Comprehensive Comparison of the Combustion Behavior for Low-Temperature Combustion of \(n\)-Nonane

Junjiang Guo,* Weijun Peng, Shijie Zhang, Jiazhi Lei, Jiantong Jing, Ruyi Xiao, and Shiyun Tang

1. INTRODUCTION

With the development of the aerospace industry, especially the acquisition of supersonic flight technology, higher technical requirements are put forward for the development and design of advanced engines. Aviation fuel gradually emerged with the birth of the aircraft at the beginning of this century. In order to ensure flight safety and long lifespan of engines, there are strict requirements on fuel quality. Linear para-\(n\)-nonane is a typical representative of \(n\)-alkanes in petroleum-based fuels,3\,4 and detailed combustion mechanism usually contains a very large number of species and reactions, the mechanism for manual construction takes a long time and is prone to errors. Conversely, this paper proposes a method to develop a high-precision low-temperature mechanism for the conditions is important because of the complexity of large hydrocarbon fuels, the kinetic models currently used to describe \(n\)-nonane combustion are extremely rare, and are primarily acquired by manual construction. Among them, Westbrook et al. developed a kinetic model (LLNL model)\,12 for describing the pyrolysis and oxidation of linear alkanes (from \(n\)-octane to \(n\)-hexadecane) over a wide temperature range; Wang et al. developed a kinetic model (JetSurf 2.0 model)\,13 for the high-temperature oxidation of linear alkanes; cyclohexane; and methyl, ethyl, \(n\)-propyl, and \(n\)-butyl cyclohexanes. Because the detailed combustion mechanism usually contains a very large number of species and reactions, the mechanism for manual construction takes a long time and is prone to errors. Conversely, this paper proposes a method to develop a high-precision low-temperature mechanism for the

Received: November 6, 2019
Accepted: February 24, 2020
Published: March 5, 2020
combustion of n-nonane using an automatic mechanism construction program.

At present, there have been a few automatic mechanism generation programs, such as EXGAS\(^{18}\) developed by Battin-Leclerc et al., MAMOX\(^{15}\) developed by Ranzi’s research group in Milan, REACTION\(^{10}\) developed by Blurock et al., RMG\(^{27}\) developed by Green et al., and ReaxGen\(^{18}\) developed by Li Xiang Yuan’s team. Among them, ReaxGen has successfully developed some low-temperature combustion mechanisms for large hydrocarbons, such as n-heptane,\(^{19,20}\) n-decane,\(^{21}\) and n-undecane.\(^{21}\) Accordingly, this paper mainly uses ReaxGen to automatically generate the new detailed mechanisms for low-temperature combustion of n-nonane. In order to verify the reliability and rationality of the new mechanisms, a few internationally published models that can be used for n-nonane combustion simulation are compared with them, such as the LLNL model\(^{22}\) and the JetSurf 2.0 model.\(^{23}\) This study aims to investigate the ignition delay time in a shock tube, the concentration of important species in the jet stirred reactor (JSR), and the propagation speed of the premixed laminar flame. Furthermore, the numerical simulation results of these combustion models are analyzed and compared with the effective experimental data in literature. Finally, the sensitivity analysis and the reaction path analysis are used to identify the types of reactions that are critical for low-temperature ignition.

### 2. MECHANISM CONSTRUCTION

The detailed combustion mechanism of hydrocarbon fuels can be constructed according to the hierarchical structure.\(^{19,22}\) The core mechanism is crucial to explain the combustion characteristics of large hydrocarbons.\(^{25}\) Generally, the mechanism construction for large hydrocarbons mainly includes two parts: the core mechanism and the expansion mechanism. The core mechanism is mainly low-carbon hydrocarbon molecules and free radicals (less than four carbon atoms). Previous studies have shown that AramcoMech 1.3\(^{24}\) and AramcoMech 3.0\(^{25}\) developed by Curran’s group have a good effect on the mechanism construction for large hydrocarbons.\(^{19}\) Therefore, the new mechanisms of n-nonane developed in this study are mainly based on AramcoMech 1.3 and AramcoMech 3.0, respectively. In addition, the expansion mechanisms are automatically generated by ReaxGen. The fundamental concept in generating a mechanism by ReaxGen is the reaction classes. The specific reaction classes in this work are mainly:

High-temperature combustion reaction classes:

1. Unimolecular decomposition of alkanes;
2. H-abstraction from C atoms in alkanes by O, H, OH, O\(_2\), CH\(_3\), C\(_2\)H\(_5\), C\(_3\)H\(_6\), and HO\(_2\);
3. Mutual isomerization of the alkyl radical;
4. Decomposition of the alkyl radical;
5. Oxidation of an alkyl radical to form an alkene;
6. H-abstraction from alkenes;
7. Decomposition of alkenes;
8. Addition of alkenes to O, OH, CH\(_3\), H, and HO\(_2\) (CH\(_3\), H, and HO\(_2\) are not included in this work);
9. Decomposition of the alkenyl radical;
10. Retro-ene decomposition reactions;
11. Mutual isomerization of the alkenyl radical;
12. Lumped consumption reaction of the diene.

Low-temperature combustion reaction classes:

13. Alkyl addition to the oxygen molecule (\(\text{R} + \text{O}_2 = \text{ROO}^*\));
14. Isomerization of \(\text{ROO}^*\) (\(\text{ROO}^* = \text{QOOH}\));
15. \(\text{ROO}^*\) reacts with \(\text{HO}_2\), \(\text{H}_2\text{O}_2\), and the fuel molecule (RH) to form a hydroperoxide (\(\text{ROO}^* + \text{HO}_2/\text{H}_2\text{O}_2/\text{RH} = \text{ROOH} + \text{O}_2/\text{H}_2\text{O}_2^*/\text{R}\));
16. \(\text{ROOH} = \text{RO} + \text{OH}\);
17. Decomposition of alkylene radicals;
18. Hydroperoxy alkyl radical addition to the oxygen molecule (\(\text{QOOH}^* + \text{O}_2 = \text{O}_2\text{QOOH}\));
19. Decomposition of hydroperoxy alkyl radicals to form alkenes and aldehydes;
20. Decomposition of hydroperoxy alkyl radicals to form cyclic ethers;
21. \(\beta\)-pyrolysis of hydroperoxy alkyl radicals to form smaller alkenes;
22. Oxidation of hydroperoxy alkyl radicals;
23. Isomerization of \(\text{O}_2\text{QOOH} = \text{HOO}-\text{QOOH}\);
24. Homolytic O=O scission of dihydroperoxy alkyl radicals;
25. Decomposition of dihydroperoxy alkyl radicals to form hydroperoxy cyclic ethers;
26. Decomposition of ketohydroperoxides;
27. Decomposition of large carbonyl radicals;
28. H-abstraction from the cyclic ether;
29. Decomposition of the hydroperoxyl cyclic ether;
30. H-abstraction from aldehydes;
31. H-abstraction from ketones.

The kinetic parameters of these reaction classes are provided in the Supporting Information. Finally, the new n-nonane combustion mechanisms, Model v1, based on AramcoMech 1.3, including 1200 species and 4615 reactions, and Model v2, based on AramcoMech 3.0, including 1506 species and 6068 reactions, are developed (provided in the Supporting Information). In these mechanisms, the thermodynamic data and transport data for species in the core mechanisms are derived from refs 24 and 25, respectively; the thermodynamic data for other species are mainly calculated by the group
contribution method proposed by Benson;\textsuperscript{27} transport data for other species are calculated through the diffusion coefficients using the approach introduced in ref \textsuperscript{28}.

3. RESULTS AND DISCUSSION

3.1. Mechanism Validation and Comparison. In order to improve the accuracy and the applicability of the mechanisms, extensive verification is needed for the experimental data on various fuels in different temperature ranges, pressure ranges, the reaction atmosphere, and the physical model. At present, the combustion reaction dynamics experiments used to verify the model involve macroscopic combustion parameters such as the ignition delay time and the flame propagation speed and microscopic combustion parameters such as species concentration. In this paper, the new mechanisms for \(n\)-nonane combustion are verified by the experiments of the ignition delay time in a shock tube, species concentration in a JSR, and the laminar flame propagation speed. At the same time, a detailed comparison is made between the new mechanisms based on automatic program construction and the international mainstream mechanisms based on manual construction.

3.1.1. Ignition Delay in a Shock Tube. Yong et al.\textsuperscript{9} systematically studied gas-phase ignition delay experiments for \(n\)-nonane/air mixtures at temperatures ranging from 684 to 1448 K; pressures ranging from 2.0 to 15.0 atm; and

![Figure 1](https://dx.doi.org/10.1021/acsomega.9b03786)  
Figure 1. Ignition delay time of \(n\)-nonane/air mixtures in a shock tube at \(\Phi = 0.5\), with pressures of (a) 2, (b) 5, and (c) 15 atm.

![Figure 2](https://dx.doi.org/10.1021/acsomega.9b03786)  
Figure 2. Ignition delay time of \(n\)-nonane/air mixtures in a shock tube at \(\Phi = 1.0\), with pressures of (a) 2, (b) 5, (c) 9, and (d) 15 atm.

![Figure 3](https://dx.doi.org/10.1021/acsomega.9b03786)  
Figure 3. Ignition delay time of \(n\)-nonane/air mixtures in a shock tube at \(\Phi = 2.0\), with pressures of (a) 2, (b) 5, and (c) 15 atm.)
equivalence ratios of 0.5, 1.0, and 2.0. The n-nonane shock tube ignition delay experiment was simulated, with the new mechanisms and the international mainstream combustion mechanisms,12,13 by the homogeneous closed reactor model in the Chemkin-Pro package.29 The assumption of adiabatic, constant volume, and homogeneous conditions is applied for high-temperature conditions. Moreover, at longer ignition delay times such as low-temperature ignition, the gradual pressure increase can have considerable effects on the ignition process. To consider this pressure increase, an average pressure rise rate of 3%/ms was considered by employing the Senkin/VITM approach.30 The comparison between the numerical simulation results and the experimental data is shown in Figure 4.

Figure 4. Comparison of the experimental and simulated results using different mechanisms for important species concentrations containing (a) n-C9H18, (b) C2H4, (c) CH2O, (d) CH4, (e) CO, (f) CO2, (g) H2, and (h) H2O in a JSR for 0.1% n-nonane diluted in nitrogen at 1 atm, \( \phi = 0.5 \), and 0.07 s residence time.

References:
1. Comparison of the experimental and simulated results using different mechanisms for important species concentrations containing (a) n-C9H18, (b) C2H4, (c) CH2O, (d) CH4, (e) CO, (f) CO2, (g) H2, and (h) H2O in a JSR for 0.1% n-nonane diluted in nitrogen at 1 atm, \( \phi = 0.5 \), and 0.07 s residence time.
numerical simulation results and the experimental data. Besides, as shown in Figure 3a, the predicted values of the LLNL model under rich combustion conditions are slightly higher than the experimental data, those of Model v1 are slightly lower than the experimental data, and those of Model v2 are in best agreement with the experimental data. However, at a pressure of 5 atm, as shown in Figure 3b, it can be found that the LLNL model and the JetSurf 2.0 model are in good agreement with the experimental data, while our models slightly underpredict the experimental data. Different combustion results are obtained because of the discrepancies in the reaction network and reaction rates in different combustion models. From the results of ignition simulation, it is seen that the new mechanisms and the LLNL model show a higher simulation accuracy.

3.1.2. Jet-Stirred Reactor Speciation. Dagaut et al. experimentally studied the oxidation of n-nonane in the JSR over a wide range of conditions, which provided the basic data for verifying the rationality of the combustion mechanism of n-nonane. In this paper, the evolution of the concentration of important components such as n-nonane, C9H20, CH4, CH3O, CO, CO2, H2, and H2O was studied. The simulations in this section were carried out by using the transient perfectly stirred reactor code with an end time of 20 s in the Chemkin-Pro package, whose method is similar to that employed by Metcalfe et al. and Sarathy et al. The measurements and predictions

Figure 5. Comparison of the experimental and simulated results using different mechanisms for important species concentrations containing (a) n-C9H20, (b) C2H4, (c) CH2O, (d) CH4, (e) CO, (f) CO2, (g) H2, and (h) H2O in a JSR for 0.1% n-nonane diluted in nitrogen at 10 atm, $\phi = 0.5$, and 0.7 s residence time.
with Model v1, Model v2, the LLNL model, and the JetSurf 2.0 model for the molar fraction profiles of \( n \)-nonane, \( C_2H_4 \), \( CH_4 \), \( CH_2O \), \( CO \), \( CO_2 \), \( H_2 \), and \( H_2O \) are shown in Figures 4–9. The simulation conditions are performed at an initial concentration of 0.1% \( n \)-nonane; equivalent ratios of 0.5, 1.0, and 2.0; pressures of 1 and 10 atm; and residence times of 0.07 and 0.7 s. It can be seen from the figures that the numerical simulation results of the new mechanisms are in overall agreement with the available experimental data, especially at atmospheric pressure and with a residence time of 0.07 s (shown in Figures 4, 6, and 8). Model v2 is found to be superior to other combustion models for \( CO \), \( CO_2 \), \( H_2 \), and \( H_2O \) predictions, except for the \( H_2O \) molar fraction in the NTC region, as shown in Figures 5h, 7h, and 9h, for which Model v2 underpredicts the experimental data. In addition, the NTC behavior of \( n \)-nonane was discovered experimentally between 600 and 750 K, which is well reproduced by the new mechanisms from the evolution of \( n \)-nonane, \( CO \), and \( H_2O \), as shown in Figures 5, 7, and 9. In contrast, the JetSurf 2.0 model cannot reproduce the NTC behavior of fuel combustion well (shown in Figures 5a, 7a, and 9a) because of the lack of low-temperature reactions in this model.

Formaldehyde is an important intermediate for the oxidation of \( n \)-nonane from low temperatures to high temperatures. As presented in Figure 4c, the formaldehyde concentration increases above 900 K and reaches the peak value at 1050 K. The predictions of the profile of formaldehyde concentration using the new mechanisms are in satisfactory agreement with the experimental data. In addition, the NTC behavior of \( n \)-nonane was discovered experimentally between 600 and 750 K, which is well reproduced by the new mechanisms from the evolution of \( n \)-nonane, \( CO \), and \( H_2O \), as shown in Figures 5, 7, and 9. In contrast, the JetSurf 2.0 model cannot reproduce the NTC behavior of fuel combustion well (shown in Figures 5a, 7a, and 9a) because of the lack of low-temperature reactions in this model.

Formaldehyde is an important intermediate for the oxidation of \( n \)-nonane from low temperatures to high temperatures. As presented in Figure 4c, the formaldehyde concentration increases above 900 K and reaches the peak value at 1050 K. The predictions of the profile of formaldehyde concentration using the new mechanisms are in satisfactory agreement with the experimental data. In addition, the NTC behavior of \( n \)-nonane was discovered experimentally between 600 and 750 K, which is well reproduced by the new mechanisms from the evolution of \( n \)-nonane, \( CO \), and \( H_2O \), as shown in Figures 5, 7, and 9. In contrast, the JetSurf 2.0 model cannot reproduce the NTC behavior of fuel combustion well (shown in Figures 5a, 7a, and 9a) because of the lack of low-temperature reactions in this model.

Formaldehyde is an important intermediate for the oxidation of \( n \)-nonane from low temperatures to high temperatures. As presented in Figure 4c, the formaldehyde concentration increases above 900 K and reaches the peak value at 1050 K. The predictions of the profile of formaldehyde concentration using the new mechanisms are in satisfactory agreement with the experimental data. In addition, the NTC behavior of \( n \)-nonane was discovered experimentally between 600 and 750 K, which is well reproduced by the new mechanisms from the evolution of \( n \)-nonane, \( CO \), and \( H_2O \), as shown in Figures 5, 7, and 9. In contrast, the JetSurf 2.0 model cannot reproduce the NTC behavior of fuel combustion well (shown in Figures 5a, 7a, and 9a) because of the lack of low-temperature reactions in this model.

Formaldehyde is an important intermediate for the oxidation of \( n \)-nonane from low temperatures to high temperatures. As presented in Figure 4c, the formaldehyde concentration increases above 900 K and reaches the peak value at 1050 K. The predictions of the profile of formaldehyde concentration using the new mechanisms are in satisfactory agreement with the experimental data. In addition, the NTC behavior of \( n \)-nonane was discovered experimentally between 600 and 750 K, which is well reproduced by the new mechanisms from the evolution of \( n \)-nonane, \( CO \), and \( H_2O \), as shown in Figures 5, 7, and 9. In contrast, the JetSurf 2.0 model cannot reproduce the NTC behavior of fuel combustion well (shown in Figures 5a, 7a, and 9a) because of the lack of low-temperature reactions in this model.

Formaldehyde is an important intermediate for the oxidation of \( n \)-nonane from low temperatures to high temperatures. As presented in Figure 4c, the formaldehyde concentration increases above 900 K and reaches the peak value at 1050 K. The predictions of the profile of formaldehyde concentration using the new mechanisms are in satisfactory agreement with the experimental data. In addition, the NTC behavior of \( n \)-nonane was discovered experimentally between 600 and 750 K, which is well reproduced by the new mechanisms from the evolution of \( n \)-nonane, \( CO \), and \( H_2O \), as shown in Figures 5, 7, and 9. In contrast, the JetSurf 2.0 model cannot reproduce the NTC behavior of fuel combustion well (shown in Figures 5a, 7a, and 9a) because of the lack of low-temperature reactions in this model.
the measurement. At the same time, under high-pressure conditions, as shown in Figures 5c, 7c, and 9c, the prediction of formaldehyde by the new models, especially Model v2, can also be in good agreement with the experimental data. Although the new mechanisms and the LLNL model can well reproduce the NTC behavior of fuel combustion, there are still some discrepancies with the experimental data. For example, the new mechanisms, especially Model v2 can well predict the speciation of all the important species, except for C2H4 and CH4 at the pressure of 10 atm, as shown in Figure 5b,d. One of the possible reasons is that the reaction network is not fully described in these mechanisms. In order to develop a comprehensive detailed mechanism suitable for a wide temperature range, a wide pressure range, and different equivalence ratio conditions, further research work needs to be undertaken. Furthermore, our research group is trying to optimize it by combining high-precision quantum chemical calculations and species concentration analysis.

3.1.3. Laminar Flame Speeds. Laminar flame speed, as an important parameter for fuel mixture reactivity, diffusivity, and heat release, is a key factor for verifying the accuracy of the combustion model. Ji et al.11 experimentally determined the premixed flame propagation speeds of C5−C12 alkanes at atmospheric pressure. This section focuses on the verification of the flame propagation speed of n-nonane with different combustion models. Simulations were performed with the Premixed Laminar Flame-Speed Calculation code of Chemkin package.29 Figure 10 shows the comparison between the simulation results and the experimental data on the laminar flame propagation speeds at the unburned mixture temperature and 0.7 s residence time.

Figure 7. Comparison of the experimental and simulated results using different mechanisms for important species concentrations containing (a) n-C9H20, (b) C7H16, (c) CH2O, (d) CH3, (e) CO, (f) CO2, (g) H2, and (h) H2O in a JSR for 0.1% n-nonane diluted in nitrogen at 10 atm, ϕ = 1.0, and 0.7 s residence time.
of 403 K and pressure of 1.01 × 10^5 Pa. It can be clearly seen that these models have different prediction values for n-nonane. Among them, the LLNL model is in good agreement with the experimental values under rich combustion conditions. Under other conditions, it has a large error with the experimental data, especially when the equivalent ratio is 0.9–1.3. The detailed mechanisms developed in this paper are in overall agreement with the available experimental data except at the equivalent ratio from 1.0 to 1.2, at which the simulation results are slightly higher than the experimental value. The JetSurf 2.0 model, based on the core mechanism USC Mech II,32 is better than the other combustion models in predicting the laminar flame speed; it has been shown that the combustion mechanisms of large hydrocarbons, such as n-heptane,18,20 isoctane,18 n-decane,18 n-undecane,18 n-dodecane,18 methylcyclohexane,33 and n-propylcyclohexane,34 developed with USC Mech II as the core mechanism, show good performance for the prediction of laminar flame propagation speed.

3.2. Sensitivity Analysis. Sensitivity analysis plays an important role in understanding the key reactions and mechanism simplification in the fuel combustion process. Considering that there is no low-temperature combustion reaction type in the JetSurf 2.0 model, the new mechanisms and the LLNL model were selected for sensitivity analysis. The specific conditions of the sensitivity analysis are the equivalent ratio of 1.0, the initial temperature of 700 K, and the pressure of 15 atm, and the result is shown in Figure 11. There are

![Figure 8. Comparison of the experimental and simulated results using different mechanisms for important species concentrations containing (a) n-C9H20, (b) C2H4, (c) CH3O, (d) CH4, (e) CO, (f) CO2, (g) H2, and (h) H2O in a JSR for 0.1% n-nonane diluted in nitrogen at 1 atm, ϕ = 2.0, and 0.07 s residence time.](https://dx.doi.org/10.1021/acsomega.9b03786)
relatively significant differences between our mechanisms and the LLNL model in the types of key reactions that are sensitive to ignition. Among them, the reaction with the maximum promoting effect on the ignition of \(n\)-nonane, in the new mechanisms, is the reaction class \(\text{ROOH} = \text{RO} + \text{OH}\), such as \(\text{s46C9H20O2} \Rightarrow \text{OH} + \text{s170C9H19ON} \) and \(\text{s52C9H20O2} \Rightarrow \text{OH} + \text{s187C9H19ON} \) in Model v1, and \(\text{s52C9H20O2} \Rightarrow \text{OH} + \text{s187C9H19ON} \) in Model v2, and in the LLNL model is the isomerization reaction \(\text{ROO} = \text{QOOH}\), such as \(\text{s9h20o2-2} = \text{s9ooh2-4} \). For the reaction with the greatest inhibition of ignition, all these mechanisms are of the reaction class \(\text{ROO} = \text{QOOH}\), such as \(\text{s12C9H20O2} \Rightarrow \text{s49C9H19O2} \) in Model v1, \(\text{s11C9H20O2} \Rightarrow \text{s43C9H20O2} \) in Model v2, and \(\text{s12C9H20O2} \Rightarrow \text{s49C9H19O2} \) in the LLNL model. It can also be seen that at temperatures below 700 K, reactions that are sensitive to ignition are the reactions in the expansion mechanism. In addition, the reaction class \(\text{RH} + \text{ROO} = \text{R} + \text{ROOH}\) also has a promoting effect on ignition, such as the reactions \(\text{s0C9H20} + \text{s12C9H19O2} \Rightarrow \text{s2C9H19} + \text{s46C9H20O2} \) in Model v1, \(\text{s0C9H20} + \text{s12C9H19O2} \Rightarrow \text{s2C9H19} + \text{s46C9H20O2} \) in Model v2, and \(\text{s0C9H20} + \text{s12C9H19O2} \Rightarrow \text{s2C9H19} + \text{s46C9H20O2} \) in the LLNL model, as shown in Figure 11a, and the reactions \(\text{s0C9H20} + \text{s13C9H19O2} \Rightarrow \text{s2C9H19} + \text{s52C9H20O2} \) in Model v1, and \(\text{s0C9H20} + \text{s13C9H19O2} \Rightarrow \text{s2C9H19} + \text{s52C9H20O2} \) in Model v2, and \(\text{s0C9H20} + \text{s13C9H19O2} \Rightarrow \text{s2C9H19} + \text{s52C9H20O2} \) in the LLNL model, as shown in Figure 11c, which is consistent with the low-temperature ignition characteristics of the \(n\)-heptane combustion mechanism. In the LLNL model,
as shown in Figure 11b, it can be seen that both the reaction classes \( RH + OH = R + H_2O \), such as \( \text{nc9h20} + \text{oh} = \text{9h19-4} + \text{h2o} \), and \( RH + H = R + OH \), such as \( \text{nc9h20} + \text{h} = \text{9h19-5} + \text{oh} \) show strong positive sensitivity. In addition, in the LLNL model, it was found that the decomposition reaction of ketones such as \( \text{c9ket2-4} = \text{oh} + \text{ch3coch2} + \text{nc5h11cho} \), \( \text{c9ket3-5} = \text{oh} + \text{c2h5coch2} + \text{nc4h9cho} \), \( \text{c9ket4-2} = \text{oh} + \text{ch3cho} + \text{c5h11coch2} \), \( \text{c9ket1-3} = \text{oh} + \text{ch2cho} + \text{nc6h11cho} \), \( \text{c9ket4-6} = \text{oh} + \text{nc3h7coch2} + \text{nc3h7cho} \), and \( \text{c9ket5-3} = \text{oh} + \text{c2h5cho} + \text{nc4h9coch2} \) all have an effect on ignition. Therefore, it can be concluded that the key reactions affecting the low-temperature ignition of the new mechanisms and the LLNL model are quite different. This indicates that these combustion models have different effects on the ignition delay due to the difference in the reaction network, which is like the previous comparative study of different n-heptane combustion models.19

### 3.3. Reaction Path Analysis

Based on the time-integrated element flux analysis,35 the reaction path of n-nonane under constant pressure ignition simulation was carried out with the C element as a flow target. The element flux results for the n-nonane/O\(_2\)/N\(_2\) mixtures were obtained under the conditions of a pressure of 15 atm, an equivalent ratio of 1.0, and a temperature of 700 K (amounts less than 5% were ignored). The reaction path analysis of the LLNL model is displayed in Figure 12. In Figure 13, the conversion fraction of complex decomposition pathways for Model v1 and Model v2 prescribed for n-nonane are shown in red font and black font, respectively.

As shown in Figures 12 and 13, the main fuel consumption paths are hydrocarbon fuels (RH) producing the alkyl radicals \( \text{R}^* \) by H-abstraction. Then, the reaction \( \text{R}^* + \text{O}_2 \rightarrow \text{ROO}^* \) took place to yield peroxy radicals \( \text{ROO}^* \), which will first isomerize to produce hydroperoxyalkyl radicals QOOH. The QOOH radicals will further yield some \( \text{O}_2\text{QOOH} \) radicals by the reaction \( \text{QOOH} + \text{O}_2 \rightarrow \text{O}_2\text{QOOH} \). It can be found that the main reaction path is almost the same, but the conversion fraction of complex decomposition pathways is quite different. Take n-nonyl radicals as an example. In the LLNL model, approximately 60% of n-nonyl radicals underwent the \( \text{R}^* + \text{O}_2 \) chemistry, and there is only 12.57% in Model v2 and only 41.17% in the Model v1. The existence of the NTC zone is mainly due to the enhanced reversibility of the reaction \( \text{R}^* + \text{O}_2 = \text{ROO} \) as the temperature increases.36 In summary, the discrepancy in the reaction flux will affect the ignition of these mechanisms.

### 4. CONCLUSION

An accurate and detailed chemical kinetic model is an important prerequisite for understanding the combustion performance of hydrocarbon fuels. Although large mechanisms can be produced manually, automatic generation provides a systematic tool that helps to simplify and systematize mechanism production. The use of a mechanism automatic
program to develop a complex large hydrocarbon combustion mechanism can effectively reduce the mechanism construction time and errors. Accordingly, in this study, combined with the core mechanisms—AramcoMech1.3 and AramcoMech3.0—and the expansion mechanisms produced by the automatic generation program ReaxGen, new mechanisms for low-temperature combustion of n-nonane are developed. In order to verify the rationality of the mechanisms, they are analyzed and compared with international mainstream combustion mechanisms. Systematic comparisons show that the low-temperature combustion mechanism of n-nonane developed by the mechanism automatic program possesses a high simulation precision in both the shock tube experiment and the species concentration generation experiment, and can be used in a wide range of conditions. Finally, through the ignition sensitivity analysis, the key reactions affecting the ignition are investigated. It is found that the reactions which have obvious effects on fuel ignition are quite different in different combustion models; and through the reaction path analysis, it can be seen that the conversion fraction of complex decomposition pathways is also distinct. Therefore, it can be inferred that different combustion models have different effects on combustion characteristics because of different reaction networks. In addition, because of some discrepancies between the predicted values and the experimental data, our research group is trying to optimize the model by combining high-precision quantum chemical calculations and species concentration analysis. A systematic method to automatically generate a mechanism for the low-temperature combustion of n-nonane could also be used to generate the mechanisms of other large hydrocarbons. Moreover, the new mechanisms of n-nonane provide a theoretical basis for revealing the nature of fuel combustion and basic data for the development of advanced engines.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsomega.9b03786](https://pubs.acs.org/doi/10.1021/acsomega.9b03786).

Mechanisms of Model v1 and Model v2 (TXT)
Rate constant expressions for main reaction classes of the expansion mechanism (PDF)

■ AUTHOR INFORMATION

Corresponding Author
Junjiang Guo — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China; Guizhou Provincial Key Laboratory of Energy Chemistry, Guiyang 550003, PR China; orcid.org/0000-0001-9401-5681; Email: junj_g@126.com

Authors
Weijun Peng — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China
Shijie Zhang — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China
Jiazhi Lei — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China
Jiantong Jing — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China
Ruyi Xiao — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China
Shiyun Tang — School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, PR China; Guizhou Provincial Key Laboratory of Energy Chemistry, Guiyang 550003, PR China; orcid.org/0000-0002-5337-4271

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03786

Author Contributions
All authors contributed equally to this work.

Funding
This work was supported by the National Natural Science Foundation of China (21963006), the Civil-Military Integration in Guizhou Institute of Technology (KJZX17-016), and the High-level Talent Research Start-up Project in Guizhou Institute of Technology (XJGC20190903)

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are thankful to the Combustion Dynamics Center of Sichuan University for providing us with the ReaxGen Program.

■ REFERENCES

(1) Guibet, J. C. Fuels and Engines; Editions Technip: Paris, 1999.
(2) Biet, J.; Hakka, M. H.; Warth, V.; Glaude, P.-A.; Battin-Leclerc, F. Experimental and modeling study of the low-temperature oxidation of large alkanes. Energy Fuels 2008, 22, 2258–2269.
(3) Xu, J.-Q.; Guo, J.-J.; Liu, A.-K.; Wang, J.-L.; Tan, N.-X.; Li, X.-Y. Construction of autoignition mechanisms for the combustion of RP-3 surrogate fuel and kinetics simulation. Acta Phys.-Chim. Sin. 2015, 31, 643–652.
(4) Rotavera, B.; Diévat, P.; Togbé, C.; Dagaut, P.; Petersen, E. L. Oxidation kinetics of n-nonane: Measurements and modeling of ignition delay times and product concentrations. Proc. Combust. Inst. 2011, 33, 175–183.
(5) Dagaut, P. On the kinetics of hydrocarbons oxidation from natural gas to kerosene and diesel fuel. Phys. Chem. Chem. Phys. 2002, 4, 2079–2094.
(6) Davidson, D. F.; Ranganath, S. C.; Lam, K.-Y.; Liaw, M.; Hong, Z.; Hanson, R. K. Ignition delay time measurements of normal alkanes and simple oxygenates. J. Propul. Power 2010, 26, 280–287.

ACS Omega 2020, 5, 4924–4936
(7) Rotavera, B.; Petersen, E. L. Ignition behavior of pure and blended methyl octanoate, n-nonane, and methylcyclohexane. *Proc. Combust. Inst.* **2013**, *34*, 435–442.

(8) He, J.; Yong, K.; Zhang, W.; Li, P.; Zhang, C.; Li, X. Shock Tube Study of Ignition Delay Characteristics of n-Nonane and n-Undecane in Argon. *Energy Fuels* **2016**, *30*, 8886–8895.

(9) Yong, K.; He, J.; Zhang, W.; Xian, L.; Zhang, C.; Li, P.; Li, X. Shock tube study of n-nonane/air ignition over a wide range of temperatures. *Fuel* **2017**, *188*, 567–574.

(10) Kathrotia, T.; Obwald, P.; Köhler, M.; Slavinskaya, N.; Riedel, U. Experimental and mechanistic investigation of benzene formation during atmospheric pressure flow reactor oxidation of n-hexane, n-nonane, and n-dodecane below 1200 K. *Combust. Flame* **2018**, *194*, 426–438.

(11) Ji, C.; Dames, E.; Wang, Y. L.; Wang, H.; Egolfopoulos, F. N. Propagation and extinction of premixed CS-C12 n-alkane flames. *Combust. Flame* **2010**, *157*, 277–287.

(12) Westbrook, C. K.; Pitz, W. J.; Herbinet, O.; Curran, H. J.; Silke, E. J. A comprehensive detailed chemical kinetic reaction mechanism for combustion of n-alkane hydrocarbons from n-octane to n-hexadecane. *Combust. Flame* **2009**, *156*, 181–199.

(13) Wang, H.; Dames, E.; Sirjean, B.; Sheen, D. A.; Tango, R.; Violi, A.; Lai, J. Y. W.; Egolfopoulos, F. N.; Davidson, D. F.; Hanson, R. K.; Bowman, C. T.; Law, C. K.; Tsang, W.; Cernansky, N. P.; Miller, D. L.; Lindstedt, R. P. A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures. *JSTurF*, version 2.0, September 19, 2010. http://web.stanford.edu/group/hawanglab/JSTurF/JSTurF2.0/index.html.

(14) Battin-Leclerc, F.; Glaude, P. A.; Warth, V.; Fournet, R.; Scacchi, G.; Come, G. M. Computer tools for modeling the chemical phenomena related to combustion. *Chem. Eng. Sci.* **2000**, *55*, 2883–2893.

(15) Ranzi, E.; Dente, M.; Goldaniga, A.; Bozzano, G.; Faravelli, T. Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures. *Prog. Energy Combust. Sci.* **2001**, *27*, 99–139.

(16) Bürrock, E. S. Reaction: system for modeling chemical reactions. *J. Chem. Inf. Comput. Sci.* **1995**, *35*, 607–616.

(17) Harper, M. R.; Van Geem, K. M.; Pyl, S. P.; Marin, G. B.; Green, W. H. Comprehensive reaction mechanism for n-butanol pyrolysis and combustion. *Combust. Flame* **2011**, *158*, 16–41.

(18) Guo, J.; Hua, X. X.; Wang, F.; Tan, N. X.; Li, X. Y. Systematic Approach to Automatic Construction of High-Temperature Combustion Mechanisms of Alkanes. *Acta Phys.-Chim. Sin.* **2014**, *30*, 1027–1041.

(19) Guo, J.; Li, S.; Tang, S.; Xiao, L.; Tan, N. Influence of Different Core Mechanisms on Low-Temperature Combustion Characteristics of Large Hydrocarbon Fuels. *Energy Fuels* **2019**, *33*, 7835–7851.

(20) Guo, J. J.; Li, S. H.; Tan, N. X.; Li, X. Y. Mechanism Construction for Low-temperature Combustion of n-Heptane. *J. Eng. Thermophys.* **2014**, *35*, 2296–2302.

(21) Guo, J. J.; Tang, S. Y.; Li, R.; Tan, N. X. Mechanism Construction and Simulation for Combustion of Large Hydrocarbon Fuels Applied in Wide Temperature Range. *Acta Phys.-Chim. Sin.* **2019**, *35*, 182–192.

(22) Westbrook, C. K.; Dryer, F. L. Chemical kinetic modeling of hydrocarbon combustion. *Prog. Energy Combust. Sci.* **1984**, *10*, 1–57.

(23) Curran, H. J. Developing detailed chemical kinetic mechanisms for fuel combustion. *Proc. Combust. Inst.* **2019**, *37*, 57–81.

(24) Metcalfe, W. K.; Burke, S. M.; Ahmed, S. S.; Curran, H. J. A Hierarchical and Comparative Kinetic Modeling Study of C1−C3 Hydrocarbon and Oxygenated Fuels. *Int. J. Chem. Kinet.* **2013**, *45*, 638–675.

(25) Zhou, C.-W.; Li, Y.; Burke, U.; Banyon, C.; Somers, K. P.; Ding, S.; Khan, S.; Hargis, J. W.; Sikes, T.; Mathieu, O.; Petersen, E. L.; AlAbbad, M.; Farooq, A.; Pan, Y.; Zhang, Y.; Huang, Z.; Lopez, J.; Loparo, Z.; Vasu, S. S.; Curran, H. J. An experimental and chemical kinetic modeling study of 1,3-butadiene combustion: Ignition delay and laminar flame speed measurements. *Combust. Flame* **2018**, *197*, 423–438.

(26) Muharam, Y.; Warnatz, J. Kinetic modelling of the oxidation of large aliphatic hydrocarbons using an automatic mechanism generation. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4218–4229.

(27) Benson, S. W. Thermochemical Kinetics, 2nd ed.; John Wiley and Sons: New York, 1976; pp 19–72.

(28) Holley, A. T.; You, X. Q.; Dames, E.; Wang, H.; Egolfopoulos, F. N. Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion. *Proc. Combust. Inst.* **2009**, *32*, 1157–1163.

(29) ANSYS Chemkin 17.0 (15151); ANSYS Reaction Design: San Diego, 2016.

(30) Chaos, M.; Dryer, F. L. Chemical-kinetic modeling of ignition delay: Considerations in interpreting shock tube data. *Int. J. Chem. Kinet.* **2010**, *42*, 143–150.

(31) Sarathy, S. M.; Vranckx, S.; Yasunaga, K.; Mehl, M.; Obwald, P.; Metcalfe, W. K.; Westbrook, C. K.; Pitz, W. J.; Kohse-Höinghaus, K.; Fernandes, R. X.; Curran, H. J. A comprehensive chemical kinetic combustion model for the four butanol isomers. *Combust. Flame* **2012**, *159*, 2028–2055.

(32) Wang, H.; You, X. Q.; Joshi, A. V.; Davis, S. G.; Laskin, A.; Egolfopoulos, F. N.; Law, C. K. USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds, 2007. http://ignis.usc.edu/USC_Mech_II.htm.

(33) Tan, N.; Wang, J.; Hua, X.; Li, Z.; Li, X. Combustion Mechanism and Kinetic Modeling Study of Methyl Cyclohexane at High Temperature. *Chem. J. Chin. Univ.* **2011**, *32*, 1832–1837.

(34) Guo, J.; Wang, J.; Hua, X.; Li, Z.; Tan, N.; Li, X. Mechanism construction and simulation for high-temperature combustion of n-propylcyclohexane. *Chem. Res. Chin. Univ.* **2014**, *30*, 480–488.

(35) Wang, Q.-D.; Fang, Y.-M.; Wang, F.; Li, X.-Y. Systematic analysis and reduction of combustion mechanisms for ignition of multi-component kerosene surrogate. *Proc. Combust. Inst.* **2013**, *34*, 187–195.

(36) Battin-Leclerc, F.; Herbinet, O.; Glaude, P.-A.; Fournet, R.; Zhou, Z.; Deng, L.; Guo, H.; Xie, M.; Qi, F.; Qi, F. Experimental confirmation of the low-temperature oxidation scheme of alkanes. *Angew. Chem., Int. Ed.* **2010**, *49*, 3169–3172.