. At temperature around 900 K or higher, there are many reactions that produce HO₂ radicals, including reactions of O₂ with radicals such as HCO, CH₂CHO, and CH₃ [42]. These radicals then react primarily via:

where R is an alkyl radical. Reaction (a) above, i.e. reverse reaction #21 in Figure 9, strongly accelerates ignition because it leads to a buildup of H₂O₂ that followed by its decomposition to produce two OH radicals, reaction 33 in Figure 9, a sequence that leads to second-stage ignition. Note reaction #21 in Figure 9 shows strong positive sensitivity due to the fact that in the mechanism this reaction is written in reverse of reaction (a) above. Given the activation energy of H₂O₂ decomposition, reaction 33 only occurs at moderate to high temperatures and, hence, the first-stage ignition delay shows no sensitivity to this reaction; while, the total ignition delay, shows very strong sensitivity to reaction 33.

H abstraction from the parent hydrocarbons via OH also exhibits high sensitivity for both first-stage and total ignition delays. These reactions, leading to the formation of in most cases alkyl radicals, may show negative or positive sensitivity depending on the products they form. The reactions of iso-hexane

(ic6h14) were examined in more detail to explain the sensitivity of various reaction paths involving H abstraction by OH (reactions 34-39). Reactions which generate alkyl radicals that lead to more reactive intermediates have negative (promoting) sensitivity, while those that lead to less reactive fragments have positive (inhibiting) sensitivity. This reactivity competition among parent radicals generated from H abstractions from various sites is common for all components of the surrogate. In the case of iso-hexane, abstractions of tertiary H atoms (reaction 36) result in alkyl radicals that cannot easily undergo the chain branching low-temperature chemistry sequence through ketohydroperoxide formation leading to OH production. These alkyl radicals lead to a preponderance of less reactive iso-butene and propene formed via β -scission. On the other hand, abstraction reactions of primary H atoms (reactions 34, 37, and 39) allow low-temperature chemistry to occur more readily and lead to a greater degree of chain branching.

The reader is encouraged to see the sensitivity analyses for the Mehl et al. [6] gasoline surrogate presented by Kukkadapu et al. [13, 41, 43] which show similar results to the present analysis at the conditions of Figure 9.

Figure 4. Comparison of RD387 experimental and simulated surrogate total ignition delay times. Experimental data were from Kukkadapu et al. [13] and Gauthier et al. [32]. Surrogate simulations were carried out using both Mehl et al. [6] and current surrogates.

Figure 5. Simulated surrogate component conversion. RCM compressed conditions for both simulations and experiment: 731 K, 20 bar, and fuel-air equivalence ratio of 0.3.

Figure 6. Comparison of experimental and simulated first stage ignition delay times. Experimental data were from Kukkadapu et al. [13] and Mehl et al. surrogate was from [6].

Figure 7. RCM pressure traces: RD387 experiment and simulations carried out with current surrogate and Mehl et al. surrogate [6]. Given temperatures are for the end of compression (time=0). Pressure at the end of compression is 20 bar and fuel-air equivalence ratio is 0.3.

Figure 8. Sensitivity of first-stage and total ignition delays to surrogate composition changes: percent change in ignition delays for a 10% increase in each surrogate component concentration by liquid volume fraction. RCM compressed conditions of 20 bar, 731 K (7a) and 850 K (7b) at equivalence ratio of 0.3.

Figure 9. Sensitivity analysis for first-stage and total ignition delays for prediction of ignition using the current mechanism under constant volume conditions at initial conditions of 731K, 20 bar, and fuel-air equivalence ratio of 0.3.

Figure 10. Predicted temperature profile for constant volume ignition carried out using the current surrogate and mechanism. Initial conditions are 731K, 20 bar, and fuel-air equivalence ratio of 0.3.

4.4. Laminar flame speed simulation and comparison with experiments

Laminar flame speed measurements for European standard commercial gasoline (EN 228) with RON/MON 95/85 were performed by Jerzembeck et al. [30] using a constant volume bomb under engine-relevant conditions. Although the composition and physical properties of the EN 228 gasoline were not reported in [30], they are not expected to be the same as RD387 because EN 228 typically contains ethanol or other oxygenates at $\sim 5\%$ by liquid volume fraction [31]. Here we have utilized the Jerzembeck et al. experiments [30] for comparisons to laminar flame speed calculations carried out with the present surrogate mixture and kinetic mechanism.

The laminar flame speed model involves an adiabatic freely propagating one-dimensional flame which is used to determine the characteristic propagation speed of the gas mixture at specified unburned temperature and pressure. The mixture average transport model, thermal diffusion (Soret effect), and windward differencing in the convective term of energy equation have been used for laminar flame speed modeling. For facilitating the laminar flame speed calculations, the detailed mechanism was reduced at high temperatures (900-2000 K), pressures of 10-40 bar, and equivalence ratios from 0.5 to 1.5 for the current and Mehl et al. [6] surrogates. As mentioned before, the detailed kinetic mechanism was developed by combining the gasoline surrogate mechanism of [38] and the n-alkane mechanism of [39],

and then the mechanism reduction was performed as suggested by [44]. The automated iterative procedure, Directed Relation Graph with Error Propagation (DRGEP) [45], was utilized for mechanism reduction by applying 1.5%, 5%, and 10% error margins in total ignition delay between the original and skeletal mechanisms. The laminar flame speeds were computed using the three skeletal mechanisms with different error margins and the difference was insignificant. It should be mentioned that mechanism reduction was performed for each surrogate separately.

Comparisons of laminar flame speed predictions from four mechanisms using Mehl et al. surrogate [6] are shown in Figure 11. The mechanisms are the detailed mechanism with 1389 species of [38], the published reduced mechanism with 312 species of [6], a new mechanism reduction at high temperatures (900-2000 K) with 348 species based on the detailed mechanism of [38], and a new mechanism reduction at high temperatures with 575 species based on the current mechanism (combination of [38] and n-alkane mechanisms of [39]). The results of both new mechanism reductions (based on the detailed mechanism of [38] and current mechanism) are very close to the detailed mechanism of [38]; however, the published reduced mechanism of [6] does not reproduce the detailed mechanism of [38]. This could be due to the removal of some important species and reactions during mechanism reduction. The detailed mechanism of [38] and the current reduction of that detailed mechanism agree for laminar flame speeds at all equivalence ratios, illustrating the accuracy of skeletal mechanisms reduced for high-temperature conditions in predicting laminar flame speeds. The reduction of the current mechanism also agrees well with the detailed mechanism of [38] and the current reduction based on [38] predicts slightly higher laminar flame speeds (<10%). Throughout the rest of this section, simulations that were carried out using the skeletal mechanisms reduced for different surrogate compositions from the current mechanism will be presented.

Figure 11. Comparison of simulated laminar flame speeds using different mechanisms.

A comparison of laminar flame speed simulations, using the current and Mehl et al. [6] surrogates, with laminar flame speed measurements carried out at an unburned temperature of 100°C, varying pressures of 10 to 25 bar, and equivalence ratios of 0.7 to 1.2 is shown in Figure 12. The decrease in laminar flame speed with increasing pressure is well reproduced. There is a good agreement between simulations and experiments for stoichiometric and lean fuel-air mixtures but both model predictions underpredict the measured laminar flame speeds for rich fuel-air mixtures at high-pressure conditions of 20 and 25 bar. These discrepancies could be due to the surrogate mixtures, designed to emulate the non-oxygenated RD387 gasoline, not adequately representing the EN 228 gasoline, which may contain ethanol (around 5%) or other oxygenated components. The laminar flame speed predictions for the two surrogates are almost identical since both of the surrogates have very similar heating value (see Table 4), molecular structure, high-temperature (above 1000 K) small molecule chemistry, and adiabatic flame temperatures over the whole range of equivalence ratios. The adiabatic flame temperature is 2360±5 K for both surrogates at equivalence ratio and pressure of 1 and 10 bar respectively.

Figure 12. Laminar flame speed simulations for current and Mehl et al. [6] surrogates at high pressures and an unburned temperature of 373 K. Gasoline experiments were from [30]. Oxygen mole fraction in air is 0.205 in experiment and simulation.

5. Conclusions

A seven component gasoline surrogate for emulation of the physical and chemical properties of RD387, a full blend non-oxygenated gasoline, has been developed. It is demonstrated that the surrogate successfully reproduces the distillation curve, H/C, density, and heating value. The surrogate also adequately reproduces the first stage and total ignition delay times, as predicted by a surrogate kinetic mechanism assembled as an ensemble of component mechanisms from the LLNL library, over the range of pressures, temperatures, and lean equivalence ratios for which experimental data exist with the exception of low temperature stoichiometric conditions where simulations overpredict measured ignition delay times. Furthermore, the surrogate model reproduces the RCM pressure traces with acceptable error margin.

The laminar flame speeds of the gasoline surrogate were also simulated and compared with experimental data at wide range of pressures and equivalence ratios and there is a good agreement

between current surrogate and gasoline laminar flame speeds, especially for lean to stoichiometric conditions.

The surrogate mixture could be utilized in internal engine combustion modeling as the surrogate model reproduces many important physical and chemical properties of the target gasoline important for predicting fuel-air mixture preparation and combustion simultaneously within computational fluid dynamics simulations.

6. Future Works

There are a couple of items that need further refinement, such as surrogate and mechanism development methodology, to have a better predictive capability for fuel-engine development. In the context of the present work, laminar flame speed and ignition delay could be added as primary targets, and hence RON/MON, which has uncertainty in definition/correlation, can be eliminated from the surrogate definition methodology. Furthermore, targets such as surface tension and viscosity, which are important in fuel spray modeling, can be included in the surrogate development methodology. Surrogate mixture composition can be refined and expanded by including additional components, such as C7 isomers which are major components in RD387 and other gasolines. Mechanism development is a major bottleneck for surrogate development, since even for well-studied components such as iso-octane and n-heptane low-temperature reactions include uncertainties and deficiencies in rate parameters. The reactions of major gasoline components such as C6, C7, and C8 isomers, cyclopentane, cyclohexane, and toluene need further development. The importance of surrogate properties in turbulent spray modeling cannot be over-emphasized. All surrogate targets need to be considered, at least computationally, to identify the controlling targets in turbulent spray ignition and combustion and acceptable error margins. These topics have been rarely studied, including, for example, the influence of surrogate/fuel distillation curve on spray penetration.

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