Optimized chemical mechanism for combustion of gasoline surrogate fuels

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A B S T R A C T

Since real petroleum fuels are composed of a huge variety of hydrocarbon components, surrogate mixtures of various hydrocarbon fuels are typically employed in computational research and in engine development to represent transportation fuels. In this study, a reduced combustion mechanism of Primary Reference Fuel (PRF) mixtures (n-heptane and iso-octane) is integrated into the published kinetic model (Narayanaswamy et al., 2010), allowing for the formulation of multi-component surrogate fuels (e.g. PRF/toluene) and for the prediction of Polycyclic Aromatic Hydrocarbon (PAH) formation in gasoline engines. In order to optimize the model performance, a recently developed optimization technique based on rate rules (Cai and Pitsch, 2014) is extended in this study. The goal is to calibrate automatically the multi-component kinetic mechanism, which also leads to a chemically consistent PRF mechanism and a computational advantage for the calibration process. In addition, this work contributes to the development of general rate rules for various hydrocarbon fuels. An ethanol model is also incorporated into the proposed mechanism. This facilitates the prediction of gasoline/ethanol blend combustion. The resulting mechanism retains a compact size and is successfully validated against experimental measurements.

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1. Introduction

Despite the increasing interest in alternative biofuels, petroleum fuel remains dominant in the transport sector. Nowadays, computational fluid dynamics (CFD) calculations are often applied in engine design to deepen the understanding of the fuel combustion process, for which accurate reaction mechanisms form the backbone [1–3]. While several global properties of practical fuels, e.g. octane number and energy density, can be either experimentally determined or numerically calculated, the detailed combustion kinetics of fuels are highly sensitive to constituents and therefore very complex. Regarding this, surrogate mixtures composed of several hydrocarbon fuels are often used in CFD simulations to represent these real fuels [4]. For gasoline fuel, generally used in spark-ignition and homogeneous charge compression ignition (HCCI) engines, the Primary Reference Fuel mixture of n-heptane and iso-octane is often suggested as the surrogate mixture [5,6]. To account for aromatic compounds in petroleum fuel, ternary mixtures of n-heptane, iso-octane, and toluene can also be found in numerous published studies to represent gasoline [7–11]. A kinetic mechanism for these surrogate mixtures should on the one hand enable high-fidelity modeling of individual fuel components and should on the other hand reflect the combustion properties of surrogate mixtures and practical fuels correctly.

A variety of kinetic mechanisms for PRF and ternary mixtures are available in the literature [5,8,12–14]. Curran et al. developed detailed kinetic mechanisms for n-heptane [15] and iso-octane [5] oxidation. The combined PRF mechanism has been applied successfully in simulations of homogeneous compression ignition engines [16]. Due to the large number of chemical species and reactions found in the mechanism, several reduced mechanisms were published based on that detailed PRF mechanism [6,17]. A detailed kinetic model for toluene oxidation was derived by Pitz et al. [18], and chemical mechanisms of n-heptane/iso-octane/toluene mixtures were studied in various publications [8,19,20]. An interesting additive to surrogate mixtures is ethanol, with which the surrogate fuel can also describe gasoline/ethanol blends in spark ignition engines [21–24]. Cancino et al. [21] and Andrae [25] proposed chemical mechanisms including the combustion chemistry of n-heptane, iso-octane, toluene, and ethanol. However, as the chemical reactions of several fuel species are included in the mechanism, both mechanisms consist of more than one thousand species and four thousand reactions. Nevertheless, the detailed reaction chemistry for PAH and nitrogen oxides (NOx) formation, which is of great interest for engine simulations, is missing in the
mechanisms. In addition, only ignition delay times were considered as validation targets in these studies. A lumped reaction mechanism was developed by Dirrenberger et al. [23] for n-heptane, iso-octane, toluene, and ethanol as well. While the model shows excellent agreement with the measured burning velocities, the validation of ignition delay times is neglected in that study.

In general, a strong variation in constituents can be found for gasoline from various sources. This variation results in different physical and chemical characteristics of gasoline, which affects the formulation of surrogate mixtures. Recently, 1-pentene [12], 2-pentene [13] and di-isobutylene [25,26] were proposed as additional surrogate components to represent the unsaturated hydrocarbons in gasoline fuels and to minimize deviations of properties between gasoline and the surrogate mixtures. While the choice of the fourth component is highly sensitive to gasoline constituents, a ternary mixture of n-heptane, iso-octane, and toluene with an optimized blending ratio is generally able to represent gasoline with different compositions over a wide variety of conditions in CFD calculations, as demonstrated in the literature [27,28]. Therefore, these three surrogate components are considered in this study.

From the standpoint of experimental investigations, a large number of studies for gasoline surrogates can be found in the literature, including measurements of ignition delay times behind reflected shock waves [7,29,30] and in rapid compression machines [9,10], laminar burning velocities [6,31,32], and stable species profiles at different pressures from flow reactors [8] and jet stirred reactors [33].

An additional aspect of the kinetic mechanism development is the continuous refinement of the model accuracy. In the recent years, automatic optimization and uncertainty quantification (UQ) techniques have been successfully established for improving predictive accuracy of chemical schemes [34–37]. In cases of rate parameter optimizations described in the literature, rate parameters of individual reactions are usually systematically optimized to obtain good agreement between experiments and simulations. This can lead to inconsistencies in rate parameters of kinetically similar reactions. Recently, Cai and Pitsch [38] demonstrated a method to calibrate rate rules that determine reaction rates of kinetically similar reactions included in one reaction class instead of rates of single elementary reactions. This leads to a chemically more consistent model calibration. The methodology also reduces the number of active parameters and therefore enables optimization of low temperature auto-ignition, where a large number of reactions appears important. For the present study, the method is applied to calibrate the PRF kinetic mechanism, in which common rule rates are incorporated for n-heptane and iso-octane. Once the general rate rules are automatically calibrated, one would expect that both kinetic models are improved. So far, few studies have focused on the calibration of multi-component mechanisms, and the published studies have been carried out mainly for small species up to C₄H₆ [39,40]. This fact can be attributed to the large number of uncertain but sensitive rate parameters of elementary reactions found in mechanism optimization of large hydrocarbon fuels, which leads to an intractable computational cost. The computational cost will be minimized in this study by using optimization of rate rules rather than individual reactions [38]. This has the advantage that kinetically similar reactions are categorized into classes of reactions with assigned rate rules and that the number of rate rules considered in model development does not increase with the number of fuels in the mechanism. Moreover, the calibration in this study contributes to a refinement of the general rate rules that can be employed to construct hydrocarbon fuel mechanisms.

Nowadays, practical reaction mechanisms for engine design are supposed to model a wide range of hydrocarbon fuels, which are necessary components of transportation fuel surrogates, with a reasonable mechanism size for CFD simulation. In addition, there is a strong demand for reaction schemes of pollutant formation for emission prognosis and control.

The goal of this study is to propose an accurate and compact chemical mechanism for gasoline surrogate fuel (e.g. PRF/toluene/ethanol). The mechanism is developed in four steps: (a) The PRF and ethanol mechanisms are adopted from the published literature and added as modules on an existing thoroughly-validated model [41] for C₁₋₈ hydrocarbon fuels and substituted aromatic species, e.g. toluene, styrene, m-xylene, and 1-methylnaphthalene. This allows for the possibility to propose gasoline surrogate mixtures with various components and to correctly predict PAH formation as well as the further growth to soot particles in engine simulations. (b) For high prediction accuracy, the optimization technique based on rate rules [38] is applied to calibrate the rate rules, which have been employed to construct the multi-component chemical mechanism that is in this study the mechanism of n-heptane and iso-octane. The mechanism is optimized against ignition delay times of n-heptane, iso-octane, and their mixtures with varying initial compositions over a wide range of conditions. (c) In order to demonstrate the performance of the resulting mechanism, it is extensively tested for laminar flame speeds and jet stirred reactor data for binary PRF mixtures as well as flow reactor data and ignition delay times for ternary mixtures. Subsequently, the ethanol sub-model in the present mechanism is validated against the ignition delay times and the adiabatic burning velocities of ethanol and also the data of ethanol-blended fuels. A large experimental database is used to evaluate the model performance of the oxidation of neat fuels and surrogate blends. (d) Appropriate surrogate model formulations are investigated and discussed in this work.

The presentation of this paper is organized as follows. First, the optimization methodology based on rate rules is introduced. Next, the development of the PRF and ethanol mechanism is described in detail. Then, the proposed mechanism is subjected to the automatic calibration process, leading to an optimized and chemically consistent PRF mechanism. Following this, numerical results using the developed model are presented and compared with experimental data of n-heptane/iso-octane/toluene/ethanol mixtures. The paper closes with a short section to assess the surrogate formulation.

2. Methodology

Recently, Cai and Pitsch [38] extended the method by Sheen and Wang [36] for automatic calibration of chemical kinetic models by performing optimization of reaction rate rules. This methodology reduces the number of uncertain parameters by categorizing kinetically similar reactions into reaction classes. It therefore enables the optimization of cases where numerous reactions appear as important, as is the case for low temperature auto-ignition of large aliphatic fuels. A second advantage of this method is that rate rules can be simultaneously optimized for several different fuels and fuel mixtures, which leads to more consistent values for reaction rate coefficients of rate rule. This methodology is described briefly in the following section.

2.1. Reaction classes and rate rules

In the present model development procedure, a well-studied kinetic mechanism including C₄₋₈ chemistry is taken as the base mechanism to describe the oxidation of the small intermediate species generally produced in fuel combustion. Then, the fuel-specific chemistry is derived using prior knowledge of similar
molecules, and all possible reactions occurring in each oxidation step of the fuel are categorized as a class of reactions with the assigned rate constant expressions. A large amount of reaction mechanisms were recently built in this way for fuels of interest [5,15,42–47]. In the currently common approach, 30 reaction classes, listed in the supplementary material, are used to construct a chemical kinetic mechanism [43].

Reaction rate constants can be determined from quantum chemistry calculations [48–52] or experimental measurements [53–55]. However, while this is practical and even desirable for a small number of reactions, it is experimentally and computationally difficult to determine the rate constants of all involved reactions due to the large number of intermediate species and reactions. For the chemical reactions included in the reaction classes, where rate data are not available, rate rules are therefore used to specify their reaction rate coefficients. The use of rate rules has, besides the obvious purpose of treating reactions with unknown rate data, another interesting advantage, which is that rate rules can be consistently supplanted when reaction rates become available from calculation or experiment. This also implies that rate rules can be treated and optimized consistently during an optimization process.

The rate rules for the individual classes are generated based on available chemical kinetic knowledge [15,43]. Several rate rules can be found for one class (e.g. Class 15: RO_2 = QOOH) with respect to a broken C–H bond and a ring strain energy barrier. However, it can also be found that only one rate is employed for a class of reactions (e.g. Class 16: RO_2 = alkene + HO_2), if limited information of similar reaction types is provided in the literature. Detailed explanations of rate rules can be found in the Supplementary material. As reported by Cai and Pitsch [38], each rule is treated as a potential active parameter of the model optimization.

To provide a reliable model, the deviations between model and experiment are typically minimized by manually tuning the sensitive rate coefficients within their uncertainties [56]. Recently, the automatic optimization and uncertainty quantification (UQ) technology has been successfully applied to replace this manual tuning process [34–36]. The rate constants of elementary reactions are thus systematically and automatically optimized for good model performance. However, as previously described, the reaction rate constants of most derived reactions in a kinetic mechanism are specified using rate rules, and a rule can be used for few to dozens of reactions in a model. Therefore, in the common reaction class based way of mechanism construction, rate constants of reaction classes and rate rules should be modified, instead of individual reactions belonging to a reaction class. Calibrating a rate rule means that the rate constants of all reactions using this rule are optimized. Thus, kinetically similar reactions are treated equally to ensure model consistency.

2.2. MUM-PCE

The method of uncertainty minimization using polynomial chaos expansion MUM-PCE by Sheen and Wang [36] is used in Ref. [38] to optimize model performance and to estimate kinetic parameter uncertainties. The MUM-PCE approach provides the possibility to utilize the experimental results and their uncertainties for model calibration and uncertainty quantification. The framework employs the Solution Mapping and the model optimization method developed originally by Frenklach [34] to calibrate the normalized pre-exponential factors, third body efficiencies, and enthalpies of formation through the minimization of the deviations between model responses and measurements. For the subsequent uncertainty quantification, the kinetic parameters are expressed using a polynomial chaos expansion with the parameter uncertainties. By propagating the quantified uncertainties of rate parameters into the model response, model uncertainties can be minimized. A detailed description of the approach is available in the Supplementary material and in previous studies [36,38]. In this work, the Arrhenius pre-exponential factors of rate rules are chosen as the kinetic rate parameters to be calibrated.

3. Mechanism development

The kinetic model for PRF mixtures proposed in this study was adopted from the available published mechanism by Curran et al. [5], which includes the detailed oxidation chemistry of n-heptane and iso-octane and has been validated extensively for various experimental configurations. The mechanism [5] is composed of 1027 species and 8472 reactions (forward and backward counted separately). While one kinetic simulation with this mechanism can be conducted within a reasonable computational time, the automatic calibration process requires a huge amount of calculations. Therefore, to reduce the computational effort, the detailed mechanism was first reduced to a skeletal level using a multi-stage reduction strategy developed by Pepiot-Desjardins and Pitsch [59] applied similarly to the work of Narayanaswamy et al. [60]. The directed relation graph method with error propagation (DRGEP) [59] selects the important reaction pathways based on the production rate analysis of species. The lumping of chemical species presented in Ref. [59] was excluded, as the isomerization of intermediates was found to be important and thus, the involved rate coefficients are of particular importance for the model predictions. The targets considered in the reduction included concentrations of different major species at experimental conditions reported by Fieweger et al. [29], Ciezki and Adamietz [57] as well as Minneti et al. [58]. This reduction process, and specifically the error propagation algorithm, ensure that only those species and reactions are eliminated, which have a minimal effect on the chemistry of the reduction targets at the relevant conditions. Ignition delay times are not direct targets in the reduction procedure, but are inherently preserved by correctly predicting the chemistry of the target species. The computed results for ignition delay times using the detailed [5] and the reduced mechanisms are compared in the Supplementary material. Over the range of interest, the reduced mechanism is found to produce negligible changes in results. The maximum deviation is less than 5% and much smaller than the experimental uncertainties [29,57,58]. The reduction procedure is performed here to reduce the computational cost using this mechanism, while keeping the accuracy of the model predictions unchanged.

Similarly to our previous studies [4,38], the PRF model is built as an additional module that is combined with the well-validated model of Narayanaswamy et al. [41] for C_6–C_8 hydrocarbon species and various substituted aromatic species. The mechanism [41] was developed without manual tuning of the rate parameters and validated by comparing against available data for many different fuels to reveal the accuracies and inaccuracies of the model [4,41]. The inclusion of the reduced mechanism into the base mechanism [41] was accomplished using an interactive tool [61] that automatically identifies common species and reactions from different mechanisms. Rate conflicts detected during the merging were always resolved in favor of the rigorously validated base mechanism, therefore leaving that part of the mechanism virtually unchanged. It should be mentioned here that the mechanism from Narayanaswamy et al. [41] provides the chemical reactions for n-heptane and iso-octane oxidation as well. However, only the lumped high-temperature reactions were included in that mechanism. Therefore, these reactions are entirely replaced here by those in the reduced mechanism. The combined mechanism consists of 314 chemical species and 2327 elementary reactions (forward
and backward counted separately). The incremental part is mainly composed of the detailed reaction pathways of n-heptane and iso-octane as well as some reactions for small molecules not included in the mechanism of Narayanawamy et al. [41]. The original mechanisms from Curran et al. [5] were established based on the concept of reaction classes and rate rules. Hence, the mechanism developed here is using the same principle.

The kinetic model for ethanol oxidation used in this study was adopted from the well-validated ethanol mechanism of Li et al. [62]. The ethanol chemistry was integrated into the mechanism also using the interactive tool from Ref. [61]. A kinetic mechanism for nitrogen oxides formation was adopted from Lamoureux et al. [63] and also included in the proposed mechanism for engine simulation. Overall, 339 chemical species among 2791 reactions (forward and backward counted separately) are found in the mechanism after the incorporation of the ethanol and NOx chemistry. Compared with similar mechanisms in the literature [5,8,12–14,21], the present mechanism includes a wide variety of alternative surrogate components and substituted aromatic species, but still retains a compact size.

The rate rules for n-heptane and iso-octane were tuned in Curran et al. [15] and Curran et al. [5], respectively to match the experimental targets, and the values for the rate rules for these mechanisms differ from each other. Still, it is desirable to have general rate rules to be determined at least for species with the same functional groups rather than for only one particular fuel. Therefore, the reaction rates for all reaction classes in the present mechanism were updated based on the revised rate rules proposed by Sarathy et al. [43] for 2-methylalkanes and alkane. Villano et al. [64,65] recently investigated the rates of reactions involving butyl peroxy and hydroperoxy butyl radicals, and suggested these as rate rules for large hydrocarbon fuels. However, in order to use these rates as rate rules for n-heptane and iso-octane, adjustment of other rate rules may be required for consistency. On the other hand, the rate rules from Ref. [43] have been successfully applied to construct a variety of chemical models [43–46] and hence employed in this study. The numerical results of the updated mechanism are shown in Figs. 1 and 2, with those of the detailed mechanism [5] and the experimental data from Ciezki and Adomeit [57], Fieweger et al. [29] as well as Minetti et al. [58]. It can be seen that this alteration of rate rules slightly improves the prediction of ignition delay times of n-heptane/air mixtures, while significant prediction improvements can be observed for iso-octane oxidation at varying initial temperatures, pressures, and equivalence ratios, especially at low temperatures. This can be attributed to the differences in the C0–C4 base chemistry [41] and the well-studied rate rules from Ref. [43]. The reaction pathways of n-heptane and iso-octane simulated using the detailed mechanism [5] and the developed mechanism with rate rules from Ref. [43] are presented and discussed in the Supplementary material for conditions of interest.

4. Computational details

In this work, the rate rules that show the highest optimization potential in the range of experimental conditions were chosen as the uncertain parameters. The optimization potential of a rate rule [38] is defined as the product of its sensitivity and uncertainty factor. A similar definition applied to elementary reactions can be found in Refs. [66,67]. For each experimental condition considered in the calibration, a sensitivity analysis of rate rules was carried out. The sensitivity, combined with uncertainty factors, indicates the contribution of the uncertainty of a rule to the uncertainty in the model prediction. A rate rule with a large sensitivity could lead to a marginal model uncertainty, if the rate uncertainty is small.

In general, two sources of uncertainty can be found for rate rules. First, uncertainties can come from the numerical or experimental estimation of the rate constants of individual reactions. Second, uncertainties can also be introduced by taking such estimated rates as rate rule for similar reactions [38]. In this study, the uncertainty factors of the reaction rate rules were assumed equal to four, as no literature values were found and large uncertainties are expected [38].

The calibration of the rate rules in the PRF mechanism is performed using the experimental data from Refs. [29,57,58] in this study. In actual, the calibration should be applied to the entire mechanism, so it should include the base mechanism, and it should be done with the complete set of experiments (>2000) for all eighteen fuels for which the base mechanism was validated in Refs. [4,41] into the calibration process plus the experimental data for the PRF fuels. This, however, is computationally intractable. Furthermore, one can expect that the base mechanism would not change in this optimization as a result of the constraints imposed by the experimental data for n-heptane, iso-octane and their mixtures [29,57,58] used in the present study. The reason is that the base mechanism would be constrained by many more experiments, which are those used in Refs. [4,41]. Therefore, both the base mechanism [41] and the validation experiments from Refs. [4,41] were not included in the optimization, leaving the accuracy of model prediction for C1–C4 species and substituted aromatic species unchanged. Note that the results for the PRF cases are found to have very low sensitivity to the reactions of the ethanol sub-mechanism because of the small amount of ethanol in the gasoline/ethanol mixtures. Therefore, these reactions also do not appear in the optimization.

The numerical calculations in this study were performed using appropriate reactor modules in the open source FlameMaster code [68].

5. Mechanism calibration

The chemistry model developed in Section 3 was calibrated automatically using the methods described in the previous
sections. The flame speeds of hydrocarbon species are highly sensitive to the reactions involving small molecules as reported in numerous studies [69,70]. Therefore, we focus on the ignition of PRF mixtures in the calibration process, for which the fuel specific pathways are dominant.

Two different calibrations each considering a different experimental data set, were conducted in this study to the unoptimized mechanism. An optimized mechanism Modelp was generated in the calibration with the experimental data of n-heptane [57,58], iso-octane [29], and PRF/air mixtures [29]. This calibration process utilized the complete available experimental data set to fully constrain the uncertainties of rate rules and further to minimize the model prediction uncertainty. A second version of a calibrated model, optimized Modelp, the comparison of the results and uncertainties of both calibrated models provides some information in how far all information about high, intermediate, and low temperature auto-ignition of neat n-heptane and iso-octane is included in the data for the mixtures.

5.1. Computational advantage

In this section, the computational advantages obtained by using optimization of rate rules rather than individual reactions are highlighted. The method reduces the number of active parameters by categorizing chemically similar reactions into one class, which is mandatory to save the calibration effort [38]. Further computational advantage is expected when applying this method to calibrate the multi-component mechanism, as in contrast to the number of reactions, the number of rate rules does not increase with the number of fuels included in the mechanism.

Fieweger et al. [29] reported auto-ignition delay times of homogeneous PRF mixtures with octane numbers (ON) of 60, 80, and 90, where the octane number is defined as the percentage of iso-octane by liquid volume in an n-heptane/iso-octane mixture. Hence, ON = 0 corresponds to pure n-heptane and ON = 100 corresponds to pure iso-octane. Ignition delay times were measured for stoichiometric mixtures and at pressures of 13.5 and 40 bar. These data were considered in the calibration processes.

Sensitivity analyses were performed to identify the important reaction rate rules for the calibration process. Rate rules that show high sensitivity (>2%) at the experimental conditions were selected for the optimization. As summarized in Table 1, 18 rate rules were chosen for calibration for the ignition delay time of a stoichiometric PRF 60 (ON = 60) mixture measured at a pressure of 40 bar and an initial temperature of 831 K, at which both the chain branching and chain breaking channels of fuel radicals play an important role. Additionally, the sensitivity analyses for n-heptane and iso-octane auto-ignition were carried out for conditions at which measurements were reported. To compare the method of optimizing rate rules to the traditional calibration of elementary reactions, sensitivity analyses were performed also with respect to elementary reactions for these cases. A threshold of 2% was also employed in these analyses to select the important reactions.

It is clearly shown in Table 1 that the numbers of sensitive rate rules that need to be considered in the calibration are similar for all cases. For these cases, the chosen rate rules are mainly identical, and include the primary and secondary H-abstraction by OH and HO₂ radicals, the fuel radical decomposition, the isomerization of alky1 peroxy radicals to form hydroperoxides through a secondary H-atom transition involving 5-, 6-, and 7-membered rings, the decomposition of hydroperoxides to yield cyclic ethers as well as the decomposition of peroxy alkylhydroperoxide radicals and keto-hydroperoxides. For iso-octane and PRF mixtures oxidation, the abstraction of ternary H atom is also of great importance. These reaction classes are generally the rate-controlling reaction steps in aliphatic hydrocarbon oxidation.

On the contrary, the number of uncertain objects increases significantly, when elementary reactions are subjected to calibration. While 17 and 25 chemical reactions are important for n-heptane model calibration at the considered conditions, 29 and 29 reactions are found to be important for the ignition delay times of iso-octane in sensitivity analyses, as the non-symmetric branched alkanes have more complex reaction pathways than the symmetric normal alkanes [5]. Furthermore, the ignition of n-heptane and iso-octane at very low temperatures requires calibration with a smaller number of uncertain parameters due to the increased ratio of chain branching to chain breaking pathways. With a decrease in temperature, decomposition channel of the fuel radical is inhibited, and only the low temperature oxidation channel is active. For PRF 60 mixture, the kinetics of n-heptane and iso-octane both are of particular importance. Therefore, the sensitivity analysis selects more elementary reactions for calibration.

Regarding the reduced number of active parameters, the optimization methodology based on rate rules enables a calibration

![Fig. 2. Ignition delay times of iso-octane/air mixtures. Symbols denote the experimental measurements by Fieweger et al. [29]. Solid lines show the numerical results for the model developed in Section 3 and dashed lines show results using the detailed model [5].](image-url)
process with improved computational cost by categorizing the chemically similar and sensitive reactions into one class. This benefit is further advanced in this study for the case of calibrating the multi-component mechanism. For the PRF mixtures, both \( n \)-heptane and iso-octane kinetics are important, and thus an increased number of sensitive reactions should be considered in the conventional calibration based on elementary reactions. However, this is not the case for rate rules. Even though a variety of elementary reactions are important here for PRF mixture combustion, the oxidation chemistry of normal and branched alkanes consists essentially of identical reaction steps at similar experimental conditions. Therefore, the number of uncertain rate rules remains unchanged, when the oxidation of binary fuel blends is investigated instead of neat fuel ignition.

5.2. Calibration and uncertainty quantification

As mentioned earlier, two calibrations were performed in this study in order to assess the improvement gained with the full experimental data set. While only the PRF mixture data [29] were considered in the partially constrained calibration, the fully constrained calibration included in addition experimental ignition delay times of \( n \)-heptane [57,58] and iso-octane [29]. Overall, 24 and 93 experiments were considered in the partially and fully constrained optimization processes, respectively. The measurements span a wide range of experimental conditions. Filtering of experiments [36] was not performed in this work. All measurements were regarded as equally important. Uncertainty estimates of ignition delays were lacking in these studies [29,57,58]. Instead, a pressure uncertainty of \( \pm 2 \) bar was reported in Ref. [57] for auto-ignition at 40 bar, which corresponded to a 2σ deviation of approximately 10% in ignition delays. This value was hence used in the calibration. The MUMPCE framework calibrates the pre-exponential factors through the minimization of the deviations between model responses and measurements. By propagating the quantified uncertainties of rate parameters into the model response, model uncertainties can be minimized.

The numerical results of ignition delay times with the predicted uncertainties obtained using the optimized mechanisms are compared with experiments in Fig. 3. The figure shows that the model uncertainties are efficiently minimized through the automatic calibration. While the unoptimized model shows large model uncertainties and fails to predict the experiments very accurately, the optimized models give satisfactory results under all conditions with a reasonable prediction uncertainty. The nominal predictions for ignition delay times using the unoptimized and optimized models are shown in the Supplementary material. Interestingly, both optimized models give almost identical results. In comparison with the partially constrained calibration process, more experimental data were considered in the calibration process with the full data set. Even though this extension of the data set does not further improve the accuracy of nominal model prediction, the increased number of experimental constraints leads to a further uncertainty minimization of the Model\( _{e} \), as seen in Fig. 3. In addition, the Model\( _{e} \) gives better agreement with experimental data for \( n \)-heptane and iso-octane ignition, as these data have been included in its calibration. Therefore, Model\( _{e} \) is the basis for the discussions in the remainder of the article.

The slight deviations at low temperatures for PRF 60 oxidation appear as outliers here and indicate the possibility of experimental uncertainties larger than those reported [29]. Note that the prediction uncertainties of the unoptimized mechanism at high temperatures are comparably smaller than those in the low and intermediate temperature regime. Since less reactions are found to be sensitive at high temperatures, a small number of rate uncertainties contributes to the overall model error.

5.3. Model performance of single component

The experimental ignition delays of \( n \)-heptane [57,58] and iso-octane [29] were also included in the calibration procedure to improve the model precision. The data sets include \( n \)-heptane ignition at 3, 13.5, and 42 bar as well as iso-octane ignition at 13 and 40 bar with equivalence ratios of 0.5, 1.0, and 2.0.

Figs. 4 and 5 depict the computed results using the unoptimized and the calibrated mechanisms compared with the experimental observations [29,57,58]. The calibration process results in a significant improvement of the prediction accuracy. For the case of \( n \)-heptane auto-ignition, the optimized Model\( _{e} \) shows a prediction advantage over the unoptimized model for a wide range of temperatures, pressures, and equivalence ratios, especially in the high temperature regime. These prediction improvements at high temperatures are mainly due to an increased value for the rate rule of \( H \) abstraction from secondary carbon sites of fuel by HO\(_2\) radicals. For iso-octane, while the deviations between experiments and measurements at low to intermediate temperatures are well minimized, the excellent agreement in the high temperature range remains unchanged after calibration. The optimized model accurately predicts the ignition delay times with an average deviation smaller than 5% and correctly reflects the influence of pressure and equivalence ratio on the ignition propensity. A comparison between the detailed mechanism from Curran et al. [5] and the optimized mechanism is shown in the Supplementary material. Over the entire range numerically investigated, the optimized model reproduces ignition delay times with a higher prediction precision. The automatic calibration framework [38] demonstrates the capability to improve the model accuracy of the multi-component mechanism by calibrating the common rate rules incorporated in \( n \)-heptane and iso-octane chemistry. The optimized PRF model will be further validated in the following sections.

5.4. Rate rules

47 rate rules have been considered in the optimization process. Detailed information about the optimized rate parameters and their uncertainties are shown in Table 2. The calibrated reaction classes contain the fuel decomposition (C1), the \( H \)-abstraction from fuel to form alkyl radicals (C2), the decomposition (C3), the isomerization (C4), and the oxidation (C11) of fuel radicals, the alkyl peroxy radical RO\(_2\) isomerization (C15), the oxidation of hydroperoxides QOOH (C26), the isomerization of peroxy hydroperoxides O\(_2\)QOOH (C27), and the decomposition of carboxylic hydroperoxides (C28). These classes represent the main consumption channels of fuel in different temperature regimes. The reaction classes 12–14 of alkyl radicals proceed through a chemically activated ROOR' adduct to yield RO, where R' is H, CH\(_3\), or alkyl radicals. These steps compete with the fuel radical oxidation at low temperatures and the fuel radical decomposition at high temperatures, respectively. While the 13th reaction class produces an \( OH \) radical and completes a chain propagation, classes 12 and 14 result in a chain termination and prolong the ignition process. In a similar way, the alternative consumption channels of RO\(_2\) (C20) and QOOH (C23) as well as the reactions of cyclic ethers with OH radicals (C29) enhance ignition delays. All these rate-controlling steps have been considered in the automatic calibration.

As shown in Table 2, the rate constants of a few rate rules remain near their mean values, while the rates of several rules approach their uncertainty limits, which indicates the minor confidence of their prior estimates. Curran et al. [5,15] prescribed the rate constant for the decomposition of hydroperoxides to form cyclic ethers and \( OH \) radicals (C23), following the recommendation of Pollard [71], in which the activation energy depends on the ring size of the formed cyclic ethers. These studies [5,15] considered
four ring sizes of cyclic ethers and thus proposed four rate rules for this class. The pre-exponential factors of rate rules were reduced by factors of 12 and 8 for \(n\)-heptane and iso-octane, respectively. The rates for iso-octane were further adopted by Sarathy et al. [43] for 2-methylalkanes and taken as prior rate rules in this study. In the calibration process, the rate rules for cyclic ethers with 4- and 5-membered rings are identified as important by the sensitivity analyses and therefore automatically calibrated. While marginal alteration is suggested by the calibration framework to the pre-exponential factor for the formation of cyclic ethers with
5-membered rings, the rate to yield 4-membered ring ethers is decreased by a factor of four. More importantly, common rate rules are determined by the calibration process and proven to work well for both n-heptane and iso-octane oxidation. Similar observations can be found for several reaction classes, e.g. classes 2 and 15. While different rate rules were prescribed for the same reaction class of n-heptane and iso-octane in the literature [5,15], common rate rules, which have been optimized automatically in the calibration process, demonstrate the capability to improve model performance.
In general, numerical and experimental studies are conducted on the rate parameters of elementary reactions. These well-estimated reaction constants with uncertainty factors of 3 \sim 5 [72,73] are taken as rate constants for similar reactions and thus as rate rules. In this study, the optimization methodology calibrates rate rules automatically. The model with the calibrated common rate rules appears satisfactory for various data sets of normal heptane and branched octane. This provides a novel possibility to determine accurate and coupled general rate rules for the model construction of hydrocarbon fuels. More common rate rules for alkane fuels can be determined by including a large number of normal and branched alkanes in one calibration process.

Nowadays, two sources of chemical inconsistency can be found in the hierarchical model construction method [5,15,74]. First, as discussed in our previous study [38], inconsistency can come from the modification of rates of individual elementary reactions, for which the same rate rules are used. It can also be introduced by using different rate rules for identical reaction classes of similar fuels, as is the case for the n-heptane and iso-octane mechanisms [5,15]. In this study, both kinds of inconsistency are removed in chemical mechanisms.

6. Validation of PRF mixtures

6.1. Laminar flame speeds

As mentioned earlier, burning velocities were not included in the calibration process, as their prediction is strongly influenced by the reactions involving small molecules. Nevertheless, they are still of great interest in engine research, especially for spark-ignition engines. Therefore, the model performance for flame speeds of PRF mixtures is evaluated in this section. The optimized PRF mechanism is validated against laminar burning velocities measured at various initial conditions.

The laminar flame speeds of PRF 90 (RON = 90) were measured by Huang et al. [31] at an initial temperature of 298 K and ambient pressure. At the similar pressure, Bradley et al. [32] reported experimental data at a higher initial temperature of 358 K. As shown in Fig. 6, the mechanism performs well in these premixed flame environments. Particularly interesting is the fact that the computed results with the optimized mechanism are in very good agreement with the experimental data, even though these experimental burning velocities are not considered in the calibration. The reason lies in the rigorously validated base mechanism from Ref. [41]. This again provides justification for the exemption of the base chemistry from the calibration processes.

PRF 87 and standard gasoline with an octane number of 90 were investigated by Jezembeck et al. [6] at a mixture temperature of 373 K and at engine relevant high pressures. The numerical results using the present mechanism are compared with the experimental data in Fig. 7. It is observed that the burning velocities of PRF 87/air mixtures and for gasoline/air mixtures are well predicted by the optimized model at all conditions. The underprediction of burning velocities at rich conditions at high pressures can be found also in previous studies [6,75] and might be attributed to larger experimental uncertainties, for instance, due to the possible occurrence of flame instabilities and the development of wrinkles for rich mixtures in the experiments as reported by Jezembeck et al. [6]. These issues make the flame analysis difficult, leading to large experimental uncertainties. In addition, the reason could also be the pressure-dependence of several elementary reactions in the H2/O2 chemistry [76] as discussed in Ref. [75].

6.2. Jet stirred reactor data

Dagaut et al. [33] studied experimentally the oxidation of n-heptane and iso-octane mixtures in a high-pressure jet-stirred reactor for a wide range of conditions covering low and high temperatures. The error in the carbon balance for the experiments was reported to be within less than 10%. The numerical results for species profiles are shown in Fig. 8 together with the experiments for the stoichiometric PRF 90 mixtures at 10 atm and with a residence time of 1 s. Cool flame and NTC regime are observed below 750 K in both simulation and experiment. Again, the present model predicts the kinetic targets quite well, and the deviations between model and experiment shown in Fig. 8 are within the experimental uncertainties reported in Ref. [33].

7. Validation of ternary mixtures

Ternary mixtures of n-heptane, iso-octane, and toluene are often used as gasoline surrogate [7,11,77]. Numerous studies have demonstrated the successful application of this ternary surrogate model in CFD calculations of gasoline engines [27,28]. The present model is developed as a module within the well-validated model of Narayanaswamy et al. [41] for oxidation of substituted aromatic species, which includes a detailed validation also for toluene. This allows the consistent formulation of a PRF/toluene surrogate using the present mechanism. In this section, the mechanism performance for combustion of the ternary mixtures in various experimental configurations is explored, which also benefits the assessment of the calibrated rate rules in the PRF mechanism.

7.1. Ignition delay times

For the validation of the present mechanism for ternary mixture oxidation, the shock tube data by Gauthier et al. [7] are used first. These data have been reported for two ternary mixtures, referred to as Surrogate A (n-heptane/iso-octane/toluene – 17%/56%/28% by mole fraction) and B (17%/63%/20%). For both surrogates, an average octane number of 87 is reported. The average octane number is determined by the average of the research octane number (RON) and the motor octane number (MON). The ignition delay times of stoichiometric ternary surrogates/air mixtures at pressures of 20 and 55 atm are shown in Figs. 9 and 10. In addition, the “customer average” regular-grade reformulated gasoline RD387 with an average octane number of 87 has been also experimentally investigated in Ref. [7]. It can be observed in Figs. 9 and 10 that the proposed model predicts the experimental data fairly well at the higher pressure of 55 atm, while the experimental
observations are slightly lower than the computed values at 20 atm.

Numerical and experimental ignition delay times of Surrogate A at 20 atm and with EGR rates of 20% and 30% from Gauthier et al. [7] are shown in Fig. 11. As reported in Ref. [7], the EGR rate is defined as the mole fraction of the exhaust gas in the fuel/air/exhaust gas mixtures, where distilled water was used as the exhaust gas. For both EGR rates, the optimized model demonstrates the capability to predict the validation targets satisfactorily.

The ignition delay times of Surrogate A have also been experimentally investigated by Kukkadapu et al. [10] at intermediate to low temperatures in a rapid compression machine. These experimental data are compared with the present model in Fig. 12. For both relevant pressures, the model developed in this study again gives satisfactory results for a variety of initial temperatures. Note that the ignition delay times computed with the present chemical mechanism in a homogeneous adiabatic isochoric reactor are slightly shorter than those reported in Ref. [10] at several temperatures. As heat loss effects are observed in the rapid compression machine, the measured ignition delay times are larger than their actual values, especially in the low temperature range, where induction times are long. The heat loss effects can be taken into account for simulations when the pressure profiles of non-reactive mixtures at these experimental conditions become available [10].

Auto-ignition of toluene-doped n-heptane/air and iso-octane/air mixtures has been experimentally investigated in a high
pressure shock tube by Hartmann et al. [30]. Experimental ignition delay times of lean and stoichiometric \( n \)-heptane/toluene mixtures with the blending ratios by liquid volume of 90/10 and 60/40 as well as iso-octane/toluene mixture with a mixing ratio of 90/10 have been reported at a pressure of 40 bar. Data are shown in Fig. 13 compared with the numerical results. Excellent agreement between simulations and experiments is again observed.

7.2. Flow reactor data

In addition, the flow reactor data by Chaos et al. [8] are used in this study to validate the present mechanism for ternary mixture oxidation. The profiles of stable species shown in Fig. 14 were measured in a variable pressure flow reactor for a stoichiometric ternary mixture (\( n \)-heptane/iso-octane/toluene – 18.23%/66.42%/15.35% by liquid volume) at 12.5 atm with a residence time of 1.8 s and 740 ppm initial fuel fraction. While the model slightly underpredicts the oxygen mole fraction at low temperatures, it predicts species concentrations at higher temperatures quite accurately.

7.3. Laminar flame speeds

The adiabatic flame speeds of a commercial gasoline TAE7000 with a research octane number of 95.6 have been measured at atmospheric pressure and a temperature of 358 K by Dirrenberger et al. [23]. To represent the commercial TAE 7000, an \( n \)-heptane/iso-octane/toluene blend with the liquid volume fraction of 13.7%/42.9%/43.4% has been proposed as the surrogate mixture, and its laminar burning velocities have also been experimentally investigated at the same condition [23].

These experimental data are presented in Fig. 15 with the computed flame speeds of the surrogate mixture. It can be seen that the measured results of the surrogate mixture agree well with those measured for TAE7000. The numerical flame speeds are in excellent agreement with the experimental determined velocities. Overall, the model proposed in this study is found to predict the combustion of ternary mixtures with a very good accuracy.

8. Gasoline/ethanol combustion

Ethanol is often used as an additive to gasoline. An ethanol addition up to 15% can be applied in conventional compression-ignition engines without the need for extensive engine modifications. Its higher octane number and oxygenated molecular structure could result in improved fuel efficiency and reduced pollutant emissions from engines. An ethanol sub-model is incorporated into the proposed mechanism, and its validation is given in this section. For the sake of brevity, the ignition delay times and the adiabatic burning velocities of ethanol are considered in the Supplementary material. The model is validated here against the data of ethanol-blended fuels.

Fikri et al. [24] and Cancino et al. [21] have experimentally determined the ignition delay times of \( n \)-heptane/iso-octane/ethanol and \( n \)-heptane/iso-octane/toluene/ethanol blends, respectively. These results are shown in Figs. 16 and 17, along with the detailed information about the mixture compositions by liquid volume and the studied conditions. As shown in Fig. 16, the model gives satis-

![Fig. 10. Ignition delay times for surrogate mixtures and gasoline oxidation at 55 atm and \( \phi = 1.0 \). Symbols denote the experimental measurements by Gauthier et al. [7]. Lines show the numerical results for the present model.](image)

![Fig. 11. Ignition delay times for surrogate A oxidation at 20 atm and \( \phi = 1.0 \). Symbols denote the experimental measurements by Gauthier et al. [7]. Solid lines show the numerical results for the present model.](image)

![Fig. 12. Ignition delay times for surrogate A oxidation at 20 atm and \( \phi = 1.0 \). Symbols denote the experimental measurements by Kukkadapu et al. [10]. Solid lines show the numerical results for the present model.](image)
factory results for the n-heptane/iso-octane/ethanol mixture covering the entire range of initial temperatures for pressures of 30 and 50 bar. For the quaternary mixtures, ignition delay times are slightly overestimated in the low temperature range at 30 bar, while the agreement between measurements and simulations remains favorable at higher pressure.

Laminar flame speeds have been reported by Dirrenberger et al. [23] for mixtures of 15 vol% ethanol with the commercial gasoline TAE7000 and its surrogate. These data have been experimentally investigated at 1 atm and 358 K, and a blend of n-heptane/iso-octane (18.23%/66.42%/15.35% by liquid volume) has been employed as the surrogate for TAE7000. The numerical results using the present model are compared with the experimental measurements in Fig. 18. Over the entire domain of equivalence ratios, excellent agreement can be observed between experiments and calculations.
9. Surrogate fuel formulation

Different surrogates have been suggested for petroleum fuels with a trend to a representation of real fuels with increasing numbers of chemical species [80]. These species can well represent various groups of chemical species in gasoline, e.g. normal and branched alkanes, olefins, as well as aromatics. Their mixtures are supposed to emulate gasoline combustion behavior accurately over a range of interest. However, concerning the computational effort in CFD calculations, surrogate models with a small number of chemical species become more attractive. While reduction techniques can be applied to reduce mechanism sizes, the magnitudes of mechanisms remain large, if reaction kinetics of several surrogate components have to be included in the model. In this section, it will be explored whether and how much the number of fuel components in the surrogate model affects the global combustion properties, e.g. ignition delay times. For this purpose, four surrogate mixtures are assessed here. The first is neat iso-octane as a single-component surrogate model. Next, the PRF 87 mixture and the Surrogate A (with an average octane number of 87) proposed by Gauthier et al. [7] are considered as two- and three-component surrogates. The properties and the compositions of these surrogate mixtures are summarized in Table 3 with those of gasoline RD387.

It can be seen in Table 3 that the averaged octane numbers of PRF 87 and Surrogate A match the one of RD387, while disagreements of RON and MON are observed. In recent studies [28,78,79], the octane index (OI) has been employed to describe the gasoline quality with emphasis on the anti-knock behavior. The OI is defined as

\[
\text{OI} = (1 - K) \times \text{RON} + K \times \text{MON},
\]

where \( K \) is a constant depending on the engine design and the operating condition. Compared with the conventional RON and MON, the octane index takes the engine design and condition into account and correlates well with anti-knock quality [78]. In order to match the OI of gasoline regardless of the engine design, surrogate mixtures are required to reproduce both MON and RON of gasoline accurately. Also Morgan et al. [27] have emphasized the necessity of surrogate models to match not only the RON, but also the MON of gasoline. Here, a new ternary surrogate mixture for RD387 is proposed to match both RON and MON and consequently also the octane index.

The RON and MON of the surrogate mixture are determined using the modified second order linear-by-volume model by Morgan et al. [27] for arbitrary mixtures of \( n \)-heptane, iso-octane, and toluene. A global optimization of the mixture composition is performed by considering RON, MON, and H/C ratio as targets. The optimization results are summarized in Table 3.

Particularly interesting is the direct determination of the surrogate composition for a set of gasoline properties, e.g. RON, MON, and H/C ratio. Morgan et al. [27] inverted their second order model to numerically solve this problem for given RON and MON. For a further simplification, a model is developed here to enable the analytical calculation of fuel composition for specified properties.

\[
\text{Toluene \ [\text{vol\%}] = 1.9528 \times \text{RON} + 1.2987 \times \text{MON} - 5.3703}
\]
\[\times \text{HC} - 0.0101 \times \text{RON} \times \text{MON} - 0.9047 \times \text{RON} \times \text{HC} - 0.1244 \times \text{MON} \times \text{HC} \]  
\text{(1)}

\[
\text{n-Heptane \ [\text{vol\%}] = -0.3592 \times \text{RON} + 1.9130 \times \text{MON} + 37.8896 \times \text{HC} - 0.0097 \times \text{RON} \times \text{MON} + 0.2760 \times \text{RON} \times \text{HC} - 0.9815 \times \text{MON} \times \text{HC} \]  
\text{(2)}

\[
\text{iso-Octane \ [\text{vol\%}] = 1 - (\text{Toluene} + \text{n-Heptane}) \ [\text{vol\%}] \]  
\text{(3)}

In comparison to the model of Morgan et al. [27], H/C ratio is also considered in this response surface model, in addition to RON and MON. The model coefficients are fitted against the data of ternary mixtures reported in the literature [27,81–86] using the least-squares method. Based on RON, MON and H/C ratio of the optimized surrogate fuel in this study, the surrogate composition calculated with Eqs. (1)–(3) is in good agreement with the composition of the optimized surrogate summarized in Table 3. Note that the mixture composition is slightly changed by directly inserting RON, MON and H/C ratio of RD387 into Eqs. (1)–(3). This can be attributed to that the response surface model is fitted to the data of ternary mixtures instead of gasoline fuels.

Fig. 19 depicts the ignition delay times computed using the four surrogate models in comparison with measured data for gasoline RD387 by Gauthier et al. [7] and by Kukkadapu et al. [9]. The experimental results by Kukkadapu et al. [10] for Surrogate A are also shown in Fig. 19. Except the single-component model, the three multi-component surrogates predict the ignition delay times with a very similar accuracy. Identical numerical results are observed at low to intermediate temperatures. The increased toluene portion in surrogate mixtures decelerates the ignition of ternary mixtures slightly in the high temperature range. Pronounced differences are revealed between iso-octane and the multi-component surrogates at intermediate temperatures. Note again that the ignition delay times computed with the present chemical mechanism are slightly shorter than those reported in the rapid compression machine [9,10] at several temperatures, as the heat loss effect in combustion chamber enlarges the experimentally determined ignition delay time.

Overall, the addition of toluene into the PRF surrogate model is found to produce negligible changes in the numerical ignition delays, while the application of iso-octane as gasoline surrogate is questionable. It should be mentioned here that the choice of the surrogate components and their number is also highly sensitive to their application in CFD calculations and the engine design. Even though the three multi-component surrogate mixtures have identical average octane numbers, the surrogate mixture proposed in this study shows the advantage of also matching the octane index. This indicates a successful application of the surrogate model in CFD calculations as demonstrated for instance in Ref. [27].
Tables of surrogate mixtures.

| Property            | RD387 [7,9] | iso-Octane | PRF 87 | Surrogate A | This study |
|---------------------|-------------|------------|--------|-------------|------------|
| RON                 | 91          | 100        | 87     | 88.8        | 90.5       |
| MON                 | 83          | 100        | 87     | 84.8        | 83.4       |
| Average ON          | 87          | 100        | 87     | 86.8        | 86.95      |
| H/C ratio           | 1.86        | 2.25       | 2.26   | 1.97        | 1.75       |
| iso-Heptane [vol%]  | 0           | 100        | 13     | 17          | 19.4       |
| Toluene [vol%]      | 0           | 100        | 87     | 63          | 42.2       |
|                     |             |            |        | 20          | 38.3       |

10. Concluding remarks

In this study, an optimized chemical mechanism for combustion of gasoline surrogates was developed. The n-heptane and iso-octane sub-mechanisms were calibrated automatically considering ignition delay times of n-heptane, iso-octane, and their mixtures. The entire mechanism was validated extensively against ignition delay times, burning velocities, and jet stirred reactor and flow reactor data of pure fuels, binary, ternary, and quaternary mixtures of n-heptane, iso-octane, toluene, and ethanol for a large range of relevant conditions. Very good agreement was observed between experimental measurements and numerical calculations. The proposed mechanism is well suitable for CFD simulations concerning its compact model size, while it still includes the detailed oxidation pathways of fuels, which enables a comprehensive kinetic analysis. The present model was built as an additional module of a well-validated mechanism for oxidation of C1–C8 hydrocarbon fuels and substituted aromatic species with emphasis on soot precursors. This allows the prediction of PAH and further soot formation, which is of relevance for direct-injected gasoline engine simulations. In addition, appropriate surrogate model formulations were briefly discussed in this work.

Another key focus in the present study is the automatic calibration of the common rate rules incorporated in the combustion chemistry of n-heptane and iso-octane. The recently developed optimization methodology for rate rules [38] based on the methods of Frenklach [34] and Sheen and Wang [36] was successfully applied to calibrate the binary PRF mechanism with an improved calibration effort, and the automatically calibrated common rate rules were shown to give satisfactory numerical results for n-heptane, iso-octane, and their mixtures covering a variety of experimental configurations. This provides the possibility to construct detailed chemical mechanisms with general rate rules for various hydrocarbon fuels.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.combustflame.2014.11.018.

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