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Article

Skeletal and Compact Validated Mechanisms for Iso-dodecane Using a Decoupling Methodology

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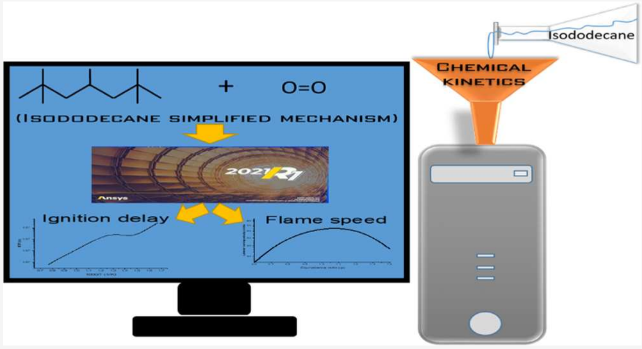
ABSTRACT: Iso-dodecane is an important component in developing surrogate fuel mixtures for conventional and alternative jet fuels. Despite some progress in recent years, there is still a requirement for a compact mechanism that is well validated in both low and high temperatures when compared to the experimental data. This paper develops a new compact mechanism with the aid of a decoupling methodology for iso-dodecane validated against available experimental data over a wide range of pressures and equivalence ratios. The ignition delay results show excellent agreement over a wide range of temperatures from 600 to 1300 K that covers low and high limits compared to the empirical data at 15, 20, and 40 bar and at lean, stoichiometric, and rich conditions. The maximum discrepancy between the simulations and the experiments by a factor of 1.7 was observed for 750 K at the rich condition at 15 bar. Laminar burning velocity simulations at two different pressures were conducted for iso-dodecane, and the results were compared with the available experimental data for alcohol-to-jet (ATJ) fuel, which is mostly composed of iso-dodecane. It was found that there was very good agreement between the modeling results and the experimental data. The final version of the new mechanism includes 158 species and 986 reactions and has potential in further functional kinetic investigations and to use for complex geometries of combustion systems such as Equivalent Reactor Network analyses.



1. INTRODUCTION

In recent years, there has been an increasing tendency to use combustor simulation tools such as computational fluid dynamics (CFD)[1] in the aviation sector, and this has had a substantial contribution to aero-engine combustion chamber design. The application has been utilized for both small-scale and industrial gas turbines[2−4] through simplified chemistry models or more complex ones. In addition to fluid mechanics, the chemical kinetics of the fuel is an essential prerequisite of the combustion numerical simulation, which demonstrates the practical utilization of a chemical reaction mechanism. In spite of technological advances and progress in the power of computational tools, it is still extremely challenging to model real jet fuels by considering all of the constituents in their structure, leading to reaction mechanisms with many hundreds to thousands of components. To avoid the complexity, stiffness, and the huge computational cost[5] of using such detailed chemical reaction mechanisms for jet fuels, researchers utilize the surrogate approach that contains a reduced form of the detailed mechanisms. The complexity of real jet fuels has also pushed researchers toward considering the use of tailor-made kinetic models for CFD simulations of gas turbine engines, which have a limited number of species and reactions while accurately emulating the real fuel specifications.

Dividing the fuel compounds into the major structural classes such as normal alkanes, iso-alkanes, naphthenes, and aromatics and allocating one representative to each class is a solution that researchers have employed, providing a compact surrogate mixture relevant to the intended combustion property targets (CPTs) of the fuel.[6,7] This highlights the importance of developing the chemical kinetics for each component of the structural class, resulting in a more accurate modeling capability for each surrogate fuel formulation in terms of ignition delay times, flame velocities, and species concentrations.

A large fraction of conventional and alternative jet fuels consist of heavy normal and iso-alkane components.[6−11] As illustrated in Figure 1, iso-alkanes are a key component of jet fuels and, as such, are of major importance in the development of appropriate surrogates for these fuels.

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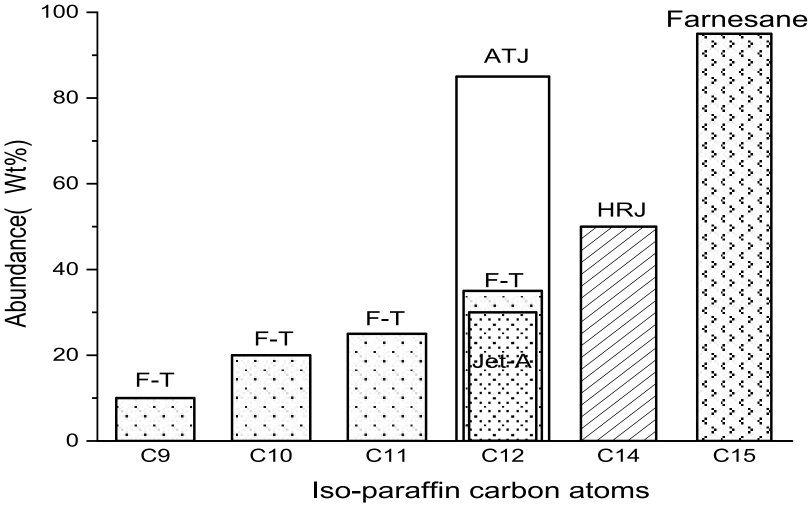


Figure 1. Iso-paraffin (iso-alkane) percentages in the composition of conventional and alternative jet fuels.[10,12]

Table 1. Physicochemical Characteristics of Iso-Dodecane in Comparison with Jet Fuels[14,15,21,22]

fuel	DCN	MW (g/mol)	H/C ratio	density (kg/m^3)	viscosity (cSt)	flash point (°C)	SP (mm)
Shell SPK	58.4	138.3	2.24	737	2.6	44	>40
Sasol IPK	31.3	148.5	2.195	762	3.6	44	>40
HRJ Tallow	58.1	163.7	2.18	758	5.3	55	>40
HRJ Camelina	58.9	167.6	2.20	751	3.3	43	>40
S-8 POSF 4734	58.7	154.5	2.14	757	4.6	49	>40
Jet A POSF 4658	47.1	157.5	1.96	806	5.2	47	22.1
JP 8 POSF 5699	49.3	154.5	1.935	790	4.1	48	23
Gevo ATJ	15.5	175.6	2.17	756	2.1	48	35
iso-dodecane	16.8	170.3	2.17	745	1.31	45	35.2

Among the candidate components for iso-alkanes in jet fuels composition, iso-dodecane is the most appropriate compound to be used as a surrogate for ATJ fuel[13−16] and as a major component in the surrogate formulation of JET A,[10,17] JP8,[18] and HRJ fuels[19,20] because of its physicochemical characteristics being similar to the average of the real fuel such as molecular weight, H/C ratio, density, and flash point. Table 1 shows various physicochemical properties of iso-dodecane in comparison with jet fuels.

During recent years, much attention has been given to the reaction kinetics of iso-dodecane, and there are several publications[23−28] that have purely been dedicated to a good understanding of the combustion characteristics and chemical kinetics of this highly branched iso-alkane. Zeppieri et al.[23] developed sub- and super-critical pyrolysis mechanisms for iso-dodecane based on the iso-octane model of Curran et al.[24] for large species reactions through utilizing fuel structure similarities, standard group additivity techniques for estimating the associated kinetic rate parameters, and the comparison of several parent fuel activation energies with ab initio calculations.

Experimental measurement of the ignition delay times (IDTs) of iso-dodecane, with the aid of a rapid compression machine (RCM), was performed by Min et al.[14] at pressures of 10 and 20 bar for lean and stoichiometric conditions. It was observed that iso-dodecane is less reactive in comparison with its similar hydrocarbon classes of n-alkane (*n*-dodecane) and light-branched iso-alkane (2,9-dimethyldecane). Won et al.[25] conducted an experimental investigation on the reflected shock ignition delay times of iso-dodecane at 20 and 40 atm over stoichiometric and rich conditions. By comparing the iso-dodecane (IC12) IDT results with a blend of iso-octane (IC8) and iso-cetane (IC16) data, it was discovered that the ignition delay times of IC12 at high-to-intermediate temperatures are similar to those of a 50/50 molar blend of IC8/IC16. Based on the shock tube ignition delay results, identical combustion property targets, and similar chemical functional group distributions for IC12 and the 50/50 blend of IC8/IC16, it was suggested that this quantitatively identical behavior of the ignition delay over high- and low-temperature regimes can be applied in developing combustion kinetic models for IC12. Iso-dodecane ignition delay data at 16 atm over the temperature range of 980−1800 K and in lean conditions were provided by Flora et al.[26] during their investigation on the effect of the fuel composition and particularly different hydrocarbon classes (*n*-alkanes, heavy- and light-branched iso-alkanes, and aromatics) on the ignition characteristics of jet fuel surrogates. Further research was conducted recently by Mao et al.[27] on iso-dodecane autoignition behavior covering both low and high-temperature regimes. They studied the IDT using RCM and shock tube facilities over a wide range of pressures, temperatures, and equivalence ratios and then developed a kinetic mechanism for the prediction of the ignition delay. This detailed kinetic mechanism, which was validated against their experimental data, consists of 729 species and 3390 reactions. Fang et al.[28] performed an experimental and numerical investigation on the autoignition of four iso-alkanes, including iso-octane, iso-nonane, iso-dodecane, and iso-cetane. The work is a valuable contribution to the understanding of the ignition characteristics of the highly branched iso-alkanes, which have

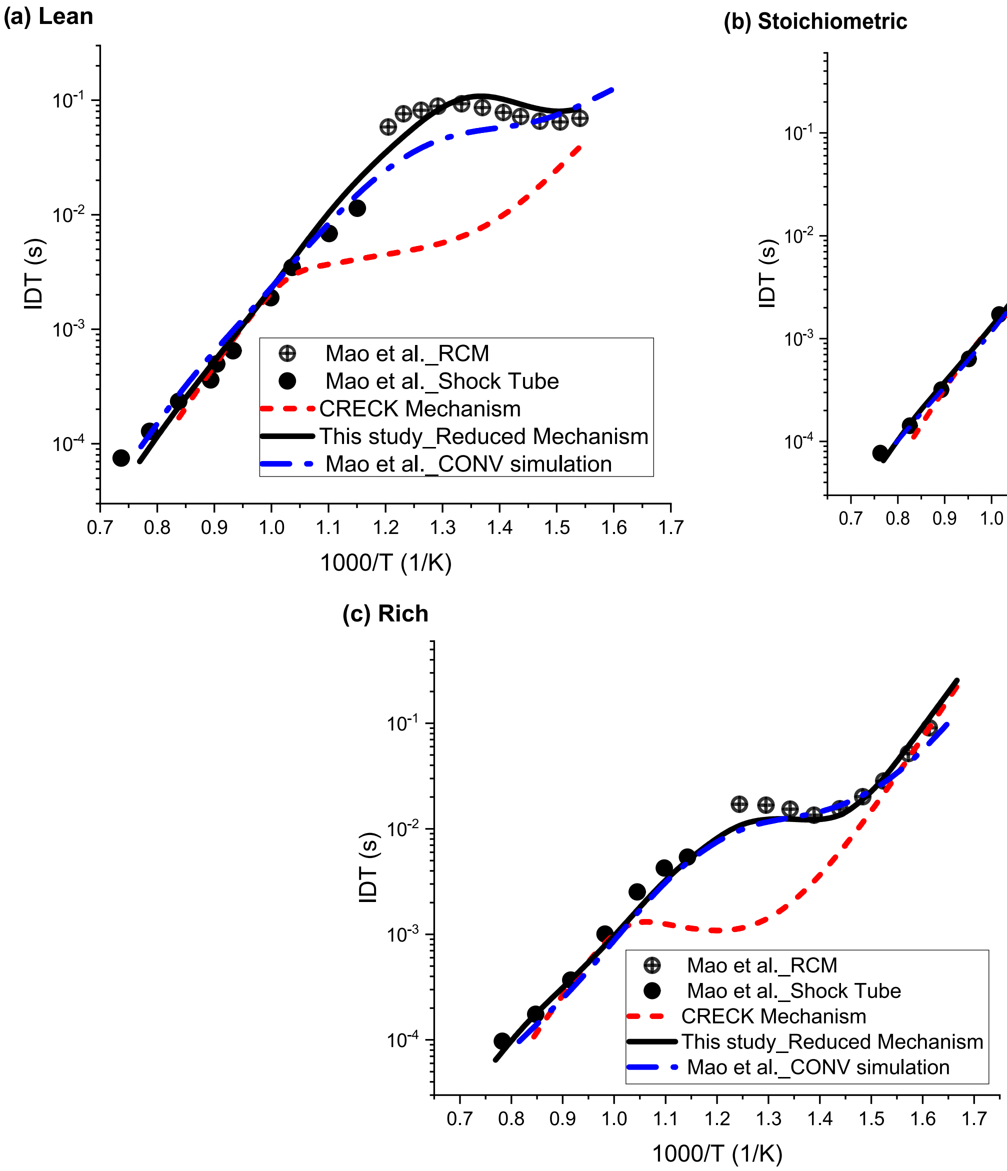


Figure 2. IDT results of the original Creck mechanism and the developed mechanism of this study against the experimental data at $P = 20$ bar for lean ($\varphi = 0.5$), stoichiometric ($\varphi = 1$), and rich ($\varphi = 1.5$) conditions.[27,29]

the potential to be used as a component for jet fuel surrogates. It also provided an opportunity to make a comparison of the autoignition behavior of different iso-alkanes at varying pressures, temperatures, and equivalence ratios. Later, in 2020, they published a comparative investigation focussing particularly on the autoignition characteristics of IC12 and IC8,[29] providing information on the influence of the fuel molecular structure on the autoignition characteristics of these two iso-alkanes at low temperatures. It was reported that IC12 has less reactivity than IC8 in a temperature window in the negative temperature coefficient regime and shows more reactivity than iso-octane outside of the temperature window. This detailed chemical kinetic mechanism includes 3252 species and 11 459 reactions. They also made their developed detailed kinetics mechanism available for iso-dodecane.

Although some previous works as described have been conducted to provide chemical kinetics mechanisms for the autoignition of iso-dodecane, especially the detailed mechanisms recently developed by Mao et al.[27] and Fang et al.,[29] there is still a lack of a compact, well-validated mechanism that would facilitate its application for CFD studies and also deliver a close emulation for the autoignition behavior of IC12 over a wide range of conditions. The conditions include pressures up to 40 bar, equivalence ratios of 0.5, 1, and 1.5, and temperatures from 600 to 1300 K, which makes the mechanism applicable for combustion systems other than jet engines working primarily in the high-temperature regime, such as diesel/HCCI engines. Therefore, this investigation is dedicated to providing a mechanism that can fulfill the requirement for a small-size mechanism and, more importantly, the need for a model producing results that accurately agree with the experimental data. In addition, this work challenges the predictive ability of the proposed mechanism for laminar flame speed simulations, since this is a very important combustion parameter, particularly for its application as an ATJ surrogate.

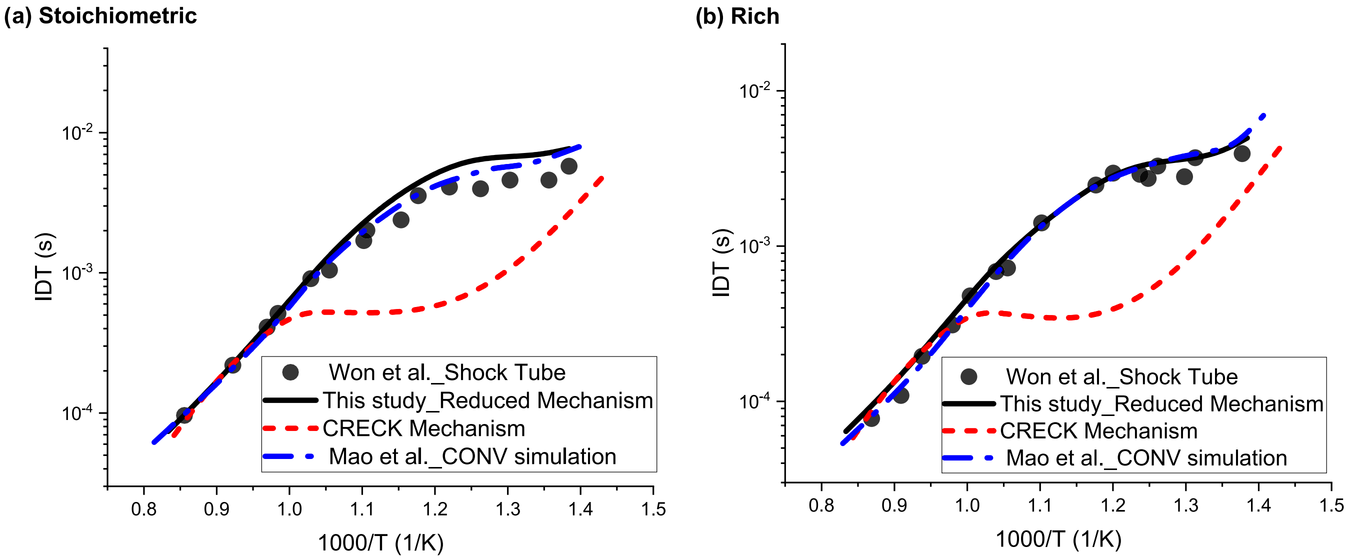


Figure 3. IDT results of the original Creck mechanism and the developed mechanism of this study against the experimental data at $P = 40$ bar for stoichiometric ($\varphi = 1$) and rich ($\varphi = 1.5$) conditions.[25]

2. MODEL DEVELOPMENT, SIMULATION, AND VALIDATION

2.1. Model Development Principles. The decoupling methodology, which utilizes coupling a detailed C_0-C_n mechanism as the core to a simplified sub-mechanism of C_n-C_m, where m is the carbon number of the intended heavy hydrocarbon, is applied to provide a compact mechanism for IC12, as this methodology is an effective approach to build a compact mechanism for heavy hydrocarbons.[30] A well-developed, simplified sub-mechanism of a heavy hydrocarbon considerably reduces the number of species and reactions in the final model by only considering the representative species required for the prediction of the intended combustion parameter of the heavy hydrocarbon. The iso-dodecane sub-mechanism of this study was developed on the basis of the IC12 kinetics model (C1−C16 HT + LT mechanism version 2003, March 2020) available in the Creck group comprehensive, detailed mechanism for the oxidation of heavy hydrocarbons[31] that includes many components for a range of hydrocarbon classes. As the mechanism focuses on the prediction of ignition delay, it keeps the number of species and reactions relatively small. The IC12 reaction mechanism is a lumped version model with a limited number of species and reactions, in which only one isomer is considered for each species, which is helpful when the goal is the development of a compact mechanism. This will benefit the optimization process in reducing the number of required modifications to provide a close agreement for the simulation of autoignition characteristics. The C6−C12 sub-mechanism development process includes the extraction of the 13 species and 65 reactions from the Creck group comprehensive, detailed mechanism (includes 492 species and 17 790 reactions), the addition of the new species and the new reactions that were recently published by Mao et al.,[27] the application of the available new rates in the literature for some reactions of the C6−C12 sub-mechanism, and, finally, the elimination of the insignificant species and reactions, which resulted in 44 species and 71 reactions for the IC12 sub-mechanism. In the Creck group mechanism, the core mechanism is extremely detailed, and that causes the overall mechanism to be very big, even after mechanism reduction. Thus, the iso-dodecane model covering the C6−C12 species has been coupled as a sub-mechanism to an alternative well-validated base model for the C0−C5 chemistry.[32,33] Because of the dominating role of small species in predicting the laminar flame speed of heavy hydrocarbons and the necessity for a detailed description of those species in emissions prediction, and the simplified nature of the core mechanism in comparison with other available detailed mechanisms, this C0−C5 model has been applied in this investigation. While the prediction ability of other detailed mechanisms is usually limited on one intended combustion parameter such as ignition delay, this C0−C5 core model could satisfactorily predict the important species mole fraction of heavy hydrocarbons,[32,33] in addition to the ignition delay and the laminar flame speed. Thus, it has the potential of being used for the prediction of species concentrations produced from IC12 combustion if experimental data would be available in the future.

2.2. Initial Simulations. The original sub-mechanism needs to be modified as its simulation results (dash lines) illustrated in Figures 2−4, in the low-temperature region, showed significant discrepancy and a large underestimation in IDT over the low to intermediate temperature regions, compared to the experimental data published in the literature.[25,27,29] Thus, some revisions are required to be applied in the IC12 sub-mechanism to improve the agreement of IDT with the experimental data.

2.3. Mechanism Optimization. Despite the fact that jet engines usually operate at high temperatures, the understanding of ignition behavior for components such as IC12 at low temperatures is of great importance, especially for its usage as a surrogate or a component in a surrogate in diesel (and HCCI) engines.[34−36] To improve the agreement of IDT with the experimental data, some revisions are incorporated into the reactions and rate constants in the IC12 sub-mechanism based on recent experimental and theoretical rate calculations.[27,29] These sources were utilized to make the reaction mechanism classes of this study complete by adding the missing reactions and to modify the rate constants of several of the reactions involving the IC12 radicals. To do this, a series of sensitivity analyses were conducted for the mechanism to identify the

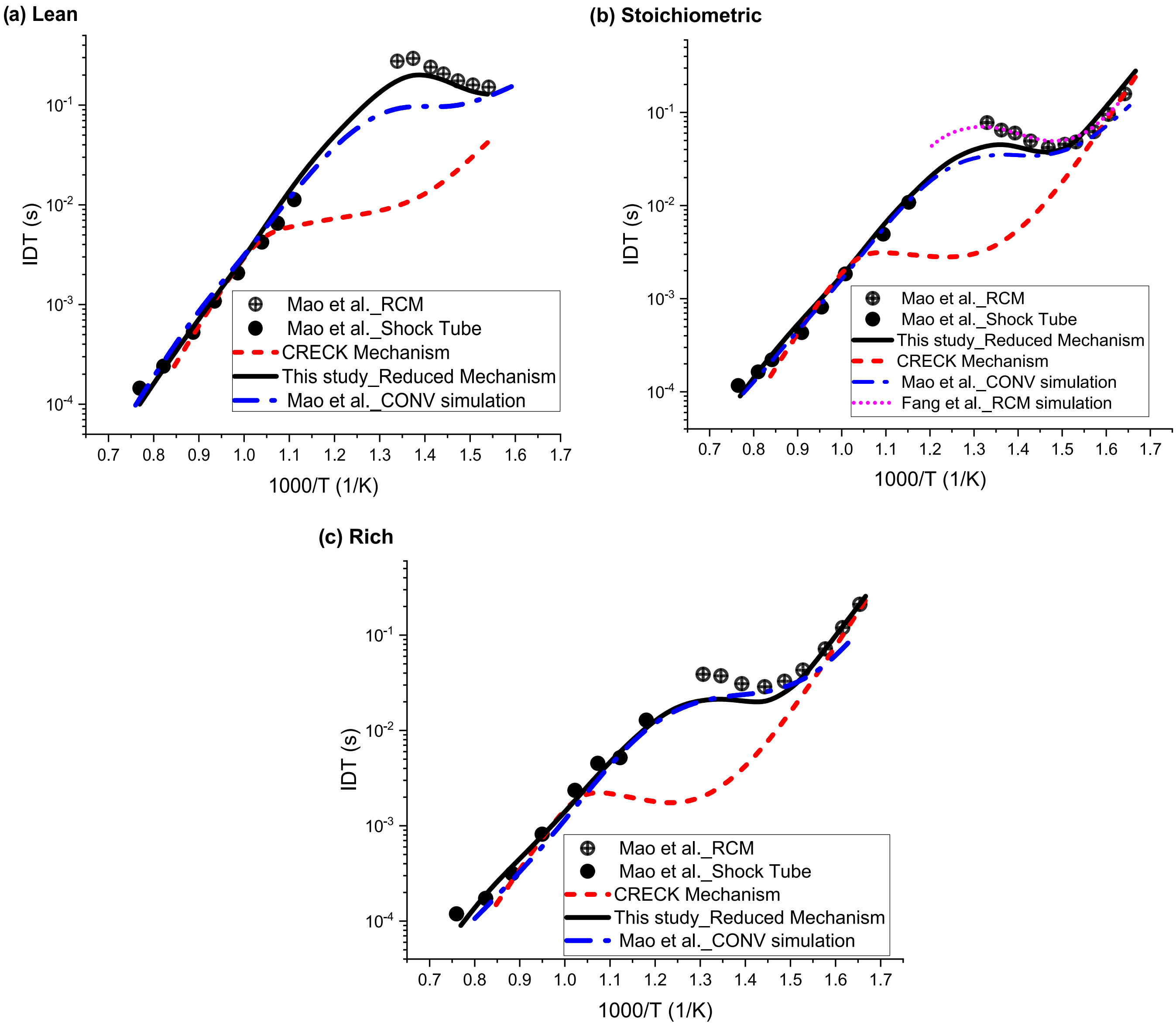


Figure 4. IDT results of original Creck mechanism and the developed mechanism of this study against the experimental data at P = 15 bar for lean (φ = 0.5), stoichiometric (φ = 1), and rich (φ = 1.5) conditions.[27,29]

most important reactions to consider for reaction rate modification. Also, the important missing reactions to add were identified by making a comparison between the reaction classes of this study and the utilized mechanisms.[27,29] The important reactions in the sub-mechanism that were added or underwent rate modification to optimize the mechanism performance and match the experimental data in a wide range of conditions are as follows:

$$IC_{12}H_{25} \rightleftharpoons H + IC_{12}H_{24} \quad (R1)$$

$$IC_{12}H_{24} + OH \rightarrow IC_{12}H_{23} + H_2O \quad (R2)$$

$$IC_{12}H_{24} + OH \rightleftharpoons TC_4H_9CHO + C_7H_{15} \quad (R3)$$

$$IC_{12}H_{24} + H \rightarrow IC_{12}H_{23} + H_2 \quad (R4)$$

$$IC_{12}H_{24} + O \rightleftharpoons TC_4H_9CHO + C_7H_{14} \quad (R5)$$

$$IC_{12}H_{24} + O \rightarrow IC_{12}H_{23} + OH \quad (R6)$$

$$IC_{12}H_{24} + CH_3 \rightarrow IC_{12}H_{23} + CH_4 \quad (R7)$$

$$IC_{12}H_{23} + HO_2 \rightarrow TC_4H_9CHO + A - C_3H_4 + T - C_4H_9 + OH \quad (R8)$$

$$IC12 - OOQOOH \rightleftharpoons HO_2 + IC12 - QOO \quad (R9)$$

$$IC12 - QOO \rightarrow TC_4H_9CHO + A - C_3H_4 + T - C_4H_9 + OH \quad (R10)$$

$$IC12 - QOOH \rightarrow OH + IC12 - QO \quad (R11)$$

$$IC12 - QO + OH \rightarrow H_2O + C_4H_9CO + C_7H_{14} \quad (R12)$$

$$IC12 - QO + HO_2 \rightarrow H_2O_2 + C_4H_9CO + C_7H_{14} \quad (R13)$$

$$IC_{12}H_{26} \rightleftharpoons C_{11}H_{23} + CH_3 \quad (R14)$$

Table 2. Modified Core Reaction Rate Parameters (cm^3, mole, s, cal/mol Units)

reaction	original rate parameters	new rate parameters	new rate reference
$HO_2 + OH \rightleftharpoons H_2O + O_2$	2.89×10^{13}, 0.0, −496.89	7.0×10^{12}, 0.0, −1092.96	37
$CH_2O + OH \rightleftharpoons HCO + H_2O$	3.43×10^{9}, 1.18, −446.94	1.72×10^{9}, 1.2, −447.0	37
$CH_3 + HO_2 \rightleftharpoons CH_3O + OH$	1.0×10^{13}, 0.0, 0.0	5.0×10^{11}, 0.3, −687.6	37
C_2H_6 (+M) $\rightleftharpoons$ $2CH_3$ (+M)	1.88×10^{50}, −9.72, 107342.26	9.21×10^{16}, −1.2, 635.8	37
$C_8H_{15} \rightarrow A\text{-}C_3H_5 + C_{50}$	2.0×10^{12}, 0.0, 29971.32	8.8×10^{13}, 2.5, 6130.0	37
$C_8H_{17} \rightarrow C_5H_{10} + N\text{-}C_3H_7$	9.431×10^{10}, 0.336, 24 031.31	5.49×10^{11}, 0.6, 28 087.1	37

$$C_{11}H_{23} \rightleftharpoons I - C_4H_8 + C_7H_{15} \qquad \text{(R15)}$$

It was found that the inclusion of reactions R9−R12 has a significant impact in improving the agreement between the model and experiment, particularly in the NTC regime of the ignition delay and on a part of the low-temperature zone. Reactions R2−R8 also had a contribution to the improvement of the IC12 ignition delay on the low- and intermediate-temperature areas. Addition of reactions R14 and R15 help to optimize the performance of the mechanism in high and intermediate temperatures. On the other hand, to provide more improvement for the high-temperature regime, the following reactions in Table 2 from the mechanism were optimized based on the reliable, detailed mechanisms developed for jet fuels by Daguat et al.[37]

Since the integration process of two separate in-house mechanisms (the sub-mechanism and the core mechanism) requires adding some reactions, especially in the interface of coupling the two mechanisms, including C_5−C_6 species, the addition of some additional reactions was applied into the core mechanism, with the aid of mechanisms previously developed for jet fuels.[31,37] The added reactions can be found at the end of the mechanism file in the Supporting Information.

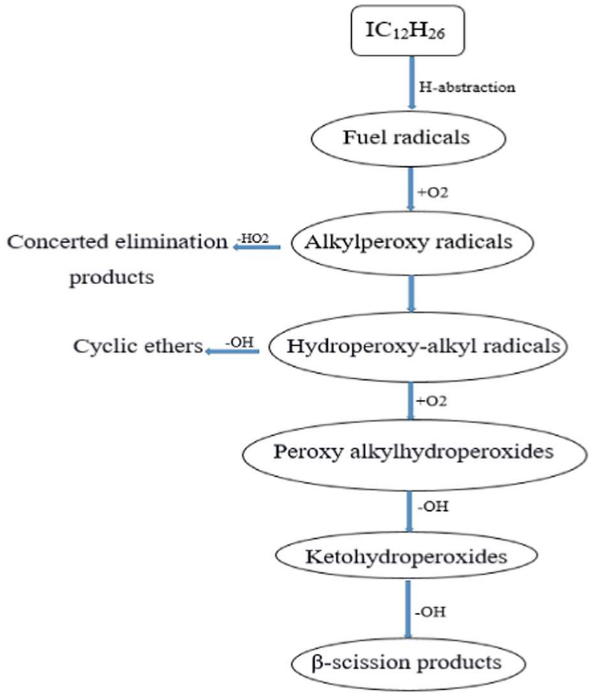
The improved IC12 mechanism, including the sub-mechanism arising from the CRECK group's IC12 mechanism coupled to a slightly expanded core mechanism, consisted of 278 species and 1860 reactions. A combination of the DRGEP and DRGPFA methods and tools available in ANSYS Chemkin-Pro for reduction purposes were applied to reduce the mechanism and provide a more compact model. The main principles of the reduction methods briefly include defining a norm, applying the norm for the definition of a directed relation graph structure, defining a set of target species, searching the directed graph, and removing the species with a coefficient below a defined threshold. The details applied for the reduction methods include ignition delay for "Target," "absolute tolerance" = 0.00001, "relative tolerance" = 30%, and end point for "value used in comparison." The final version of the developed mechanism after reduction has 158 species and 977 reactions. This reduced version follows the IDT results of the main mechanism with negligible differences. The new kinetic model is able to predict oxidation over low to high temperatures for a wide range of conditions in a more compact size compared to the available IC12 mechanisms.[25,27,29] Finally, this mechanism has been validated comprehensively using all of the currently available experimental data. In general, the mechanism developed with the aid of the decoupling methodology demonstrates a close agreement compared to the experimental data for 15, 20, and 40 bar, at three equivalence ratios (φ) of 0.5 (lean), 1 (stoichiometric), and 1.5 (rich), in the wide range of temperature from 600 to 1300 K, which can prove the approach is a promising method for the development of a reaction kinetics mechanism for heavy hydrocarbons. In comparison with the modeling results in the literature,[27] this study shows a considerable improvement at the lean condition for 15 and 20 bar and also a minor improvement at other conditions.

2.4. Optimized Mechanism Results.

Simulations for the IDT of IC12 were conducted at varying conditions with the aid of the new proposed kinetic model using the closed homogeneous batch reactor model in ANSYS Chemkin-Pro 2019 R1 software and were validated against the available experimental data in the literature, see Figures 2−4. The performance of the model was investigated at the three regimes of low, intermediate, and high temperatures. In spite of some discrepancies under certain conditions, the model shows, in general, a good agreement with the experimental data at different pressures and equivalence ratios. Typical NTC behavior was observed for all of the conditions in accordance with the experimental data, along with the reduction in the IDTs for higher pressures over the temperature regime covering the NTC behavior. At 15 bar, the simulated IDT for 750 K and 800 K is slightly shorter at lean and stoichiometric conditions and longer at the rich condition than the RCM empirical data, and a part of this can be related to the experimental uncertainty of the RCM measurements reported by the authors. Indeed, the considerable heat loss effect in the RCM tests[27] during the compression stroke, especially for the low pressure of 15 bar where there are relatively longer IDTs, might account for it, although using a lumped mechanism restricts the performance of the mechanism at some temperatures. To improve the performance of the model, more fundamental kinetics studies on the contribution of individual reactions to the behavior of the iso-dodecane at the pressure of 15 bar or less should be conducted, and this approach has been recommended recently when working on the autoignition of IC12.[27] Considering the discrepancies, the proposed kinetic model demonstrated an acceptable and reasonable behavior, especially at 20 bar, in predicting the IDT. The predictive capability of this mechanism, as well as its compact size, makes it a suitable candidate for application as a surrogate for fuels and CFD simulations.

In addition, there is a notable discrepancy between the RCM data and ST data at $\varphi = 0.5$ in the work of Mao et al., which may be due to the invalidity of the homogeneous core assumption of the RCM due to the mass loss in the facility crevices or heat loss through the walls, and the inhomogeneity and boundary layer phenomenon in the shock tube.[38] This issue was reported previously for the other fuels having low reactivity or high octane number,[38−41] and more research in the future should be performed to identify the reasons for this discrepancy. The experiments show nonideal pre-ignition pressure rise at low temperatures around 900 K due to the inhomogeneous ignition phenomenon[42,43] and therefore cannot be accurately modeled using zero-dimensional simulations.[38]

(a) Main low temperature pathways:



(b) Main high temperature pathway:

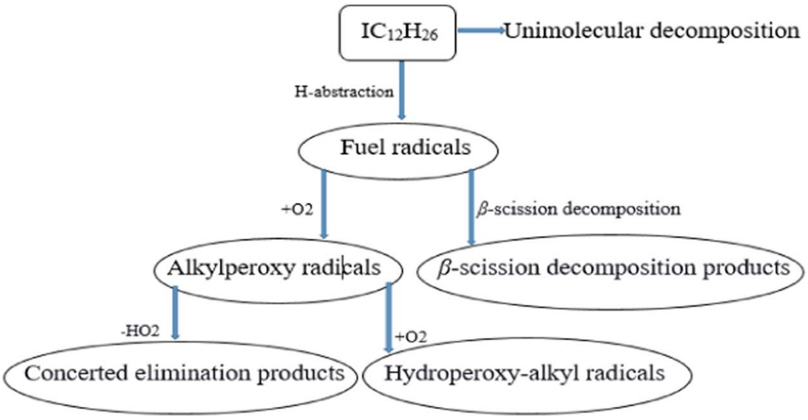


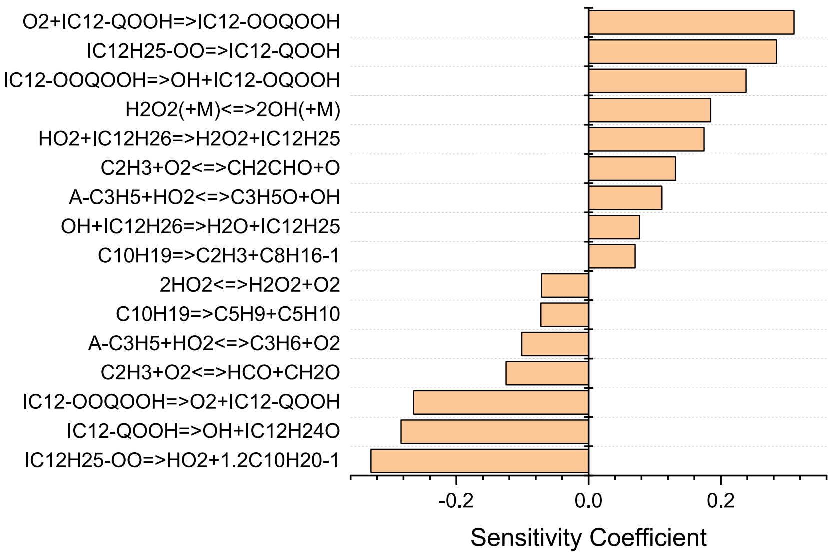
Figure 5. Main low and high pathways of the mechanism developed in this study, at (a) 800 K and (b) 1200 K.

3. KINETIC ANALYSIS

Reaction pathway analysis is a tool that can provide a better understanding of reaction mechanisms by determining the contribution of each reaction to the production and consumption of every species with the aid of a rate-of-production analysis. Therefore, a reaction pathway analysis was performed based on the rate-of-production data produced within Chemkin-Pro, in stoichiometric conditions at 20 bar with a closed homogeneous batch reactor at 800 K as representative of low and intermediate-temperature regimes, and at 1200 K as representative of the high-temperature regime. An overview of the main reaction routes is given in Figure 5.

Analysis of the reaction pathway for a stoichiometric iso-dodecane/air mixture for the developed model for this study at 800 K shows that H-atom abstraction, in particular, by the OH radical that leads to the formation of fuel radicals, is responsible for the majority of fuel consumption. Due to the first O_2 addition process, the formed radicals generate alkylperoxy radicals (RO_2), which is the start of the chain branching reaction sequence of low temperature, and this is the reaction channel contributing to the consumption of nearly all of the produced radicals. These form alkylhydroperoxy radicals (QOOH) via an intramolecular hydrogen abstraction that are mainly consumed in two ways: the production of a cyclic ether or the formation of peroxy-alkylhydroperoxides (OOQOOH) via a second O_2 addition process. Following the decomposed route, the OOQOOH radical forms an OH and ketohydroperoxides, which finally decompose to the β-scission products rather than the common low-temperature branching (OOQOOH → 2OH + RO), which shows that the iso-dodecane is less reactive. The presence of the tertiary carbon-hydrogen bond can be attributed to this result, as reported by previous authors.[44] An alternative isomerization route for OOQOOH and a similar outcome is also provided in this study, although its contribution remains trivial and, in general, the rate

(a) 800 K, φ=1.0, 20 bar



(b) 1200 K, φ=1.0, 20 bar

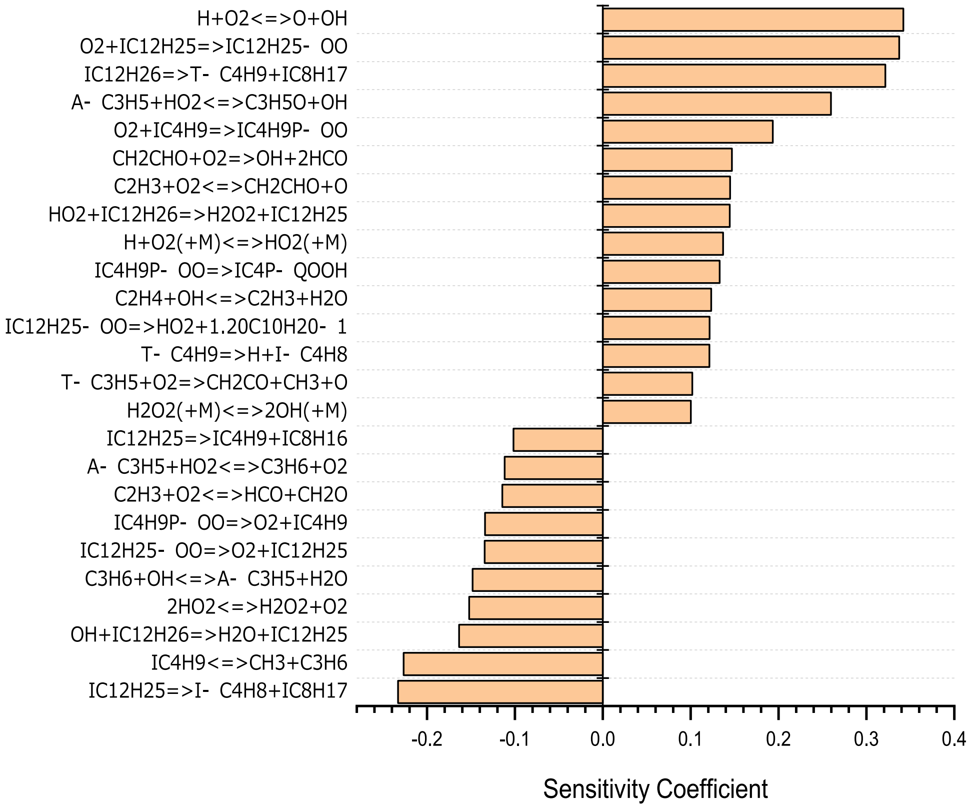


Figure 6. Sensitivity analysis at 20 bar for stoichiometric condition at (a) low and (b) high temperatures.

constant of this reaction branch has little information. In addition to the isomerization of RO_2 (RO_2 → QOOH channel) as the main route of the RO_2 consumption, the concerted elimination reaction is another significant channel of RO_2 decomposition that has a contribution for the NTC behavior of IC12 by the formation of more stable alkenes, which in turn leads to the reduction in the overall reactivity. It appears that the competition between this reaction class, the cyclic ether formation reaction, and degenerate chain branching reactions forms the NTC behavior.

Concisely, for the main low-temperature pathway, the R + O_2 ⇌ RO_2 strongly favors RO_2, as does the QOOH + O_2 favoring O_2QOOH, and this leads to the low-temperature chain branching that enhances the rate of the fuel consumption. As the temperature increases, these equilibria favor the separate R + O_2, QOOH + O_2, thus reducing the

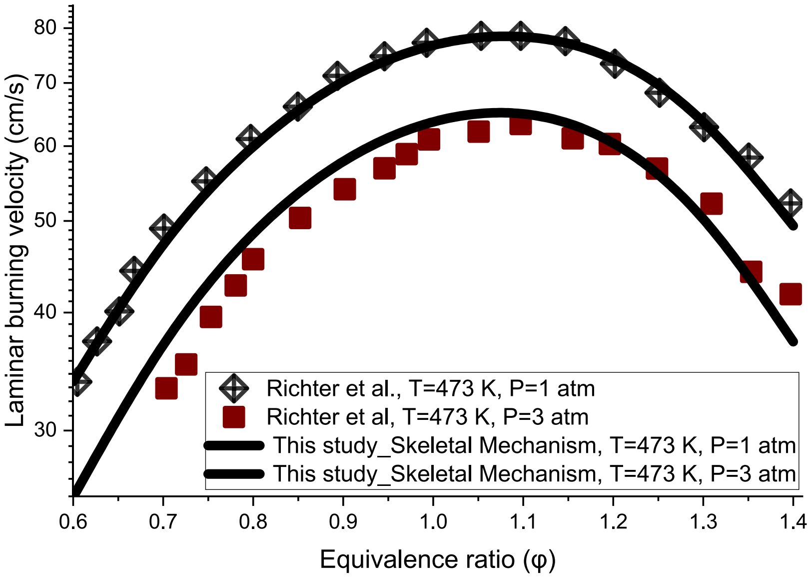


Figure 7. Laminar flame speed simulation results of the developed mechanism of this study at the unburned temperature of 473 K against the experimental data of ATJ fuel at P = 1 and 3 bar.[45]

chain branching processes and hence slowing the overall reaction rate, even though the temperature has increased. The formation reactions of cyclic ethers and the concerted elimination reactions appear to be the important side reactions that compete with the main low-temperature pathways.

Based on the reaction routes at 1200 K for stoichiometric iso-dodecane/air mixture, as illustrated in Figure 5b, unimolecular decomposition and H-atom abstraction that dominate the fuel conversion (mostly by the OH abstractor) are the channels that consume IC12 and have a substantial contribution to the combustion chemistry in the high-temperature regime. The resulting $IC_{12}H_{25}$ radicals undergo an O_2 addition process (forming alkylperoxy radicals) and β-scission decomposition. The C−C and C−H bonds in the $IC_{12}H_{25}$ radicals are opened via β-scission and then generate olefins and alkyl radicals, which in turn undergo successive β-scission reactions, ultimately decomposing to generate small molecules and radicals that are depleted according to the provided core mechanism. Therefore, the β-scission reactions and the reactions of small species play a significant role in the high-temperature regime. Further, in the sensitivity analysis, it can be observed how much the small species reactions, such as $H + O_2 \rightleftharpoons O + OH$, contribute greatly to controlling the combustion chemistry in the high-temperature regime.

To identify the key reactions relevant to the ignition of iso-dodecane, sensitivity analyses were performed for the ignition delay time of the developed skeletal mechanism at the same temperatures and conditions of the reaction pathway analysis. Figure 6 demonstrates the top reactions that have a greater impact on the ignition delay time according to the magnitude of their sensitivity coefficients. It can be seen from Figure 6a that the reactions with the greatest promoting effect on the ignition delay time are the isomerization of alkylperoxy, the second oxygen addition, and the isomerization of OOQOOH to the ketohydroperoxides. The H abstraction reactions have a relatively great promoting effect, especially by the HO_2 abstractor that leads to the generation of hydrogen peroxide which in turn boosts the combustion process by producing two reactive OH radicals through $H_2O_2 \rightarrow 2OH$. The reaction of $C_2H_3 + O_2 \rightleftharpoons CH_2CHO + OH$ that the C_2H_3 radicals undergo in the branching reaction to form two reactive radicals has also a relatively great promoting effect.

Since the fuel radicals at higher temperatures break down directly without going through the low-temperature pathways, the rate of OH production is decreased in the low-temperature pathways. Thus, in spite of the OH production, which has a promoting effect on fuel consumption through H abstraction reactions in the reaction forming cyclic ethers, this reaction has a very strong inhibiting effect. The concerted elimination reaction of the alkylperoxy radicals is the strongest inhibitor and reduces the overall reactivity via the formation of more stable alkenes. This higher inhibiting effect of the concerted elimination than the cyclic ether formation is because of the lower reactivity of the produced HO_2 radicals compared to the generated OH radicals, which compensate a part of the decreased reactivity by the reaction of cyclic ethers. IC12-OOQOOH → O_2 + IC12-QOOH is the third reaction that is among the strongest inhibitors.

As discussed in the reaction pathway analysis, the reactions of small species dominate the reactivity of the system in the high-temperature regime and show strong promoting and inhibiting effects, as illustrated in Figure 6b. Among the top-ranked promoter reactions are the small species reactions of the coupled core mechanism, which only generate more active radicals. The unimolecular decomposition of iso-dodecane and the formation of the alkylperoxy radicals are the strong promoting reactions at this temperature. As can be seen in the figure, the importance of the reactions in the low-temperature chain branching pathways (which demonstrated a significant promoting/inhibiting effect at 800 K) becomes trivial at the high-temperature regime, and H abstraction by HO_2 and OH still has a considerable promoting and inhibiting effect at this temperature. On the other hand, in addition to some small species reactions (such as those that produce stable alkenes) showing a strong inhibiting effect, the β-scission of the fuel radicals also indicated a strong inhibiting effect.

4. FLAME SPEED

The simulations of the laminar flame speed given in Figure 7 were conducted at 1 and 3 bar for the unburned combustion temperatures of 473 K and a range of equivalence ratios from 0.6 to 1.4. Due to the lack of empirical data for the laminar flame speed of IC12, the results were compared to the results of the available experimental data for ATJ fuel,[45] which consisted predominately of iso-dodecane in excess of 90% and thus can be expected to provide a close approximation for the flame speed behavior of IC12. Similar to the rate optimization process implicated for the ignition delay, the procedure was conducted for laminar flame speed to provide an improved mechanism that can simulate the flame speed behavior of IC12 with a close agreement. The selection of candidate reactions for optimization was done by considering the sensitivity analysis results, the availability of different rate constants, and the fact that the modifications should not negatively affect the results of ignition delay significantly. In this regard, the reactions of $HCO + H \rightleftharpoons CO + H_2$ and $CH + CO (+M) \rightleftharpoons HCCO (+M)$ were optimized based on the available rate constants in the literature.[29,36]

The skeletal mechanism demonstrates an excellent simulation for the laminar flame speed at 1 bar and a relatively close emulation at 3 bar compared to the empirical data, although discrepancies are found at the fuel-lean side for 3 bar. However, more experimental data on the laminar flame speed of pure iso-dodecane is needed to have a certain interpretation of the prediction ability of the provided mechanism for the laminar flame speed.

5. CONCLUSIONS

A compact reaction kinetic mechanism covering both the low-temperature and the high-temperature reaction schemes was developed based on the decoupling methodology for iso-dodecane as an important surrogate component of conventional and alternative fuels. A well-validated core mechanism was coupled to a provided sub-mechanism of IC12. Modifications, including a change of a few of the reaction rates and adding some reactions to the core and sub-mechanisms, were applied to improve the performance of the developed mechanism to emulate the empirical data of the IC12 ignition behavior. The improved mechanism could follow closely the experimental data over the low-to-high temperature, and it is in reasonable agreement for lean, stoichiometric, and rich conditions at different pressures. However, some discrepancies are still observed between the new modeling and experimental results for a certain temperature at 15 bar, especially for rich conditions, which might be related to the reported uncertainties in the experimental results. Despite the discrepancies, this compact mechanism is an improvement over existing mechanisms in terms of an overall good agreement for IDT of iso-dodecane in a wide range of conditions. The kinetic analysis includes the analysis of the reaction pathways, and a sensitivity analysis was conducted to identify the main pathways and the key reactions of the developed mechanism. The simulations of the laminar flame speed were conducted at 1 and 3 bar and were compared against the empirical data for ATJ fuel that contained over 90% IC12; the results were found to be in good agreement with the experimental data. The improved mechanism was reduced by DRGEP and DRGPFA reduction methods available in Chemkin-Pro so that the final version of the developed mechanism includes only 158 species and 986 reactions. In conclusion, the predictive capability and the compact size of the developed mechanism make it a useful tool for use in the application as a surrogate for fuels and also for some CFD simulation works, including complex geometries of combustion systems (such as Equivalent Reactor Network analysis).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c03539.

> Chemical kinetic mechanism files: Chemkin-Pro format of the skeletal and the compact mechanism files, thermodynamics data for the mechanism file, and transport data for the mechanism file (ZIP)

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

ATJ = alcohol to jet
CFD = computational fluid dynamics
CPT = combustion property target
DCN = derived cetane number
DRGEP = directed relation graph error propagating
DRGPFA = directed relation graph path flux analysis
H/C = hydrogen-to-carbon ratio
IC8 = iso-octane
IC12 = iso-dodecane
IC16 = iso-cetane
IDT = Ignition delay time
LES = large Eddy simulation
MW = molecular weight
NTC = negative temperature coefficient
OOQOOH = peroxy alkylhydroperoxides
QOOH = hydroperoxy-alkyl radicals
RCM = rapid compression machine
RO_2 = alkylperoxy radicals
ST = shock tube

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