Title:

Development and validation of a reduced reaction mechanism with a focus on diesel fuel
/ syngas co-oxidation

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Abstract

A reduced reaction mechanism has been developed for modeling Reactivity Controlled Compression Ignition (RCCI) engine combustion with diesel fuel and syngas. Employing n-heptane as a single representative chemical surrogate for diesel fuel, a comprehensive mechanism was reduced such that the reaction mechanism of syngas oxidation is included as a sub-mechanism with emphasis on the interaction of oxidation reaction pathways of syngas and n-heptane. Important reaction pathways to be kept in the reduced mechanism to maintain the performance of the detailed mechanism were identified through ignition delay curve sensitivity analysis. In addition, reaction steps to which ignition delays of multi-fuel blends are sensitive were identified and the importance of predictability of co-oxidation of multi-fuels in the mechanism reduction process was demonstrated.

The reduced mechanism, with 81 species and 312 reactions, was validated against experimental ignition delay times available in the literature. The reduced mechanism was also applied to simulate diesel-syngas RCCI engine combustion, employing a multi-component surrogate model to accurately model the physical properties of diesel fuel sprays. Predicted pressure and heat release rate results were compared with engine experimental data and good agreement was observed. The present reduced mechanism gave reliable performance for combustion predictions of RCCI engine operation to help further the fundamental understanding of the process occurring in reformed-fuel RCCI combustion and increase the computational efficiency of multi-dimensional computational fluid dynamics simulations. The reaction mechanism development outlined highlights the importance of considering co-oxidation in generation of reduced reaction mechanisms for applications to dual-fuel combustion.

Key words: reactivity controlled compression ignition, reaction mechanism, autoignition, co-oxidation, multi-fuel, surrogates.

1. Introduction

Premixed charge compression ignition (PCCI) combustion strategies are an attractive advanced combustion technique to simultaneously achieve emissions reduction and combustion controllability. Particulate matter (PM) emissions can be reduced by timing auto-ignition to occur after the fuel and air are mixed below the PM formation threshold and the oxides of nitrogen (NO_x) emissions can be reduced by reducing the combustion temperature by running under highly dilute conditions. Employing the strategy of premixed charge compression ignition, for example, with the use of a fully premixed charge prepared before introduction to the cylinder or a more advanced/retarded direct injection timing than for conventional diesel, this emissions reduction can be successfully achieved [1-7]. Although PCCI combustion is a promising technique to simultaneously achieve high efficiency and low NO_x and soot levels, difficulties controlling the combustion phasing and duration have limited their widespread use.

To address these issues Inagaki et al. [9] and Kokjohn et al. [10] proposed blending two fuels with different auto-ignition characteristics inside the cylinder. This in-cylinder blending allows combustion phasing control by varying the ratio of the two fuels and combustion duration control by introducing spatial stratification into the fuel reactivity (i.e., auto-ignition) distribution [15]. Consequently, they termed this alternative combustion mode “reactivity controlled compression ignition,” or RCCI combustion. Kokjohn et al. [10] compared RCCI and conventional diesel combustion in a heavy-duty diesel engine and showed a reduction in NO_x by three orders of magnitude and a reduction in soot by a factor of six. An improvement in gross indicated efficiency by 16.4% was demonstrated due to reductions in heat transfer losses and improved control of combustion phasing and duration. In addition to high efficiency and low emissions, another advantage of RCCI combustion is its fuel flexibility. A number of combinations of conventional and alternative fuels have been studied in RCCI engine combustion [11-14,17-23].

Although dual fuel RCCI combustion shows many beneficial features, the requirement to carry two fuels remains a limiting factor for some applications where a shortage of one fuel causes critical problems. As a viable way to address this technical challenge, utilization of the low reactivity fuel doped with a small amount of appropriate cetane improver to replace the high reactivity fuel has been suggested [24,25]. Splitter et al. [24] used ditertiary butyl peroxide (DTBP) as an additive (up to 3.5 % by volume) to pump gasoline and demonstrated the feasibility of using a single fuel as both the high and low reactivity fuels. Hanson et al. [25] used 2-ethylhexyl nitrate (2-EHN) as a cetane improving additive and demonstrated low load single fuel RCCI operation on a heavy-duty engine.

As another method to achieve “single fuel” engine operation, use of an on-board fuel reformer to generate the low-reactivity fuel from a high reactivity fuel stream has been suggested [26]. Based on the thermodynamic analysis of thermochemical exhaust heat recuperation performed by Chakravarthy et al. [27], thermochemical recuperation to drive the endothermic fuel reforming reactions can increase the second law efficiency by up to 11%. Further, this approach has the potential to enable RCCI operation with the reformed fuel. The low reactivity syngas generated from the reformer is introduced into the cylinder as a pre-mixture before direct injection of the high reactivity fuel, allowing single fuel RCCI operation with improved fuel flexibility. Combustion phasing and duration of reformed fuel RCCI is controlled by varying the ratio of syngas to the high reactivity fuel and the spray injection strategy.

To develop a reformed fuel RCCI combustion system, computational fluid dynamics based optimization is needed. For optimization purposes, tens of thousands of simulations are required. Accordingly, computational cost prohibits use of detailed reaction mechanisms that consist of several hundred species and several thousand reactions. A common approach used for exploration of new fuel blends is the use of reduced reaction mechanisms created and validated for single fuels. For example, Nieman et al. [23]

performed RCCI combustion calculations of blends of methane and diesel fuel using a reaction mechanism developed and validated for n-heptane that contained methane reaction pathways. The mechanism reproduced n-heptane and methane ignition delay adequately and was deemed acceptable for use. To date, little attention has been paid to predictability of the chemistry interactions between fuels. The work shows that the chemistry interaction of multiple fuels is of great importance when two fuels with substantially different reactivity are used in engine combustion (e.g., in the case of RCCI combustion using diesel fuel and syngas).

In the present study, single fuel RCCI engine combustion with diesel fuel and its reformed gas fuel is studied. In order to model the physical properties of the diesel fuel sprays realistically, a multi-component surrogate model was employed. The oxidation reaction kinetics was modeled using a reduced reaction mechanism for a single representative component for diesel fuel. Employing the GCR combustion model by Ra and Reitz [28], n-heptane was selected for the single component chemistry surrogate. The reaction mechanism for n-heptane oxidation processes was reduced from a comprehensive mechanism such that the reaction mechanism of syngas oxidation is included as a sub-mechanism. When developing the reduced mechanism, emphasis was put on the interaction of oxidation reaction pathways of multi-component fuels with large reactivity differences. The reduced mechanism was applied to simulate diesel-syngas RCCI engine combustion and predicted results are compared with measured data.

2. Reaction mechanism formulation

2.1. Comprehensive mechanism

A comprehensive detailed kinetic mechanism for n-heptane oxidation processes [29] was used as the base mechanism for the present reduced mechanism. The mechanism consists of 540 species and 2526

reactions to fully describe the fundamental chemical processes involved in n-heptane oxidation, and has been validated against various experimental data from laboratory devices. In the mechanism, 25 major classes of elementary reactions were identified. Classes 1–9 are associated with the high temperature oxidation and classes 10–25 are linked to the low temperature oxidation.

Fig. 1 shows the flux diagram for fuel (RH) oxidation. A double arrow indicates that the reaction step involves isomerization. The reactions in the dashed line box indicate high temperature reaction pathways, while those in the dash-dotted line box are for low temperature reaction pathways. A double-arrow indicates that the reaction step involves isomerization. In the diagram, RH denotes fuel, $R\cdot$, $R'\cdot$, $R''\cdot$, Q and Q' denote alkyl radicals. S, S', and S'' are olefins and, in particular, S_c and $S_c\cdot$ are the conjugate olefin of the fuel and its radical, respectively. P_1 and P_2 are decomposition products of olefins.

2.2. Mechanism reduction

To generate skeletal mechanisms, mechanism reduction was performed using the directed relation graph (DRG) method of Lu and Law [30] and the methods by Ra and Reitz [28, 31]. The reduction sampling point for the DRG method was set to a stoichiometric n-heptane/air mixture at initial conditions of 800 K and 40 bar. nC_7H_{16} , CO, H_2 and OH were used as the search-initiating species in the reduction process. Multiple generations of reduction processes were performed with varying user-specified error tolerance. It was observed that the size of resulting reduced mechanisms are similar for a given error tolerance regardless of the reduction history of error tolerance setting. Moreover, the results reduced from the base comprehensive mechanism using increasing tolerances are similar to those obtained in a sequential manner where the reduced mechanism obtained in the previous generation is used as the starting mechanism in the next reduction generation.

With increasing error tolerance, the size of the reduced mechanism decreases. In Fig. 2, the reduction ratio of the size of reduced mechanisms compared to those of the base comprehensive mechanism is shown for each sequential reduction generation up to the 28th generation. An error tolerance of 0.25 allowed the mechanism to be reduced below 100 species. Note that, since the reduction processes start with a smaller tolerance than the user-specified value in each generation, it is possible to generate a reaction mechanism with a smaller number of species and reactions, but with a smaller error tolerance value, as can be seen between generations 21 (tolerance = 0.06) and 22 (tolerance = 0.05) in the figure.

As the extent of reduction increases, more species and reaction pathways are removed, and thus the performance of the reduced mechanisms tend to deviate from that of the base mechanism, although the discrepancy varies depending on the fuels that are modeled by the sub-mechanisms included in the reduced mechanisms. Fig. 3 compares predicted ignition delay times for several reduced mechanisms under constant volume conditions at two equivalence ratios. The calculations were performed with the SENKIN code [32]. As shown in Figs. 3(a) and (b), ignition delay prediction for syngas/air mixtures is not affected by the reduction extent. On the contrary, the n-heptane ignition delay prediction is significantly affected by the mechanism size. Up to the 17th generation with an error tolerance of 0.03, no significant difference of ignition delay times is observed. However, the 18th generation reduced mechanism (error tolerance remains the same, 0.03) begins to show noticeable discrepancy in the low to mid temperature range (see the solid and dotted lines in Figs. 3(c) and (d)) and the predicted ignition delay times deviate more from the baseline values with further reduction. Note that the deviation does not necessarily change in a monotonic fashion. It is seen in the figure that ignition delay times are slightly overpredicted by the 18th generation mechanism, then significantly underpredicted in the NTC region by the 24th and later generations. It is also seen that the prediction error spreads over the entire temperature range such that ignition delay times at high temperatures ($T > 1000$ K) are unacceptably overpredicted by the 28th generation mechanism. Another noticeable difference between the base

mechanism and the reduced mechanisms of the 24th and higher generation is that the variation of ignition delay times at low temperatures ($T < 850$ K) became steeper and the NTC region starts at higher temperatures compared to the base mechanism case. This indicates that important species and reaction pathways of the base mechanism are missing and the oxidation processes were altered in the reduced mechanisms, detailed characteristic behavior of which will be discussed later in the paper. As a balance between computational efficiency and accuracy, the target size of the reduced mechanism was set to ~100 species. Instead of using the 27th generation mechanism obtained using the DRG method that has species under 100, the 26th generation mechanism (115 species and 357 reactions) was chosen for further reduction by isomer lumping.

A reduced mechanism of 77 species and 254 reactions was created by lumping isomers and relevant reactions and this mechanism will be referred to as Ver-1 mechanism in the remainder of the paper. In the lumping process, isomers of $R\cdot$ (C_7H_{15}), S_c (C_7H_{14}), RO_2 ($C_7H_{15}O_2$), $QOOH$ ($C_7H_{14}OOH$), O_2QOOH ($O_2C_7H_{14}OOH$) and ketohydroperoxides (C_7ket) in Fig. 1 were lumped into the corresponding single generic species and their thermodynamic properties were represented using those of 2nd-carbon-site isomers. Note that, although ketohydroperoxides were lumped to single species, the variety of their decomposition reactions were retained as much as possible by considering decomposing products described by the reactions before lumping. In Ver-1 mechanism, the hydrogen abstraction reaction by heptylperoxides ($nC_7H_{16} + C_7H_{15}O_2 = C_7H_{15} + C_7H_{15}O_2H$) was added to complement the mechanism.

Following Ra and Reitz [28], the reaction rate constants of Ver-1 mechanism were adjusted to match the ignition delay times of the base mechanism. The sensitivity of ignition delay curves of selected n-heptane oxidation reactions of Ver-1 mechanism is shown in Fig. 4. In each figure, ignition delay curves for three cases of pre-exponential factors of the reaction of interest are compared; i) base value, ii) base value $\times 10$ (shown as $A \times 10$), and iii) base value $\div 10$ (shown as $A \times 0.1$). The hydrogen abstraction

reaction by OH radicals ($nC_7H_{16} + OH = C_7H_{15} + H_2O$) influences ignition delay in the low to intermediate temperature range. It is seen in Fig. 4(a) that the NTC behavior is most sensitive to the reaction. On the contrary, the abstraction reaction by HO_2 radicals ($nC_7H_{16} + HO_2 = C_7H_{15} + H_2O_2$) affects ignition delays at mid to high temperatures. Oxygen addition to heptyl radicals ($nC_7H_{15} + O_2 = C_7H_{15}O_2$) or heptylhydroperoxides ($C_7H_{14}OOH + O_2 = O_2C_7H_{14}OOH$) mainly changes the ignition delays in the NTC temperature range (Figs. 4 (c) and (e)), with relatively little variation of the depth of the NTC behavior. Similar ignition delay sensitivity is seen in heptylketoperoxides formation reaction ($O_2C_7H_{14}OOH = C_7ket + OH$). Ignition delays at low temperatures are most sensitive to the heptylperoxide isomerization reaction ($C_7H_{15}O_2 = C_7H_{14}OOH$), as shown in Fig. 4(d). The rate constants of selected reactions in Ver-1 were adjusted to capture the ignition delay times of n-heptane oxidation at stoichiometric conditions. Details of rate constant adjustment are listed in Table A-1

In order to validate the performance of the Ver-1 reduced mechanism in prediction of n-heptane/syngas co-oxidation, five fuel mixtures were simulated for ignition at constant volume. Table 1 shows the mixture compositions. Note that Mixture-1 and Mixture-3 have the same syngas amount and Mixture-3 and Mixture-5 have the same n-heptane amount. Thus, ignition delay comparison between Mixture-3 and Mixture-5 allows investigation of the effects of syngas (low reactivity fuel) in the co-oxidation of n-heptane (high reactivity)/syngas (low reactivity) fuel mixtures. Similarly, Mixture-1 and Mixture-3 can be compared to isolate the effects of n-heptane (high reactivity fuel) addition in oxidation of syngas (low reactivity fuel). The effect of equivalence ratio on n-heptane/syngas fuel mixtures can be observed by comparing Mixtures 2 to 4.

Fig. 5 shows calculated constant volume ignition delay times of the five mixtures using the base mechanism, 26th generation reduced mechanism, and Ver-1 mechanism. The initial pressure for calculations was 40 bar. The ignition delay times of Mixture-1 (neat syngas) monotonically decrease as

temperature increases. Mixture-5 (neat n-heptane) shows a characteristic negative temperature coefficient (NTC) behavior. It is notable that ignition delay times of syngas become shorter than those of n-heptane at high temperatures. For temperatures less than the high end of the NTC region, ignition delay times of Mixture-3 are predicted to be longer than those of Mixture-5. Considering that the amount of n-heptane in Mixture-3 and Mixture-5 are the same, this indicates that the existence of syngas acts as a reaction suppresser in n-heptane/syngas co-oxidation. However, at high temperatures the addition of syngas enhances reactivity such that ignition delay times of the syngas blends become shorter than that of neat n-heptane. It is also observed that the NTC behavior of the n-heptane/syngas fuel mixture is much weaker than that of the n-heptane-only case, which is thought to be due to the influence of non-NTC characteristics of syngas oxidation. The effects of equivalence ratio variation are clearly seen from the results of Mixtures-2, 3 and 4. By further increasing the n-heptane amount from Mixture-5, the reactivity of the n-heptane/syngas fuel mixture becomes stronger than that of Mixture-5. It is seen that Mixture-2 oxidation shows a weak NTC behavior. Note that the quantitative dependency of ignition delay times of n-heptane/syngas fuel mixture on equivalence ratio variation could not be validated due to lack of experimental data and further validation is left for future study.

The 26th generation reduced mechanism was used to simulate the same conditions as in Fig. 5(a) and its ignition delay curves are shown in Fig. 5(b). It is seen that the ignition delay behavior of n-heptane/syngas fuel mixture is predominantly influenced by the n-heptane oxidation, especially low to medium temperatures such that ignition delays tend to be over-predicted at low temperatures ($T < 800$ K) while those are significantly under-predicted for higher temperatures ($800 < T < 1200$ K). This results in a much weaker NTC behavior of n-heptane/syngas fuel mixtures by the 26th generation mechanism than the base mechanism.

Ignition delay times predicted using Ver-1 mechanism show similar characteristics to those of the 26th generation reduced mechanism, as shown in Fig. 5(c). As mentioned above, the ignition delay times of n-heptane oxidation were matched to those of the base mechanism by adjusting the reaction rate constants of selected reactions in Ver-1 mechanism (see Table A-1). The adjustment of n-heptane oxidation in the NTC region increased the ignition delays of Mixtures-2, 3 and 4 in both low and the NTC temperatures, resulting in much weaker NTC behavior of Mixtures-2, 3 and 4. It is clearly seen in the figure that differences in ignition delay times between Mixture-3 and Mixture-5 became substantially larger than in the base mechanism case for temperatures less than 950 K. Note that ignition delay times of Mixture-1 were identical to those of the base mechanism. Thus, it can be stated that the n-heptane/syngas co-oxidation processes are governed by the more reactive n-heptane oxidation processes modeled in the reduced mechanism.

The implication of this behavior is that typical reaction mechanism reduction methods used for single-component fuels remove species and reaction pathways that are important for co-oxidation. Use of these methods does not necessarily guarantee the same level of predictability of co-oxidation of two fuels with a large reactivity difference. In the following section, the key reaction pathways that affect the co-oxidation process are identified and added to the reduced mechanisms in order to retain the low temperature oxidation characteristics of the base mechanism.

In order to identify the key species and reactions that affect the co-oxidation behavior, reduced mechanisms of generations earlier than the 26th were investigated using the elimination method. In Fig. 6, variation of ignition delay curves of Mixture-3 during the reduction process is shown. When the 23rd reduced mechanism is generated, ignition delays at low temperatures start to deviate noticeably from the previous generation mechanism. This reduction of reactivity was found to be due to omission of the reaction pathways to generate ketohydroperoxides with 6-carbons (e.g., C₆ket; HOOC₆H₁₁OOH) and

their decomposition reactions. It was found by Ra and Reitz [31] that the overall reactivity of n-heptane oxidation is dominantly sensitive to the reaction pathways related to heptyl ketohydroperoxides and the ketohydroperoxide reaction pathways at levels below heptyl ketohydroperoxides can be reasonably eliminated to form a reduced mechanism at minor expense of prediction accuracy.

However, in the co-oxidation process of n-heptane and syngas, it was found that ignition delay times of Mixture-3 are sensitive to the omission of the reaction pathways of ketohydroperoxides smaller than heptyl ketohydroperoxides, to an extent comparable to that of Mixture-5. For instance, using the 22nd generation mechanism, which includes the reaction pathways of hexyl ketohydroperoxides, the omissions of the pathways increased the ignition delay times of Mixture-3 and Mixture-5 at initial temperature of 800 K by 10% and 21%, respectively.

With additional low-temperature branching pathways, this larger sensitivity could be resolved and the low temperature oxidation of n-heptane become more balanced. An effective way used in the present study was to retain the reaction pathways for immediate lower level ketohydroperoxides, i.e., hexyl ketohydroperoxides in the mechanism. Hexyl radicals (C_6H_{13}) are produced by reactions, $nC_7H_{16} + M = C_6H_{13} + CH_3 + M$, $C_7H_{14} + OH = CH_2O + C_6H_{13}$, and $C_7H_{15}O = CH_2O + C_6H_{13}$. Formation of $C_7H_{15}O$, through reactions, $C_7H_{15}O_2 + CH_3O_2 = C_7H_{15}O + CH_3O + O_2$, $C_7H_{15}O_2 + C_7H_{15}O_2 = O_2 + C_7H_{15}O + C_7H_{15}O$ (note that these reactions are modeled as one-way reactions in the detailed mechanism), and $C_7H_{15} + HO_2 = C_7H_{15}O + OH$ leads to hexyl radical generation mainly via $C_7H_{15}O = CH_2O + C_6H_{13}$. Hexyl radicals are generated through the reaction, $C_7H_{14} + OH = CH_2O + C_6H_{13}$, as well (this reaction is also modeled as one-way reaction in the detailed mechanism). However, this reaction is not as influential as $C_7H_{15}O$ -related reactions, as is described below. Formation of hexyl radicals through direct decomposition of heptane is active at high temperatures, and thus its influence is quite limited at low temperatures. As in the modeling of heptyl ketohydroperoxide pathways, considering one major hexyl ketohydroperoxide in a

lumped species form was found to be effective enough to minimally increase the mechanism size in the present reduced mechanism.

Another substantial change of reactivity was observed when the 24th generation reduced mechanism was created, as shown in Fig. 6(b). Ignition delay times in the NTC range of temperature were significantly reduced while those for low temperatures were not influenced much. Interestingly, further reduction reduced the error in ignition delays in the NTC region and increased the error at low temperatures. This trend can be seen from the 26th generation case shown in Fig. 6(c).

The reduction of ignition delays in the NTC region was found to be due to omission of reactions related to conjugate alkene (C_7H_{14}) of n-heptane from the low-T reaction pathways. Heptenes are generated mainly through $C_7H_{15} = C_7H_{14} + H$ and $C_7H_{15} + O_2 = C_7H_{14} + HO_2$, but they play a critical role in $C_7H_{15}O_2 = C_7H_{14} + HO_2$ and $C_7H_{14} + HO_2 = C_7H_{14}OOH$, especially the latter reaction. Formation of C_7H_{14} from $C_7H_{14}OOH$ or $C_7H_{15}O_2$ slows down the progress of low-temperature branching because $C_7H_{14}OOH$ is intercepted by the reaction. The 23rd generation mechanism indicates that 57.1%~85.1% of heptyl hydroperoxides form conjugate alkenes, as shown in Table 2. Neglecting this pathways make all of heptyl hydroperoxides react with O_2 to form $O_2C_7H_{14}OOH$, which enhances the degenerate branching reactions, and thus shortens ignition delay. Interestingly, consideration of further oxidation pathways of heptenes did not affect the overall reactivity of n-heptane when the two conjugate-alkene formation reactions are retained in the reduced mechanisms, which indicates that alkenes' contribution to the reproduction of active radicals is relatively low at low temperatures.

Considering conjugate-alkene formation serves as a buffer reaction step to control the amount of heptylperoxides and their isomers in the low-temperature branching process. Similarly, but to a lesser extent, inclusion of propylperoxides formation ($C_3H_7O_2 = C_3H_7 + O_2$ and $C_3H_7O_2 = C_3H_6OOH$) and decomposition ($C_3H_6OOH = C_3H_6 + HO_2$) influenced the ignition delay of n-heptane and n-

heptane/syngas oxidations. Thus, the reaction pathways were retained in the present reduced mechanisms regardless of the imposed reduction ratio.

2.3. Interaction of oxidation pathways of multi-component fuels

In order to investigate the interaction of oxidation processes of multi-component fuels, the sensitivity of ignition delay curves to reactions of fuel with active radicals was calculated.

In Figs. 7 and 8, ignition delay curve variations with reaction rate change of reactions fuel + OH and fuel +HO₂ are shown. Reaction rate change was obtained by increasing/decreasing the pre-exponential factors of the reactions of interest by a factor of 10.

Increasing the reaction rate of $\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$ did not change the ignition delay times of Mixture-1 (syngas only) or Mixture-5 (n-C₇H₁₆ only). Decreasing the reaction rate only slightly increases the ignition delay times of Mixture-1 at high temperatures, as can be seen in Fig. 7. However, ignition delay times of Mixture-3 (50/50 syngas/n-heptane at $\phi = 1.0$) are significantly affected by this reaction. By reducing the consumption of OH radicals by H₂ molecules, the ignition delay behavior tends to become closer to that of n-heptane. That is, since the reactivity of neat n-heptane is higher than that of syngas at low to intermediate temperatures, but lower than that of syngas at high temperatures (see Fig. 5(a)), ignition delay times become shorter at low to intermediate temperature and slightly longer at high temperatures. This indicates that consumption of OH radicals by the reactions of the lower reactivity fuel hinders progress of the oxidation process of the higher reactivity fuel. Interestingly, reduction of the reaction rate of $\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$ by a factor of 10 makes the ignition delay times of Mixture-3 (50/50 syngas/n-heptane at $\phi = 1.0$) slightly shorter than those of Mixture-5 (neat n-C₇H₁₆) at low to intermediate temperatures (not shown here). This means that syngas oxidation has a slight enhancing effect on the overall reactivity of the fuel blends. This implies that accurate estimation of the reaction

rate constants of $\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$ is of critical importance in correct modeling of co-oxidation processes of high-low reactivity fuel blends.

Similar behavior is seen for the reaction, $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$. Ignition delay times of pure syngas and n-heptane are minimally sensitive to the reaction, while ignition delay times of blends of syngas and n-heptane are increased when this reaction rate is increased. However, its sensitivity is much lower than that of the $\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$ reaction. Additionally, ignition delay times of Mixture-5 (neat n- C_7H_{16}) are significantly affected by the reaction $\text{nC}_7\text{H}_{16} + \text{OH} = \text{C}_7\text{H}_{15} + \text{H}_2\text{O}$ at low to intermediate temperatures. It is seen in Fig. 7(c) that the NTC behavior is mainly governed by the reaction. As can be expected, increasing the reaction rate of $\text{nC}_7\text{H}_{16} + \text{OH} = \text{C}_7\text{H}_{15} + \text{H}_2\text{O}$ enhance the overall reactivity of Mixture-3, which is an opposite trend compared to that of the syngas+OH reactions. Note that reactions of H_2 , CO and n- C_7H_{16} with OH radicals are exothermic reactions, but they have quite different reaction characteristics. That is, OH reaction with CO is oxygen atom addition processes, but for n- C_7H_{16} it is a hydrogen abstraction process to initiate the oxidation process in the n-heptane case, and thus has a significant influence in determining its reactivity. For OH reactions with H_2 , it can be viewed as either oxygen atom addition or hydrogen abstraction.

Ignition delay sensitivity to reactions of fuel species with HO_2 radicals is shown in Fig. 8. It is seen that syngas ignition delay times (Mixture-1) are significantly affected by reactions, $\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{H}$ and $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$, in particular, the enhancing effects are dominant compared to the reactions with OH radicals (see Fig. 6). Oxidation of Mixture-5 is less sensitive to reactions, $\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{H}$ and $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$, but, as expected, markedly sensitive to reaction, $\text{nC}_7\text{H}_{16} + \text{HO}_2 = \text{C}_7\text{H}_{15} + \text{H}_2\text{O}_2$, especially at intermediate to high temperatures, as can be seen in Fig. 8(c). It is seen that oxidation of Mixture-3 is affected by fuel+ HO_2 reactions over the entire range of temperature considered with enhancing overall reactivity of the blended fuels with increasing reaction rates of individual fuel+ HO_2

reactions. This indicates that the competition between the two fuels to consume HO_2 radicals is very minor. Reaction with HO_2 promotes the progression of oxidation by either producing other active radicals (H or OH) or alkyl radicals (C_7H_{15}). This assisting effect is more evident considering that reactions, $\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{H}$ and $\text{nC}_7\text{H}_{16} + \text{HO}_2 = \text{C}_7\text{H}_{15} + \text{H}_2\text{O}_2$, are endothermic.

Similarly, the ignition delay sensitivity to reactions of fuel species with H and O radicals was investigated. Ignition delay times of Mixtures 1,3 and 5 (not shown in the paper) were found to be relatively insensitive to fuel+O and fuel+H reactions, which is mainly attributed to the fact that the concentrations of O and H radicals is much lower than other active radicals during the oxidation process.

Sensitivity of ignition delay times of Mixtures 3 to the major n-heptane reactions in the low-T branching pathways is shown in Fig. 9. The Mixture-3 sensitivity was found to be similar to that of Mixture-5 (not shown here). The largest sensitivity at low temperatures is seen from the isomerization reaction, $\text{C}_7\text{H}_{15}\text{O}_2 = \text{C}_7\text{H}_{14}\text{OOH}$. On the contrary, reaction, $\text{O}_2\text{C}_7\text{H}_{14}\text{OOH} = \text{C}_7\text{ket} + \text{OH}$, is most influential in the NTC temperature range, while the oxygen addition reaction to heptylhydroperoxide, $\text{O}_2\text{C}_7\text{H}_{14}\text{OOH} = \text{C}_7\text{H}_{14}\text{OOH} + \text{O}_2$, most dominantly affects the ignition delay times of n-heptane in the NTC range.

One characteristic reaction of interest is the reaction of CO with the oxygen molecule to form CO_2 and an O radical, i.e., $\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$. It is observed that syngas oxidation is sensitive to this reaction while n-heptane and its blends with syngas have significantly less sensitivity to the reaction, as shown in Fig. 10. The adjustment of reaction rate constants of this reaction allows improvement of validation of syngas ignition delay prediction, while limiting the influence of the adjustment on n-heptane and the other fuel blends.

As expected, it was observed that radical branching reactions or radical termination reactions influence the co-oxidation of syngas/n-heptane blend fuels, as well as individual single fuel oxidation, due to their position in the hierarchical structure of the reaction mechanism. Fig. 11 shows the sensitivity of ignition delay times to two major chain branching reactions ($\text{H} + \text{O}_2 = \text{O} + \text{OH}$, $\text{H}_2\text{O}_2(+\text{M}) = \text{OH} + \text{OH}(+\text{M})$) and a radical termination reaction ($\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$) in the oxidation of Mixture-1, Mixture-3, and Mixture-5. Enhancing chain branching and chain termination reactions reduces and increases ignition delay times, respectively, for all charge mixtures. It is also seen that ignition delay times vary substantially over the entire temperature range considered. In particular, enhancing the forward reactions of $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ and $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$, has much more influence than suppressing them, while suppressing the hydrogen peroxide decomposition reaction has more effect than enhancing reaction. The radical termination reaction has a strong influence on the ignition delay of n-heptane oxidation (Mixture-5), while its effects on syngas (Mixture-1) and blend fuel (Mixture-3) are relatively small.

Note that, in the present reduced mechanisms, the reactions of H_2 and CO oxidation were not adjusted at all since i) they are the lowest oxidation pathways in the hierarchy of the reaction mechanisms, affecting the oxidation processes of all hydrocarbon fuels, and ii) the reaction rate constants of those reactions have been quite well established, although there are still being updated for accuracy improvement. Hence, the reaction sensitivity in multi-chemistry is indicative of the emphasis of necessary attention and the direction of research on the determination of reaction rate constants.

3. Validation of the reduced mechanism

Including the key reactions that affect co-oxidation in the reduced mechanism, isomers and their relevant reaction were lumped to generate another reduced mechanism, called Ver-2 mechanism, consisting of 81 species and 312 reactions, as shown in Tables A-2 and A-3 of Appendix A [43]. The Ver-2 mechanism was validated for ignition delay calculation of the five mixtures in Table 1 and n-

heptane/air mixtures of equivalence ratios of 0.5, 1.0 and 2.0. Fig. 12 shows predicted ignition delay times. It is seen that the Ver-2 mechanism captures the experimental ignition delay times of Ciezki et al. [33] for the three equivalence ratios tested (Fig. 12(a)). The trend of ignition delay times of n-heptane/syngas fuel mixtures for various temperatures and equivalence ratios were also reasonably well captured by Ver-2 mechanism (Fig. 12(b)), although the NTC behavior is slightly under predicted for Mixture-2 compared to the base detailed mechanism (see Fig. 5(a)). Note that, considering the log scale used in the figure, the quantitative difference of ignition delay times between the detailed and the present Ver-2 mechanisms would look larger in linear scale plot, which was not employed in the present study.

The performance of the present mechanism is also compared with other reduced mechanisms available in the literature. The ignition delay times of the five n-heptane/syngas mixtures in Table 1 predicted by the LLNL-reduced mechanism [42] and the mechanism of Ra and Reitz [31] are shown in Figs. 12(c) and 13(d), respectively. It is seen that the reactivity of Mixtures 2~3 is significantly over-predicted by the LLNL-reduced mechanism over the entire temperature range, especially at intermediate and high temperatures. In addition, the NTC behavior is not predicted for the mixtures of n-heptane/syngas fuels by the LLNL-reduced mechanism, as shown in Fig. 12(c). On the contrary, the mechanism of Ra and Reitz shows similar behavior to that of detailed mechanism (see Fig. 5(a)) at high temperatures, while the ignition delay times tend to be over-predicted at low temperatures and under-predicted in the NTC temperature range. It is also seen that the sensitivity of the ignition delay times to equivalence ratio is significantly under-predicted and the ignition delay times of Mixture-2 (lean) are significantly under-predicted. The poor performance of the two reduced mechanisms is attributed to the fact that the mechanisms were validated for stoichiometric neat n-heptane/air mixtures only without considering the effects of multi-component chemistry effects of fuels with large reactivity difference.

In order to test the present mechanism in simulations of syngas autoignition, experiments by Kromns et al. [34] were used. In their study, ignition delay times for $\text{H}_2/\text{CO}/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures was measured using rapid compression machines and shock tubes at pressures from 1 to 70 bar, over a temperature range of 914–2220 K and at equivalence ratios from 0.1 to 4.0. Among the experimental syngas compositions, four cases were chosen for validation with H_2 ratio ranged from 5 to 100 %, as shown in Table 3. Initial mixture temperatures tested ranged from 900 to 2200 K and three initial pressures after the end of compression or the passage of reflected shock wave were simulated. Lean ($\phi=0.5$) and stoichiometric conditions ratios were considered in the validation simulations. In the simulations, reactions to form excited OH radicals (OH^*) from ground OH radicals [34] were incorporated into the present reduced mechanism and ignition delay times were defined as the time lapsed to reach a local peak concentration of OH^* as suggested in the experiments [34].

Figure 13 shows comparison of predicted and measured ignition delay times of the mixtures listed in Table 3. It is seen that the crossing behavior with respect to pressure change is well captured by the model in all cases considered. Effects of temperature variation are excellently predicted, although ignition delay times tend to be overpredicted for very lean $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures in the range of the low-to-high temperature transition. It is also seen that ignition delays of CO-dominant syngas blends (Case-D) at 1 bar initial pressure tend to be underpredicted at high temperatures. However, overall a good quantitative agreement is observed for the conditions more relevant to engine operations.

4. Modeling of diesel fuel-syngas RCCI combustion

4.1. Diesel fuel spray modeling

Diesel fuel is modeled as mixtures of surrogate components, whose properties are calculated using a discrete multi-component (DMC) fuel model [35]. Following the methodology of Anand et al. [36] and Su et al. [37], surrogate components and their composition are chosen to match measured distillation

profiles and properties of the target fuel such as density, vapor pressure, surface tension, latent heat of vaporization, liquid and vapor phase specific heat capacity, viscosity and thermal conductivity, lower heating value, hydrogen to carbon (H/C) ratio, cetane number, etc.

Distillation profiles, which are a graphical depiction of boiling temperatures against the volume fraction distilled, are obtained by calculating the evaporation history of a single drop under a boiling condition (true boiling point) by setting the drop interior temperature to a superheated state [36] in order to model the temperature configuration near the boiling surfaces of batch distillation. Uniform liquid temperatures in the batch distiller (e.g., by using a stirrer) are effectively modeled by setting a uniform temperature in a drop. The temperature distribution across the liquid/vapor interface is modeled by the temperature change from a superheated liquid in the drop interior, to the boiling temperature at the drop surface, and to the temperature of the surrounding gas mixtures. For detailed description, readers are referred to Fig. 3 in Ref. [36]. Properties of the mixture are calculated from the properties of the individual pure components [36]. The models were implemented into an in-house CFD code, KIVA-ERC-CHEMKIN [38], and applied to simulate the distillation profiles of diesel fuel. All the thermo-physical properties of the representative hydrocarbon species were taken from Daubert and Danner [39] and were incorporated in the code's fuel library.

The class contents of the diesel fuel used in the engine experiments, measured by the GC/MS method [40], are shown in Table 4. Among the class contents, the paraffins are the most numerous chemical class (~75.9%) and the next largest portion of the components belong to mono-aromatics that are mostly alkylbenzenes. About 5% naphthenes are found in the fuel, which are modeled using one mono-naphthene (methylcyclohexane) and one poly-naphthene (decalin), neglecting possible heavy naphthenes beyond C7. The oxygenates (~5.9%) and the remainder of unknown species (~3.6%) were not modeled in the present study. Instead, they were added to the n-alkanes, distributing over the modeled n-alkanes

in proportion to the mass fraction of individual components. A 14-component diesel fuel surrogate model was developed and its detailed composition is shown in Table 5. In the table, the chemical class and boiling temperature of each component are listed as well. The two most prevalent components of the surrogate model are iso-cetane (heptamethylnonane, ~18.1%) and cetane (hexadecane, ~17.4%).

Fig. 14 shows the comparison of the measured [40] and predicted distillation curve by the present surrogate model. Excellent agreement is seen between model prediction and measurement over the entire boiling temperature range. Other major properties are compared between the model and measurement in the table accompanying Fig. 14. Overall, a very good agreement with measured data was obtained by the model, although density and viscosity are seen to be underpredicted, while the other properties are somewhat overpredicted. It should be noted that the estimated cetane number is higher than the measured value due to the fact that i) oxygenates and unknown remainder species (~9.5 % of total mass) were modeled as n-alkanes, most of which are heavy and thus, of high CN, and ii) CN was estimated as a mole-weighted average without considering non-linear effects of the mixture cetane number [41], which needs to be taken into consideration when evaluating the CN of the physical surrogate model. However, note that the CN of the physical surrogate model becomes irrelevant when a single chemistry surrogate is used in reaction calculation, as will be described next.

4.2. Combustion simulations

While the spray behavior of diesel fuel is modeled using the 14-component surrogate model mentioned above, the oxidation processes of the fuel were modeled using single surrogate component chemistry in the present study. In the approach, the vapor components of the model fuels are assigned into n-heptane (CN~52) in the chemistry domain, which well represents the average reactivity of the test diesel fuel. The reduced reaction mechanism (Ver-2) described earlier was used to calculate the chemistry of n-heptane.

The present reduced reaction mechanism was applied to simulate dual fuel combustion. Experiments were performed in a heavy-duty single-cylinder research engine. The engine has a bore of 13.7 cm, a stroke of 16.5 cm, and a compression ratio of 14.9. To ensure the reduced model is predictive over a range of conditions, experiments were performed in both the low temperature combustion regime (LTC) and high temperature combustion regime. In both sets of experiments, syngas, consisting of a 50/50 blend of H_2 and CO (by volume), was injected into the intake manifold and mixed with air before being introduced into the cylinder.

Low temperature dual-fuel combustion was achieved by premixing syngas and direct-injecting diesel fuel at -56° after top dead center (ATDC). In these experiments, the injection pressure was held constant at 500 bar. These cases will be referred to as RCCI combustion. High temperature dual fuel combustion was achieved by premixing syngas and direct injecting diesel fuel at -10° ATDC. The injection pressure was held constant at 1000 bar and the syngas quantity was swept from 0% to 79%. Both sets of experiments were performed at an engine speed of 1300 rev/min and a nominal load of 7.3 bar gross indicated mean effective pressure (GIMEP). Detailed specifications of the engine and operating conditions are given in Table 6.

Simulations used a relatively coarse, $1/7^{\text{th}}$ sector computational grid with a total of 8,140 cells at BDC. The crevice volume was resolved as an elongated top land region, which was adjusted to match the effective compression ratio of the engine. Figure 15 shows the computational grid used in the simulations. The initial and boundary conditions were obtained from the measured data. The trapped residual gases were estimated based on the in-cylinder charge pressure. The internal EGR gases were added to the fresh fuel/air to specify the gas composition at IVC. The mixture at IVC was assumed to be

completely homogeneous and the computations were performed from intake valve closure (IVC) to exhaust valve open (EVO).

The predicted profiles of pressure and heat release rate of diesel/syngas RCCI engine combustion are compared with measured data in Fig. 16. For comparison, results obtained using the Ver-1 mechanism are plotted in the figure as well. As expected, the spray evaporation behavior is so similar between the two simulations that the vaporized fuel profiles are almost identical (Fig. 16(a)). However, the predicted combustion behavior is substantially different. It is seen in Fig. 16(b) that the timings of cool flame and main ignition, peak cylinder pressure, and expansion pressures are well captured by the model prediction using the Ver-2 mechanism, while ignition is substantially retarded, fuel mixtures are partially burned and expansion pressures are underpredicted using the Ver-1 mechanism, which does not reflect the multi-component effects correctly, as described above. The reaction of injected diesel fuel is predicted by the Ver-2 mechanism, which can be noticed from the increased in-cylinder CO amount and local maximum gas temperatures at crank angles from -20° ATDC, as shown in Fig. 16(c). The cool flame behavior predicted by the Ver-2 mechanism is clearly seen from the small jump of the local maximum gas temperature profile near -20° ATDC (see Fig. 16(d)). On the contrary, the reactivity of the local diesel fuel/syngas mixtures is significantly under-predicted by the Ver-1 mechanism and no noticeable cool flame behavior is observed before the main ignition timing ($\sim 2.5^\circ$ ATDC). This under-prediction subsequently affects the main ignition due to altered local distributions of active radicals such as OH and the mixture temperature, and thus, the overall reaction progress is substantially slowed, resulting in excessive unburned CO.

In-cylinder distributions of equivalence ratio, CO and OH mass fractions on the spray axis plane predicted by the Ver-1 and Ver-2 mechanisms are compared in Fig. 17. The equivalence ratio was

calculated considering all species that contain C, H and O atoms including CO₂ and H₂O, and thus its distributions indicate the distributions of injected fuel, regardless of combustion.

As can be expected from the profiles of vaporized fuel amount (see Fig. 16(a)), the predicted equivalence ratio distributions are very similar to each other, as shown in Fig. 17(a). The distributions prior to ignition (figure for -20° ATDC) are nearly identical. As the piston moves closer to TDC, the size of the region bounded by an equivalence ratio iso-contour of $\phi=0.5$ increases faster for the Ver-2 case due to the gas expansion after combustion. Although the differences in the fuel distribution are small, large differences are seen in the CO distribution, as shown in Fig. 17(b). A CO-rich region formed by diesel fuel oxidation is seen at the top-center region of the cylinder at -10° ATDC in the Ver-2 case, while no noticeable increase of local CO concentration is observed in the Ver-1 case. The subsequent oxidation of CO in the CO-rich region drives the ignition process that accelerates the consumption of the low-reactivity syngas in the surrounding regions (note that the initial CO concentration was distributed uniformly). Similarly, the increase of local OH radical concentration during the cool flame period that drives the ignition process is correctly predicted by the Ver-2 mechanism, while OH generation is substantially suppressed by the Ver-1 mechanism, as shown in Fig. 17(c).

The performance comparison between the present mechanism and the reduced mechanisms of Refs [31] and [42] is shown in Fig. 18. As can be expected from the ignition delay results in Figs. 12(c) and 13(d), it is predicted that ignition occurs much earlier and the peak pressures are much higher in the cases of LLNL-reduced [42] and Ra and Reitz [31] mechanisms. Since the overall mixture equivalence ratio is lean, it is seen that the prediction error of the Ra and Reitz mechanism tends to be more than that of the LLNL-reduce mechanism, and thus the ignition occurs earlier in the Ra and Reitz mechanism case (Fig. 18(a)). It is also seen in Fig. 18(b) that both the Ra and Reitz mechanism and the LLNL-reduced

mechanism predict excessive heat release during the cool flame period, which tends to drive the main ignition much faster.

For the same injection conditions, the fuel concentration distributions in the cylinder (plots not shown here) are almost identical until the point of noticeable pressure rise (~ -15.5 deg atdc) of the Ra and Reitz mechanism case, and thus the profiles of fuel mass contained in mixtures with $\phi \leq 0.5$ (ϕ -1 range) and with $0.5 < \phi \leq 1.0$ (ϕ -2 range) are seen to be identical, as shown in Fig. 18(c). Note that all the mixtures fall in ϕ -1 range initially since the initial equivalence ratio of the syngas/air pre-mixture is 0.304. The fuel mass in ϕ -2 range mixture, which is the ignition-driving mixture, increases from zero up to CA = -36.5 due to evaporation of injected diesel fuel, then decreases due to either further dilution by mixing with ϕ -1 range mixture or its consumption by reaction. On the contrary, the mass of ϕ -1 range mixture drops first from the initial value of 0.152 g (initial syngas amount in the cylinder) as a part of it becomes richer due to diesel evaporation, then increases until it falls due to consumption by the main ignition reaction. Note that the mass of ϕ -1 range mixture is expected to increase up to the total fuel mass of 0.174 g if there is no consumption by reaction. Therefore, the falling time of the ϕ -1 range mixture mass profile is dependent on the reactivity prediction and, until that time, the fuel distribution keeps changing by mixing. This implies that the fuel mixture distributions at the time of main ignition and subsequent temperature distributions would be quite different in the three mechanism cases.

Indeed, over-prediction of reactivity of the ignition-driving mixtures (ϕ -2 range) by the Ra and Reitz mechanism significantly alters its mass profile, deviating it from those predicted by the other mechanism cases. The subsequent early main ignition occurs during the rise of fuel mass in the ϕ -1 range mixture, while the main ignition by the present mechanism occurs when the fuel mass in the ϕ -1 range mixture reaches close to the overall fuel mass.

As mentioned above, this difference in reactivity prediction for the same spray injection conditions leads to substantial difference in local mixture temperature prediction. The change of volume of local mixtures with $1100\text{ K} \leq T_g < 1900\text{ K}$ (T-1 range) or $1900\text{ K} \leq T_g < 2400\text{ K}$ (T-2 range) is compared for the three mechanism cases in Fig. 18(d). With over-prediction of reactivity of lean mixtures at low temperatures in the Ra and Reitz and LLNL-reduced mechanism cases, the volume fraction of T-2 range mixtures increases rapidly at a earlier phase than that of T-1 range mixtures due to burning at time with less dilution and more amount of the ϕ -2 range mixtures. At TDC, it is seen that the volume fractions of T-2 range mixtures are more than 3-times of T-1 range mixtures. For the present mechanism, the burned gas distribution between T-1 and T-2 ranges opposite of the other two mechanisms. With more mixing time before the main ignition, the fuel/air mixtures dilute more (see Fig. 18(c) where it is shown that ϕ -1 range mixtures increase up to 0.1725 g) and their burned gas temperatures are reduced. Accordingly, the burned gas temperature of the majority of charge mixtures falls in the T-1 range. Note that the volume fraction of T-1 range mixture prevails at crank angles later than ~ 10 deg atdc due to mixing of burned gases. However, it is also notable that the accuracy of prediction of the local temperature history is important since the emissions prediction are significantly affected by local burned gas temperatures.

The Ver-2 mechanism was further tested for high temperature combustion conditions. For the test, various amounts of the diesel fuel were substituted by the syngas, ranging from zero to 79 %. For all the cases, the start of injection was fixed at -10 deg atdc. Figure 19 shows comparison of the predicted and measured pressure and HRR profiles of the diesel combustion. Typical diesel combustion behavior, i.e., premixed burn and subsequent mixing controlled burning, is predicted for all cases considered. The trend of diesel substitution in pressure profiles is well captured by the simulation. That is, the peak cylinder pressure increases with increase of syngas fuel energy, as shown in Fig. 19(a). In order to demonstrate the performance of the model, the pressure and heat release rate profiles of the cases with diesel fuel only (100/0), 50% (50/50) and 79% (21/79) syngas substitution are compared in Fig. 19(b). In all three cases, the predicted and measured results are in good agreement, except that the peak

cylinder pressure is slightly overpredicted and the expansion pressures are slightly under-predicted in the case of 21/79 fuel split. It is seen that, overall, the diesel fuel/syngas combustion behavior is well predicted by the present reduced mechanism.

5. Conclusions

A reduced reaction mechanism was developed for modeling a single fuel RCCI engine combustion with diesel fuel and its reformed gas fuel. Employing n-heptane as a single representative chemical surrogate for diesel fuel, a comprehensive mechanism was reduced to a mechanism with 81 species and 312 reactions such that the reaction mechanism of syngas oxidation is included as a sub-mechanism with emphasis on the interaction of oxidation reaction pathways of syngas and n-heptane.

Five fuel mixture compositions were suggested such that the effects of equivalence ratio and the addition of low and high reactivity components on the co-oxidation in the multi-chemistry could be investigated systematically. Systematic detailed mechanism reduction investigation revealed;

- 1) Retaining the reaction pathways for immediate lower level ketohydroperoxides of the high reactivity fuel, i.e., hexyl ketohydroperoxides in the present mechanism, is important to maintain the co-oxidation predictability at low temperatures.
- 2) Conjugate-alkene formation plays a role of buffer reaction step to control the amount of heptylperoxides and their isomers in the low-temperature branching process.
- 3) Conjugate-alkene formation reactions need to be retained to maintain the overall progress of low-temperature branching of n-heptane.
- 4) Similarly, but to a less extent, inclusion of propylperoxides formation and decomposition in the reduced mechanism was important in predicting the reactivity of n-heptane/syngas oxidation.
- 5) In co-oxidation of two fuels with a large reactivity difference, reactions with OH and HO₂ radicals play an important role in determining the co-oxidation behavior of fuel mixture. Reaction with OH radicals have competing effects while reactions with HO₂ radicals have

assisting effects. On the contrary, reactions with O and H radicals have very minor effects on the overall reactivity of the fuel mixture.

- 6) Additional constraints mentioned above need to be considered in the automatic reduction processes to be able to generate reduced mechanisms that capture multi-chemistry characteristics.

The reduced mechanism was validated against experimental ignition delay times and applied to simulate diesel-syngas RCCI engine combustion, employing a multi-component surrogate model to model the physical properties of diesel fuel sprays realistically. Predicted pressure and heat release rate results were in good agreement with experimental data. The present reduced mechanism gave reliable performance for combustion predictions of RCCI engine operation to help further the fundamental understanding of the process occurring in reformed-fuel RCCI combustion and improve computational efficiency.

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Table 1. Conditions of five fuel mixtures simulated for co-oxidation behavior.

Mixture No.	Mixture composition [%]	Overall equivalence ratio
1	Syngas/air, $\phi=0.5$	0.5
2	(Syngas/air, $\phi=0.5$):(n-heptane/air, $\phi=0.5$)=50:50	0.5
3	(Syngas/air, $\phi=1.0$):(n-heptane/air, $\phi=1.0$)=50:50	1.0
4	(Syngas/air, $\phi=2.0$):(n-heptane/air, $\phi=2.0$)=50:50	2.0
5	n-heptane/air of $\phi=0.5$	0.5

Table 2. Reaction fluxes of heptyl hydroperoxides in the 23rd generation mechanism.

Heptyl hydroperoxide formation	Heptyl hydroperoxide consumption	Reaction flux (%)
$C_7H_{15}O_2-1=C_7H_{14}OOH1-2$	$C_7H_{14}-1+HO_2=C_7H_{14}OOH1-2$	85.1
	$O_2C_7H_{14}OOH1-2=C_7H_{14}OOH1-2+O_2$	14.9
$C_7H_{15}O_2-2=C_7H_{14}OOH2-3$	$C_7H_{14}-2+HO_2=C_7H_{14}OOH2-3$	57.1
	$O_2C_7H_{14}OOH2-3=C_7H_{14}OOH2-3+O_2$	42.9
$C_7H_{15}O_2-3=C_7H_{14}OOH3-2$	$C_7H_{14}-2+HO_2=C_7H_{14}OOH3-2$	57.1
	$O_2C_7H_{14}OOH3-2=C_7H_{14}OOH3-2+O_2$	42.9
$C_7H_{15}O_2-3=C_7H_{14}OOH3-4$	$C_7H_{14}-3+HO_2=C_7H_{14}OOH3-4$	59.0
	$O_2C_7H_{14}OOH3-4=C_7H_{14}OOH3-4+O_2$	41.0
$C_7H_{15}O_2-4=C_7H_{14}OOH4-3$	$C_7H_{14}-3+HO_2=C_7H_{14}OOH4-3$	59.9
	$O_2C_7H_{14}OOH4-3=C_7H_{14}OOH4-3+O_2$	40.1

Table 3. Test conditions for H₂-CO oxidation simulation [34].

Case	Fuel (H ₂ /CO) [%]	ϕ	H ₂ [mol %]	CO [mol %]	O ₂ [mol %]	N ₂ [mol %]	Ar [mol %]	Initial temperature [K]	Initial pressure [bar]
A	100/0	0.1	0.81		4.03		95.16	900-2200	1, 4, 16
B	100/0	0.5	3.47		3.47	93.06		900-2000	1, 4, 16
C	50/50	0.5	1.74	1.74	3.47		93.06	900-1800	1, 4, 16
D	5/95	0.5	0.17	3.30	3.47		93.06	900-2200	1, 4, 16

Table 4. Chemical class contents of diesel fuel [40].

Class	Mass fraction [%]		
	Measured	C-range	Model
n-Alkane	50.50	C9~C21	60.80
i-Alkane	25.38	C8~C20	24.95
Naphthene	4.97	C7~C16	4.64
Aromatic	7.23	C7~C12	7.15
Tetralin	1.52	C10~C11	1.58
Olefin	1.66	C9~C19	1.05
Oxygenated	5.87	C9~C20	0
Other	3.61	C9~C20	0

Table 5. Composition of diesel fuel surrogate model.

Species	Tboil [K]	Mass fraction
iso-Octane	372.39	0.0581
1-Octene	394.44	0.0105
cis-Decalin	468.97	0.0464
n-Pentylbenzene	478.61	0.0290
Tetralin	480.77	0.0149
n-Dodecane	489.47	0.1407
Naphthalene	491.14	0.0415
n-Tridecane	508.62	0.0067
Heptamethylnonane	519.50	0.1814
n-Tetradecane	526.73	0.0100
n-Hexadecane	560.01	0.1739
n-Octadecane	589.86	0.1474
Phenanthrene	613.45	0.0010
n-Eicosane	616.93	0.1393

Table 6. Engine specifications and operating conditions of the experiment.

Engine specification	
Displacement [L]	2.44
Bore x Stroke [mm x mm]	13.7 x 16.5
Piston Bowl Type	Open
Compression ratio	14.9:1
Spray included angle [degree]	148
Operating conditions	
Engine speed [rev/min]	1300
Swirl ratio	0.7
O ₂ @ IVC [%]	20.4
Gross IMEP [bar]	7.3
DI injection timing [deg atdc]	-56.0
Injection pressure [bar]	500 (RCCI), 1000 (Diesel)
Diesel fraction [%]	12 (RCCI) 21 ~ 100 (Diesel)

Figure 1. Schematic representation of n-heptane oxidation of Ref. [29].

Figure 2. History of reduction ratio and error tolerance using the DRG method.

(a)

(b)

(c)

(d)

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(a)

(b)

(c)

(d)

(e)

(f)

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(a)

(b)

(c)

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