A PRF+Toluene Surrogate Fuel Model for Simulating Gasoline Kinetics

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The use of Primary Reference Fuels mixtures (PRF, n-heptane and iso-octane) plus toluene (hereafter referred to as PRF+1 mixtures) as a surrogate fuel for gasoline combustion research is investigated. The reasoning behind the selection of toluene as a third surrogate component and its physical and kinetic effects on the PRF components are explained. Experiments in a Variable Pressure Flow Reactor (VPFR) are reported at relevant temperature and pressure conditions using pure components as well as PRF+1 mixtures with appropriate C/H ratios matching those of real gasoline compositions. A minimized/optimized chemical kinetic model is presented that predicts the behavior of PRF+1 mixtures at pure toluene, n-heptane, and iso-octane content, as well as at the optimal PRF+1 composition used to emulate gasolines. In constructing the model, the prior published mechanisms for n-heptane and iso-octane developed by Curran et al. [Combustion and Flame 114 (1998) 149-177; Combustion and Flame 129 (2002) 253-280] were minimized, optimized and combined to reproduce PRF results. Special attention was then given to modifying and validating a toluene sub-mechanism based upon earlier work of Klotz et al. [Proceedings of the Combustion Institute 27 (1998) 337-344], as it was found that existing models failed to accurately represent the newly collected data. The PRF+1 kinetic model described herein is shown to reproduce pure component as well as PRF+1 experimental data from a variety of experimental venues, including data published subsequent to its development. The importance of “co-oxidation” reactions of alkanes and toluene is also discussed. The present paper describes contributions that improve the experimental and kinetic database on pure components and PRF+1 mixtures.

1. Introduction

Practical fuels, such as gasoline, are mixtures of very large numbers of different hydrocarbon components [1] that can vary widely depending on the refining process, the crude oil source, geographical location of purchase and season [2]. Due to its broad availability and well-established infrastructure, gasoline is a likely candidate for use in emerging technologies such as Homogeneous Charge Compression Ignition (HCCI) engines. It is clear, however, that the values of Research Octane Number (RON) and Motor Octane Number (MON) are insufficient in characterizing autoignition behavior under HCCI conditions [3]. Therefore, as computational
design of advanced engines becomes more important, refined combustion chemistry models for gasoline will be of continuing interest. Extensive efforts have been focused on studying the kinetic behavior of single component or simple mixtures of components that can represent that of gasoline. Primary Reference Fuel (PRF) mixtures (comprised of $n$-heptane and iso-octane) are at the foundations of rating gasoline octane number; however, due to differing physical and chemical properties, the behavior of PRF mixtures in homogenous charge and spark ignition engines is significantly different than that of gasoline itself. Consequently, more complex mixtures of individual species representing different molecular groups have been suggested as surrogate fuels for gasoline [4]. Such efforts attempt to represent each class of hydrocarbon found in gasoline (i.e. alkanes, iso-alkanes, alkenes, cyclo-alkanes, and aromatics) by a single component so that the different molecular structures are embodied. The intent is that the mixture distributions can be varied, primarily to match research and motored octane numbers as well as representative chemical structural composition. It is also possible to model the physical properties of gasoline (i.e. distillation curve, viscosity, etc.) through surrogate formulations with larger numbers of components; similar approaches are suggested for modeling diesel and aviation fuels, e.g., see [5, 6]. For such complex surrogates, the dimensional character of the kinetic model becomes large and the collective uncertainty of kinetic and thermochemical parameters increases dramatically. Moreover, the validation process then requires comparisons against a large experimental database for pure components and their mixtures, for which the needed target data are mostly lacking.

In this work, we have been driven by the above issues to consider an approach that minimizes the number of surrogate components to three, including the original PRF components. We began investigation of using PRF+toluene (PRF+1) mixtures as surrogates for gasoline combustion research as early as 2000. Initial work on the problem showed that there were significant limitations of existing models for the oxidation of pure PRF components, their mixtures and pure toluene. Furthermore, there was a continuing need for additional validation target data, particularly for ternary mixtures. Subsequently, we initiated a 36-month detailed research program to develop and validate a PRF+1 kinetic model and to generate approaches for formulating PRF+1 mixtures that would emulate specific gasoline combustion properties. Recently, a team of scientists from industry, government, and academia assembled to evaluate the status of current surrogate fuel efforts has recommended that these same components are the appropriate initial species for development of more complex surrogate mixtures [7]. Similar evaluations are currently underway for diesel [8] as well as jet fuels [9].

We report here our basis for selecting these ternary components to model gasoline behavior. New experimental results obtained in a Variable Pressure Flow Reactor (VPFR) on binary ($n$-heptane+toluene, iso-octane+toluene) as well as ternary ($n$-heptane+iso-octane+toluene) mixtures and a small number of reference laminar flame speed measurements on PRF+1 mixtures, performed to support the PRF+1 kinetic model development effort, are reported. The developed PRF+1 model is validated against these data, as well as data appearing in the literature from flow reactor, stirred reactor, shock tube, and flame experiments. Additional comparisons against new experimental data that have appeared since model development are also presented, and the importance of “co-oxidation” reactions of alkane and toluene is further addressed.
2. Component Selection

The overall C/H mass ratio of proposed complex surrogates has typically not been scrutinized so as to align it with the C/H mass ratio of the gasoline of interest. Gasoline C/H mass ratios vary considerably by source, even though the Research Octane Number (RON), Motored Octane Number (MON), and (RON+MON)/2 (Road Octane Number) of various gasoline compositions may be nearly the same. The C/H mass ratio of PRF mixtures themselves is functionally dependent on octane number. PRF C/H mass ratio lies between 5.213 (n-heptane, PRF0) and 5.296 (iso-octane, PRF100) (here the number notation after PRF corresponds to the molar percentage of iso-octane in the PRF mixture). C/H mass ratios for gasoline are usually considerably larger, on the order of 6 and above. This is an important property to consider, as the adiabatic flame temperature of a fuel/air mixture is not only dependent on equivalence ratio but also on the C/H mass ratio of the fuel [10], see Fig. 1. Furthermore, C/H mass ratio also affects mass transport issues in terms of the definition of the local air/fuel stoichiometry and overall air/fuel flow rates in actual engine modeling. Selection of the air flowrate along with valve geometry and lift affect chamber turbulence initialization and mass burning rates in homogeneous charge spark ignition engines. Without matching C/H ratio of surrogate and gasoline, these overall parameters cannot be properly matched in modeling engine combustion measurements, which are known to be affected by in-cylinder turbulence. While the coupling of turbulence with homogeneous charge compression ignition behavior is less direct, it is known to be of importance to HCCI behavior.

We chose toluene (C₆H₅CH₃) as a third component to add to the primary reference fuel baseline with the intent of matching the following properties to those of gasoline: C/H ratio, low and high temperature autoignition behavior, homogenous reaction heat release rate and reference laminar flame burning rate. As shown in Fig. 1, toluene can be added to PRF mixtures to adjust the overall C/H mass ratio. A molar concentration of approximately 10-20% toluene is needed to adjust the C/H mass ratio of a PRF mixture to that of conventional gasoline. Moreover, toluene is typically the most abundant simple aromatic found in gasoline.

Toluene itself exhibits no negative temperature coefficient (i.e. two-stage ignition) kinetic behavior, but inhibits both the low temperature and hot ignition behavior of PRF components. The octane behavior of a PRF+1 mixture that replicates C/H mass ratio can be independently adjusted by changing the ratio of n-heptane and iso-octane without varying the toluene molar fraction. The presence of toluene in PRF+1 mixtures couples with n-heptane and iso-octane kinetics through the radical pool composed principally of OH, O, H, HO₂, and CH₃ species. Toluene scavenges radical species that are produced in the reaction of alkanes at low and intermediate temperatures and therefore suppresses the negative temperature coefficient behavior of a PRF+1 mixture relative to the PRF mixture without toluene. Toluene also has a higher hot ignition temperature than either PRF component. The addition of toluene to PRF mixtures also increases the hot ignition temperature of the mixture through an inhibition of hydrogen peroxide formation rate. Of all of the possible species that could be added to PRF components to achieve the above target properties, toluene has also received the most detailed kinetic modeling efforts [11-16].
3. Detailed Kinetic Model Formulation

We initiated kinetic development of the PRF+1 model from the baseline iso-octane mechanism developed by Curran and co-workers [17]. A minimized version of this model was generated using an approach described in detail elsewhere [18, 19]. A series of zero-dimensional computations were performed for the range of initial conditions of interest to emulate a selected set of experimental conditions that encompassed those used in the original detailed model development. For each computation, individual reaction rates were analyzed at each integration time step. An elementary reaction step was retained in the minimized scheme if the following conditions were satisfied at each integration step for all conditions considered:

\[
\begin{align*}
|R_{f,i}| &> \varepsilon_R |R_{Ref}| \\
|R_{r,i}| &> \varepsilon_R |R_{Ref}| \\
|R_{Net,i}| &= |R_{f,i} - R_{r,i}| > \varepsilon_R |R_{Net,Ref}| \\
|\dot{Q}| &> \varepsilon_Q |\dot{Q}_{Ref}|
\end{align*}
\]  

(1)

Where \(i\) is the reaction index, \(R_{f,i}\) the forward reaction rate, \(R_{r,i}\) the reverse reaction rate, \(R_{Net,i}\) the net reaction rate, \(\dot{Q}_i\) the heat release associated with the \(i\)th reaction, and \(\varepsilon_R\) and \(\varepsilon_Q\) are assigned minimization parameters. Reference reaction rates \(R_{Ref}\) and \(R_{Net,Ref}\) and reference heat release rate \(\dot{Q}_{Ref}\) were taken to be the maximum values (amongst all of the reactions present in the mechanism) of the corresponding rates at the current integration time step. This procedure provided a clear, robust, and physically sensible means for identification and removal of unimportant reactions from large reaction schemes. As reactions were removed, the mechanism was also searched for “orphan” species and associated thermochemistry data that were no longer required in the minimized model. It should be emphasized that because the reactions that were removed did not contribute significantly to either species fluxes or heat release for a wide range of conditions, the performance and quality of predictions of the resulting minimized reaction set...
against the original experimental targets remained essentially that of the original detailed mechanism. Moreover our research group has employed the same minimization approach to generate minimized models from the detailed PRF mechanisms produced by Curran and co-workers as they appear on the Lawrence Livermore National Laboratories (LLNL) website [20]. For example, following the procedure described above, Zhao et al. [21] performed the first validation of the early PRF model developed by Curran et al. [22] against flame speed data.

of Minimized versions for iso-octane (derived from [17]) and n-heptane (derived from [23]) were identified, and a suitable combination of these mechanisms was tested and optimized to reproduce combustion characteristics of pure component (PRF0 and PRF100) as well as those of PRF mixtures. In the process, our recent update to hydrogen/oxygen kinetics [24] was also implemented in the combined mechanism. During development of the PRF+1 model, however, no public-domain toluene submodel could be found that reproduced high pressure toluene oxidation data produced in the VPFR [8-13].

Starting from the baseline reaction set of Klotz et al. [12], an in-house sub-mechanism for toluene oxidation was developed, based on the current (and, still, incomplete) level of conceptual understanding of the oxidation of aromatic single ring species [25, 26]. The redevelopment process included several steps: 1) a basic mechanism structure was established for main species (toluene, benzyl, benzaldehyde, benzene, and their derivatives) by assigning appropriate reaction rate coefficients based on an extensive up-to-date literature review [27-38]; 2) thermochemistry was adopted from the Burcat [39] and LLNL databases [14], where possible; 3) a cyclic C5 sub-mechanism was added based on implementations by Alzueta et al. [29] and Djurisic et al. [33] with updated thermochemistry for the cyclopentadienyl radical (C5H5) from Roy et al. [40] and Kiefer et al. [41]; 4) benzoquinone (C6H4O2) chemistry and additional branching channels during low temperature toluene oxidation involving benzyl (C6H5), phenoxy (C6H5O), and HO2 radicals were added based on the theoretical work of Skokov et al. [25]. The resulting set was then integrated with the PRF model, linking it to C3, C2, and C1 intermediates and final products producing the PRF+1 mechanism reported here which consists of 469 species undergoing 1,221 reactions.

4. Experimental Methods

The new experiments on PRF+1 mixtures reported herein were performed in the Princeton VPFR. Only a brief discussion of these experiments is given below as there exist numerous prior publications providing detailed information on the VPFR instrumentation and experimental methodology (e.g. [42]).

Nitrogen carrier gas is heated by a pair of electrical resistance heaters and directed into a reactor duct. Oxygen is also introduced at the duct entrance. The carrier gas/oxygen mixture flows around a baffle plate into a gap serving as the entrance to a diffuser. In the present study, liquid fuel (consisting of either binary or ternary mixtures of n-heptane, iso-octane, and toluene) is volumetrically metered to a liquid vaporizer system located within the VPFR pressure shell. The metered liquid flow is gas-blast atomized using heated nitrogen. The nitrogen and fuel vapor mixture is introduced through the center tube of a radiation shielded fuel injector assembly and injected radially outward into the gap where it rapidly mixes with the carrier gas and oxygen. The reacting mixture exits the diffuser into a constant area test section. The reactor is surrounded by electrical resistance thermostated heaters which maintain the reactor the wall
temperatures within close proximity (< 50 K) of gas temperatures. Axial temperature distribution through the reactor test section is determined to be uniform within ±1 K (relative) with all flows established, absent of fuel vapor.

Near the exit of the test section, a water-cooled sampling probe is positioned on the reactor centerline to continuously extract and convectively quench a small percentage of the flow. At the same axial location, the local reaction gas temperature is measured with a type R thermocouple accurate to ±3 K. The extracted sample gas flows via heated Teflon lines to analytical equipment including a Fourier transform infrared spectrometer (FTIR), an electrochemical O2 analyzer, and a pair of non-dispersive infrared analyzers for CO and CO2. Additional stable species of interest (e.g. CH4, H2O, and small molecular weight hydrocarbons and hydrocarbon oxygenates) can be measured continuously using on-line FTIR spectrometry. Upstream of the above analytical equipment and immediately upon exiting the sampling probe, the sample stream flows through heated multiport sampling valves (MPV). The system is designed to trap and store as many as 30 individual gas samples for subsequent off-line gas chromatographic (GC) analyses. The gas chromatograph equipped with flame ionization detectors was used in this study to determine and quantify larger molecular weight hydrocarbons. The measurement uncertainties for the data reported here are: fuel species – ±4%, O2 – ±2%; CO – ±2%; CO2 – ±2%; H2O – ±5% of reading; higher hydrocarbons and fuel species – ±4%. For all experiments reported, the total carbon and oxygen balances experimentally determined at each residence time were within 15% and 5% of the specified input, respectively. This somewhat large discrepancy in the carbon balance is not representative of experimental difficulties but of limitations in quantifying all intermediate species. For example, during the oxidation of aromatic species, combination of radicals (such as cyclopentadienyl and phenoxy) may form low vapor compounds [11] that cannot be sampled by the water-cooled probe.

Two types of VPFR experiments are reported here: 1) “species-time history” experiments at constant initial reaction temperature and reactant concentration where the distance between the point of fuel injection and the sampling position is varied by moving the fuel injector probe (with attached mixer/diffuser assembly) relative to the fixed sampling location. Mean axial velocity measurements along the centerline of the reactor are used to determined reaction residence time as a function of reaction distance. By this means, profiles of stable species and temperature versus reaction residence time can be determined experimentally. The uncertainty in the residence time is approximately 5%; 2) “reactivity” experiments where initial reactant concentrations are held constant and the initial reaction temperature is varied while keeping the residence time constant. This mode of operation is more fully described in [22, 43].

As discussed in the Introduction, a small number of flame speed measurements were performed on PRF+1 mixtures to aid in the development of the kinetic model described below. These measurements were performed using a single jet-wall stagnation flame similar to that used by Egolfopoulos et al. [44] and Particle Image Velocimetry (PIV) was applied to extract flame speed information. A detailed description of the experimental methodology can be found in [45].

5. Results and Model Validation

In this section, predictions obtained using the mechanism described above are compared against a wide range of experimental data, including shock tube studies, premixed flames, and species profiles obtained in the VPFR. For shock-tube ignition delay simulations, the systems were
modeled assuming isochoric, homogeneous, and adiabatic conditions. Since ignition delay times are monitored and defined differently among the research groups considered here, a simulation code was developed, coupled with CHEMKIN II [46] packages, to directly compute ignition delay based on the following criteria: time to maximum rate of increase in pressure, time to maximum OH and CH concentrations, and time to maximum rate of increase in concentration of OH and CH. For all the conditions considered in this study, these definitions yield values that differ by no more than 10%. Laminar burning velocity predictions were obtained using PREMIX [47]. Transport parameters were taken from the Sandia database [48] as well as from the studies of Curran et al. [14, 22, 23]; Soret effects and multi-component diffusion were also included in the computations. To assure a fully converged flame speed prediction, a minimum of 1,000 grid points was imposed in the PREMIX calculations. Finally, VPFR experimental data were modeled using SENKIN [49] under isobaric and adiabatic conditions.

Figure 2 shows combined CO and CO$_2$ mole fractions as a function of initial reaction temperature for PRF, PRF+1, and toluene oxidation at fixed residence time in the VPFR [50, 51] compared against model predictions. The change in reactivity of the different fuels is captured well by the model. It should be noted again that the hot ignition temperature of toluene is much higher than that for either of the PRF components and toluene itself exhibits no low temperature chemical activity on the time scale of Fig. 2. Reactivity data presented in Fig. 2, show that the addition of toluene to a PRF mixture affects the chemistry controlling low temperature phenomena, as well as that determining the hot ignition temperature. It suppresses low temperature reactivity and increases the hot ignition temperature, both of which are significant in defining autoignition-related phenomena in homogenous charge reciprocating engines. The present model also shows good agreement with the PRF flow reactor data presented in Curran et al. [22] and Callahan et al. [43] as well as with the jet stirred reactor experiments of Dagaut et al. [52-54] (comparisons not shown here for the sake of brevity).

![Figure 2: PRF, PRF+1, and toluene VPFR oxidation at 12.5 atm, $\phi = 1.0$, $X_{O_2} = 0.015$, residence time = 1.8 s. Experimental [50, 51] (symbols) versus model predictions (lines) of the extent of oxidation by conversion to CO and CO$_2$ as a function of inlet temperature. Dashed lines correspond to open symbols.](image)
High pressure shock tube ignition of PRF fuels at temperatures that include negative temperature coefficient (NTC) behavior has been a topic of continued interest. Here we show comparisons of calculated ignition delays against the data of Fieweger et al. [55] (Fig. 3). The change in low and intermediate temperature ignition characteristics is properly captured by the model for neat PRFs (i.e. \(n\)-heptane and \(iso\)-octane) as well their blends. We recently reported [56] an analysis of the chemistry controlling the first and second stage ignition characteristics observed in the predictions shown in Fig. 3 for \(n\)-heptane using the models of Curran et al [23] and Peters et al. [57]. Other shock tube studies of neat PRF fuel ignition (i.e. \(n\)-heptane/air and \(iso\)-octane/air) have recently appeared in the literature [58-60]. The agreement of present model predictions against such data is similar to that shown in Fig. 3 and indicates that the model involves the same ignition kinetic pathways in the high pressure, intermediate temperature regime (which are of relevance to HCCI combustion). Furthermore, the model also compares well against the large number of experimental studies of PRF ignition found in the literature in high-temperature shock tubes studies (e.g. [61, 62]; as reviewed by Chaos et al. [63]) and rapid compression machine experiments [64, 65].

![Figure 3: Computed ignition delay times for stoichiometric PRF/air mixtures at 40 bar pressure compared with experimental shock tube measurements [55]. Dashed line corresponds to open symbols.](image-url)

It is important to examine the performance of the toluene kinetic model developed in this study against experimental data. As discussed above and shown in Figure 2, the model captures the lack of NTC chemistry although it predicts a slightly lower hot ignition temperature than is experimentally observed. Figure 4 compares predictions of species-time histories against a representative VPFR experiment for lean toluene oxidation at 12.5 atm and 920 K. Major species profiles are well reproduced whereas the model under-predicts benzene and formaldehyde intermediates by approximately a factor of 2 (not shown). The model also compares well against the high temperature, atmospheric pressure flow reactor measurements of Klotz et al. [12]. Formaldehyde is predicted to be formed mostly from the toluene side chain, while carbon atoms in the ring follow direct routes to CO and CO\(_2\) (due to the lack of CH\(_2\) groups produced from them). Formaldehyde predictions could be improved by exploring alternative channels leading to its formation. It is noted, however, that computed profiles present
a dramatic improvement over results found using available literature models [13, 15, 16] as evidenced by the O$_2$ profiles shown in Fig. 4.

![Graph showing O$_2$ profiles](image)

Figure 4: Toluene oxidation under flow reactor conditions, $P = 12.5$ atm, $T = 920$ K, $\phi = 0.6$, $X_{C_6H_5CH_3} = 0.14\%$. Symbols represent experimental data; lines are the results obtained using the present model. Predicted O$_2$ profiles (gray lines) using models found in Refs. [13] (solid line), [15] (dash-dot line), and [16] (dashed line) are also shown. Model predictions have been shifted by 0.32 s.

Toluene ignition has been studied by Burcat et al. [66], Pengloan et al. [67], and, more recently, by Hanson and co-workers [58, 68]. Most of the experiments were conducted in the 1-3 atm pressure range with the noticeable exception of the study by Davidson et al. [58] who reported ignition delays of toluene/air mixtures at pressures in excess of 55 atm. The equivalence ratios of studied mixtures covered a range from 0.3 to 1.5. Here we choose the data sets for stoichiometric toluene/air ignition of Davidson et al. [58] (high pressure) and Vasudevan et al. [68] (low pressure) to demonstrate comparisons against model predictions (Fig. 5); similar levels of agreement are obtained in modeling the data of Burcat et al. [66] and Pengloan et al. [67] (not shown). Davidson et al. [58] found that all toluene oxidation models they considered failed to predict their high-pressure ignition data.

A common target used to partially validate kinetic mechanisms is the reference laminar burning velocity. In this study, laminar burning velocities were calculated for toluene/air mixtures over a wide range of equivalence ratios at both atmospheric conditions (i.e. room temperature and pressure) and at an initial temperature and pressure of 3 atm and 450 K, respectively. These conditions correspond to experiments performed by Davis et al. [69] and Johnston and Farrell [70]. Figure 6 compares experiments and computations. Very good agreement is observed although a slight shift towards the rich side is noticeable when considering the model results at higher pressure and unburned gas temperature (not observed in the atmospheric pressure case).

The model validations presented above only considered pure fuels. The remainder of this section addresses the performance of the mechanism against data for binary (i.e. n-heptane/toluene and iso-octane/toluene) as well as ternary (i.e. $n$-heptane/iso-octane/toluene, PRF+1) mixtures. Figures 7 and 8 show species profiles at fixed residence time as a function of initial reaction temperature in the VPFR for mixtures of $n$-heptane/toluene and iso-octane/toluene, respectively.
Overall, the agreement is very good for the initial reactants and major products and the NTC region is properly reproduced in the case of \(n\)-heptane/toluene (Fig. 7).

![Figure 5: Toluene ignition delays.](image)

Data have been normalized to the values shown using published parameters.

![Figure 6: Measured (symbols) and modeled (lines) laminar flame speeds of toluene/air mixtures.](image)

- Data [69] for atmospheric pressure and temperature flames;
- Data [70] for flames at an initial pressure and temperature of 3 atm and 450 K, respectively.

During the preparation of the present manuscript, a very recent study on shock tube ignition of \(n\)-heptane/toluene/air mixtures has appeared in the literature [71], presenting opportunity to test model predictions against new data not utilized in its development. Figure 9 compares modeling predictions against these new data [71]. Agreement is reasonable (within a factor of 2) considering that the present model has not been optimized \textit{a priori} against this set of data. For stoichiometric mixtures, the model captures the NTC turnover temperatures very well although agreement deteriorates at lower temperatures and higher pressures. These results require further study, and our present speculation is that refinement might be needed in the \(n\)-heptane sub-
mechanism and its effect on coupling reactions between toluene and $n$-heptane involving small radicals.

Figure 7: Reactivity profiles during VPFR oxidation of a $n$-heptane/toluene (90%/10%) mixture at 12.5 atm, 1.8 s residence time, $\phi = 1.0$, and 670 ppm initial fuel fraction. Symbols are present experimental measurements with lines showing modeling results; dashed lines correspond to open symbols.

Figure 8: Reactivity profiles during VPFR oxidation of a iso-octane/toluene (90%/10%) mixture at 12.5 atm, 1.8 s residence time, $\phi = 1.0$, and 620 ppm initial fuel fraction. Symbols are present experimental measurements with lines showing modeling results; dashed lines correspond to open symbols.

In a companion paper to [71], Andrae et al. [72] developed a PRF+toluene mechanism that was used to model the ignition delay data shown in Fig. 9. The PRF model developed at Lawrence Livermore National Laboratories (LLNL) [73] coupled with the toluene model of Sivaramakrishnan et al. [16] were chosen as starting mechanisms. As discussed above, the PRF model [73] was minimized and tested by Zhao et al. and shown not to reproduce flame speed measurements [21]. We have shown here that the model of Sivaramakrishnan et al. [16] fails to reproduce toluene oxidation data collected in the VPFR (see Fig. 4). Moreover, Herzler et al.
Found that the \( n \)-heptane model of Curran et al. [23] (a subset of the PRF model [73]) overpredicted high pressure (~50 bar) \( n \)-heptane/air ignition delays in the intermediate and high temperature regimes. Also, Conley et al. [74] showed that the \( n \)-heptane model [23] could not reproduce VPFR reactivity measurements. Nonetheless, Andrae et al. [72] decided to turn their attention solely to improving the toluene sub-mechanism so that good agreement with pure toluene [59] as well as \( n \)-heptane/toluene [71] ignition data could be obtained. In the process, the most relevant changes performed were to a) reduce the rate of hydroperoxy addition to the benzyl radical \( C_6H_5CH_2 + HO_2 = C_6H_5CH_2O^- + OH \) (R1) to \( 2.0 \times 10^{12} \text{ cm}^3/\text{mol}/\text{s} \), adopted from Hippler et al. [75]; b) add decomposition pathways of the alkoxy benzyl radical to H and CH_2O, \( C_6H_5CH_2O^- = C_6H_5CHO + H \) (R2), \( C_6H_5CH_2O^- = C_6H_5 + CH_2O \) (R3); c) include a step adding molecular oxygen to the benzyl radical, \( C_6H_5CH_2 + O_2 = C_6H_5 + CH_2O + O \) (R4). It is also worth noting that the mechanism developed in [72] consists of 1,083 species and 4,635 reactions, dimensionally much larger than the model developed here.

![Graph showing ignition delay times for \( n \)-heptane/toluene/air mixtures. Symbols represent experiments [71] with lines showing predictions from the present model; dashed lines correspond to open symbols. Experimental data has been normalized to the pressures shown using \( P^{0.833} \) for \( \phi = 0.3 \) and \( P^{1.08} \) for \( \phi = 1.0 \) [71].](image)

The reduction in the rate of reaction (R1) is warranted since in the study of Sivaramakrishnan et al. [16] this rate was increased to its collision limit of \( 3.67 \times 10^{14} \text{ cm}^3/\text{mol}/\text{s} \). Reaction (R1) is one of the most sensitive reactions during the ignition of toluene at high pressures. In the model developed here, the rate of reaction (R1) was increased from the value adopted by Hippler et al. [75] to \( 2.0 \times 10^{13} \text{ cm}^3/\text{mol}/\text{s} \). This higher value is consistent with similar \( R + HO_2 \) reactions and with recent transition state theory calculations [25]. The value chosen by Andrae et al. [72] for (R1) still could not reconcile their modeling predictions against data for neat toluene [59]. They realized that additional branching needed to be included in the mechanism which led to the introduction of reaction (R4). This complex lumped reaction generates a reactive O radical as well as formaldehyde, both of which lead to increases in the overall branching of the system. The rate of reaction (R4) was adjusted to achieve ignition delay predictions that match the data [59, 71]. As discussed by Hippler et al. [75], however, oxidation of benzyl radicals does not proceed through the formation of peroxy or alkoxy radical by molecular oxygen addition at any significant rate; therefore reaction (R4) is not a likely contributing path to branching in toluene oxidation.
More importantly, in an earlier publication, Andrae et al. [76] developed a similar model to that discussed in [72] to describe the autoignition of \(n\)-heptane/toluene mixtures in a HCCI engine. In that effort, the toluene model of Dagaut et al. [13] was added to the PRF model from LLNL [73] (which, again, we have shown to be inadequate in replicating VPFR toluene oxidation experiments, see Fig. 4) and further adjustments were made to the composite model. In order to increase the reactivity of the model, Andrae et al. [76] argued that “co-oxidation” or cross reactions involving H abstraction from one of the fuel molecules by large alkyl (and benzyl) radicals formed from other fuel molecules present in the system could be an important pathway in HCCI combustion. From the modeling results they claimed that inclusion of co-oxidation reactions was needed in order to match observed engine ignition at low intake pressures and high intake temperatures.

Such a condition has been considered using our PRF+1 model and is shown in Fig. 10. Modeling was performed using a single zone approach with engine and initial pressure/temperature parameters as described in [76]. For the conditions shown in Fig. 10, no ignition could be predicted by the model of Andrae et al. [76] unless co-oxidations reactions were incorporated. Figure 10 shows that the present PRF+1 model (which includes no co-oxidation reactions) predicts ignition at approximately 20 crank angle degrees (CAD) before that seen experimentally. This is expected as the modeling does not consider heat losses such as convective transfer from the gas to the cylinder walls, a more physically realistic treatment. Introducing heat loss to the cylinder walls following the correlations found in [77] for the heat transfer coefficient and assuming a cylinder wall temperature of 425 K yields a much better prediction, as seen in Fig. 10.

![Figure 10: Experimental (bold solid line) [76] and calculated pressures as a function of crank angle in a HCCI engine at the conditions shown. Solid and dashed lines show present model predictions with and without treatment of cylinder wall heat transfer, respectively.](image)

The above discussions support the argument that toluene coupling with PRF autoignition chemistry occurs through the small radical pool and not through participation of large radical species. We conclude, consistent with the prior literature that co-oxidation reactions are not significant, as is also now claimed in the more recent paper of Andrae et al. [72]. The discrepancies seen in the studies of Andrae et al. [72, 76] are due to inadequacies of the selected
toluene models and introduction of co-oxidation reactions or reactions such as (R4) appear not to be good approaches to resolving these differences.

![Figure 11: Reactivity profiles during VPFR oxidation of a ternary mixture emulating 84 ON gasoline (n-heptane/iso-octane/toluene – 18.23%/66.42%/15.35%) at 12.5 atm, 1.8 s residence time, \( \phi = 1.0 \), and 740 ppm initial fuel fraction. Symbols are present experimental measurements with lines showing modeling results; dashed lines correspond to open symbols.](image1)

![Figure 12: Oxidation of a ternary mixture emulating 84 ON gasoline (n-heptane/iso-octane/toluene – 18.23%/66.42%/15.35%) under flow reactor conditions, \( P = 12.5 \text{ atm}, T = 820 \text{ K}, \phi = 1.0 \), 740 ppm initial fuel fraction. Symbols represent experimental data, lines are the results obtained using the present model; dashed lines correspond to open symbols. Model predictions have been shifted by \(-0.11 \text{ s}\).](image2)

Lastly, the performance of the model developed herein is evaluated against experimental data obtained using ternary mixtures. Reactivity of a sample ternary mixture emulating an 84 ON gasoline (termed Ternary 84) along with speciation results are shown in Figs. 11 and 12, respectively. The model shows good agreement for initial reactants, principal reaction
intermediates and products. Also the effect of iso-octane and toluene on diminishing the mixture reactivity in the NTC region is reproduced well by the model. Although not shown, the characteristic reaction time scales and their dependences on equivalence ratio and initial temperature are properly captured by the model. Prediction of minor intermediates is less satisfactory as evidenced by the formaldehyde profile in Fig. 11, as might be expected, given the current understanding of some of the kinetic details involved in the toluene mechanism (e.g. phenyl and benzyl ring oxidation \[25, 26\]).

As explained above, preliminary laminar flame speed measurements were obtained using PRF+1 mixtures. No such measurements are available in the literature for ternary mixtures. Data were taken for Ternary 84 mixtures at selected equivalence ratios, unburned gas temperatures, and N\textsubscript{2} dilution levels to simulate exhaust gas recirculation (EGR) effects. The present mechanism was used to model these data and the results are shown in Fig. 13. Very good agreement is observed with the exception of the case for an unburned gas temperature of 550 K, where the model overpredicts the flame speed by approximately 9\% for $\phi=1.10$.

Present model predictions have also been tested against shock tube ignition delay measurements of ternary mixtures [59], as shown in Fig. 14. These data appeared in the literature after development of the present model and no optimization has been performed against them. While agreement is very good, the model tends to over-predict the experimental results for lower pressure and lean conditions. The model is seen to correctly emulate ignition delay dependence on pressure and equivalence ratio.
6. Conclusion

A three-component surrogate fuel consisting of \( n \)-heptane, \( iso \)-octane, and toluene has been proposed to emulate combustion characteristics of gasoline. Toluene provides a means to adjust the mixture C/H mass ratio and low as well as high temperature ignition characteristics independently, all of which are important properties to reproduce for gasolines. Experiments have been performed in a Variable Pressure Flow Reactor at 12.5 atm and temperatures relevant to HCCI combustion. A detailed chemical kinetic model has been developed consisting of 469 species and 1,221 reactions. No suitable toluene sub-mechanism could be identified during development of the present model and considerable efforts were placed in updating and improving toluene kinetics, enhancing the theoretical foundation of the mechanism as well as its predictive capabilities. The model has been comprehensively validated and tested against an expanded database including the experiments reported herein as well as data appearing in the published literature since its development.

It has been shown that comparisons with flow reactor, ignition delay, and laminar flame speed results are very good, and all of the validation comparisons in all of the various experimental configurations are significant improvements over other mechanisms presently in the literature, especially for mixtures involving toluene. Our results continue to support that there is little coupling of toluene kinetics with alkane kinetics other than through small species chemistry [12], contrary to the earlier suggestions of Andrae et al. [72], now apparently retracted [76]. The erroneous conclusion of their initial work [72] can be attributed to the limitations of the toluene models in replicating high pressure toluene oxidation adequately. The approach to increase branching from the reactions of phenyl and benzyl radical oxidation, as suggested by their more recent work [76] is not supported by present estimates for the elementary reaction of these species with molecular oxygen. While the toluene model that we demonstrate here is an improvement in terms of predictive ability at higher pressures, significant refinements remain to be made to achieve higher fidelity predictions. Finally, it should be mentioned that the approaches taken here were not developed for and will not be successful in simultaneously emulating physical or aerosol/particulate emission properties of gasolines. Further
considerations are necessary to provide appropriate chemical kinetic surrogate models to include these properties, a subject of present interest in our laboratory and elsewhere. Nonetheless, minimized/optimized models based upon a minimal number of components, such as the one shown here, can be utilized in 3-D CFD cylinder computations (e.g. [78]) and will remain valuable tools for engine designers.

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