Research Article

Effects of High-Concentration CO₂ on Ignition Delay Time of 70% n-Heptane/30% Toluene Mixtures

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In order to research the high-concentration CO₂ effects on ignition delay time (IDT) of diesel surrogate fuel (70% n-heptane/30% toluene), a carbon dioxide effect (CDE) model is established, which considers fuel and ambient gas concentration, density, and temperature influence on autoignition under CO₂/O₂ atmosphere. Firstly, a chemical model of n-heptane/toluene is established, and the coupling, reduction, and simulation processes are carried out in chemical kinetic software with the IDT as the target parameter. Secondly, a constant volume combustion chamber (CVCC) visualization platform is built by incorporating a high-speed camera system and different working conditions are set in the CO₂ volume fraction range (40%-70%) at 3.0 MPa and 850 K for an autoignition experiment. Thirdly, experiment and simulation results are discussed in air, 60% CO₂/40% O₂, 50% CO₂/50% O₂, and 40% CO₂/60% O₂ atmospheres, including the IDT, CO₂ effects, temperature sensitivity, and OH radical rate of production (ROP). The results show that the CDE model well predicts the 70% n-heptane/30% toluene IDT under the CO₂/O₂ atmosphere and the average error in 60% CO₂/40% O₂ atmosphere is 5.29%. Besides, when the CO₂ volume fraction increases from 40% to 60%, the CO₂ thermal effect plays a leading role in the IDT prolongation and the OH radical ROP peak of R4 (O+H₂O→2OH) decreases by 180%.

1. Introduction

Diesel engines play an indispensable role in industrial development, but the CO₂ emission poses a great threat to the lives of workers in such as underground, underwater, and other closed environments [1]. When the CO₂ concentration reaches 5% in a closed environment, it causes severe damage to body functions, loss of consciousness, and even death [2, 3]. In order to solve the CO₂ emission problem in closed environments, Pei and Liu [4] proposed a closed cycle diesel engine (CCDE) system with liquid oxygen carbon sequestration whose working principle is that diesel burns in the “artificial atmosphere” (only O₂ and CO₂). In addition, the combustion process takes advantage of the CO₂ high specific heat and the flame retardant properties to avoid diesel excessive combustion in the oxygen-rich atmosphere, and the CO₂ in the diesel exhaust is cooled and collected by using the physical properties of liquid oxygen vaporization heat absorption. The vaporized O₂ and the remaining unsolidified CO₂ are sent to the cylinder for the next combustion cycle through exhaust gas recirculation. The unique advantage of the closed cycle system is
that the emission of pollutants such as nitrogen oxides and soot is almost "zero" during the working process. Unfortunately, the CCDE has the problem of unstable combustion and unpredictable autoignition in practice [5], so in-depth research on diesel IDT under the CO$_2$/O$_2$ atmosphere is necessary.

Diesel is a complex mixture composing hundreds of different components, which is not feasible to consider the oxidation chemistry of all the compounds [6, 7]. Encouragingly, n-heptane is commonly adopted as DSF due to it having a similar cetane number to diesel and the oxidation reaction is well known [8–11]. Additionally, the aromatic compounds in diesel account to about 30% [12], and the most representative substance with a simple structure is toluene. In general, binary mixed fuel can potentially provide a better representation of autoignition delay properties than those on the basis of a single fuel. In order to simulate the diesel C/H ratio and the physical and chemical properties in the actual autoignition process as accurately as possible, binary mixed fuel becomes a hot topic in diesel IDT research [13–19], especially toluene reference fuels (TRFs) [20–23]. Therefore, the IDT of 70% n-heptane/30% toluene under the CO$_2$/O$_2$ atmosphere needs to be further investigated to provide a reference for the optimized design of future diesel engines.

Researchers made extensive studies on the IDT of n-heptane/toluene mixtures in air. Herzler et al. [24] studied the n-heptane/toluene mixtures IDT by using a high-pressure shock tube (HPST), which laid a foundation for developing and improving the DSF autoignition kinetic model. Later, Hartmann et al. [25] employed the HPST experiment to prove the toluene inhibitory effect on autoignition in a low-temperature environment by adding toluene to n-heptane, and they explained the nonlinear effects on the IDT of n-heptane/toluene mixtures. In addition, Di Sante [26] obtained the n-heptane chemical properties that dominated the toluene/n-heptane mixture when the toluene content was low through a rapid compression machine (RCM) experiment, while the effect of toluene content change on IDT was not significant when the temperature was higher than 800 K. Malliotakis et al. [27] combined HPST and RCM experiments to study the variation of n-heptane/toluene mixtures IDT with toluene content at different pressures and equivalence ratios using reaction paths and sensitivity analysis (SA) methods, and they also described the key aspects of toluene oxidation and explained its characteristics as reaction inhibition. Besides, Hernandez et al. [28] adopted 50% n-heptane/50% toluene as DSF to conduct an autoignition experiment in a single-cylinder engine and proved that toluene eliminated numerous active groups through the dehydrogenation reaction of OH radical at low temperatures, which remarkably prolonged the IDT. Subsequently, Hellier et al. [29] further researched the interaction between toluene and n-heptane during the compression autoignition process by changing the toluene content, which caused the changes in IDT. The result proved that a distinct two-stage autoignition process appeared with the increase of toluene content, and the toluene content exceeded 50% without spontaneous combustion. Further, Zhang et al. [30] selected n-heptane and toluene (6:4 by mass) as DSF using a numerical simulation to study the diesel autoignition in different oxygen concentrations, and the oxidation process of the mechanism was verified by the CVCC experiment.

In recent years, many studies have been reported on ignition and combustion under the CO$_2$/O$_2$ atmosphere. Zhou et al. [31] investigated the ignition characteristics of single-particle slitme in a tube furnace at initial temperatures of 923-1173 K and O$_2$ volume fractions of 5%-80% and showed that the IDT and ignition temperature decreased significantly with increasing ambient temperature and oxygen concentration. But Liu et al. [32] studied the ethane IDT variation with the change of equivalence ratio and pressure through a shock tube experiment. Hu and Wei [33] further investigated the CO$_2$ effects on the propane laminar flow flame speed by Bunsen burner experiment, and the results concluded that the CO$_2$ thermal effect is the determining factor, followed by the chemical effect and finally the radiation effect. Additionally, Chen et al. [34] studied the diesel combustion process through optical engine experiments, and the results showed that the engine power loss was minimized and the IDT was shortened obviously in the 50% CO$_2$/50% O$_2$ atmosphere. Peng et al. [35] compared the autoignition delay of butane in CO$_2$/O$_2$ and air atmosphere by HPST experiment and analyzed the equivalence ratio and CO$_2$ effect on the IDT. Subsequently, Zhao et al. [36] studied the ignition characteristics of n-heptane by the visualization platform experiment of CVCC, and the results showed that the IDT in 35% CO$_2$/65% O$_2$ atmosphere was significantly shortened by 50% than that in air. Moreover, Liu et al. [37] studied the effects of CO$_2$ concentration on the combustion characteristics of diesel in different CO$_2$/O$_2$ atmosphere through the CVCC experiment.

Although researchers extensively studied the n-heptane/toluene mixtures auto-ignition characteristics in air, few reports under CO$_2$/O$_2$ atmosphere, especially in a high-concentration CO$_2$ environment. Thus, the goal of the present work is to propose a model that is appropriate for calculating the diesel IDT under the CO$_2$/O$_2$ atmosphere. Firstly, the CDE model of 70% n-heptane/30% toluene is established in the CO$_2$/O$_2$ atmosphere. Then, the n-heptane and toluene chemical models are coupled and reduced. Finally, the CVCC visualization experiment platform is built to verify the CDE model, and the important factors affecting the IDT are specifically analyzed and discussed. The discussion focuses on the autoignition process, the flame natural luminosity, calculation and validation of IDT, CO$_2$ effect, temperature sensitivity, and OH radical ROP.

2. Simulation

2.1. CDE Model. The CDE model is used to calculate the diesel IDT from the Arrhenius formula [38] as shown in Equation (1). Later, Ryan and Callahan [39] creatively converted the pressure effect into the gas concentration and ambient density effects on IDT on the basis of Equation (1). Besides, the influence of fuel concentration, oxygen concentration, and ambient temperature and density on IDT is considered as shown in Equation (2).
\[
\tau_{id} = A p^n \exp \left( \frac{E_a}{RT} \right),
\]

(1)

where \( A \) and \( n \) are calibration coefficients, which vary with fuel type, test method, and test condition; \( p \) and \( T \) are the gas average pressure and temperature before fuel spontaneous combustion, Pa, K; \( R \) is the universal gas constant, J/(mol·K); and \( E_a \) is the global activation energy, kJ/mol.

\[
\tau_{id} = b_0 C_{O2}^b C_{fuel}^b \rho^b \exp \left( \frac{b_4}{T} \right),
\]

(2)

where \( b_0, b_1, b_2, \) and \( b_3 \) are regression coefficients; \( b_4 \) is global activation energy over \( R \) (universal gas constant); \( C_{O2} \) and \( C_{fuel} \) are the oxygen concentration and the fuel concentration before fuel spontaneous combustion, moles/m³; \( \rho \) is the average gas density before fuel spontaneous combustion, kg/m³; and \( T \) is the average gas temperature before fuel autoignition, K.

However, Equation (2) describes the IDT in air without considering the special CO₂/O₂ atmosphere, where the CO₂ concentration is much higher than that in air and CO₂ has a higher specific heat capacity compared to N₂. Additionally, in a high-temperature environment, CO₂ cracks and directly participates in the reaction, which affects the oxidation process. Thus, the CDE model is established as shown in Equation (3), which considers the CO₂ retardant effect on autoignition.

\[
\tau_{CDE} = b_0 C_{O2}^b C_{fuel}^b \rho^b \exp \left( \frac{b_4}{T} \right) C_{CO2}^{b_5},
\]

(3)

where \( \tau_{CDE} \) is the ignition delay time, s; \( C_{CO2} \) is the carbon dioxide concentration at the ignition moment; and \( b_5 \) is the regression coefficient.

The CDE model considers the coupled effects of gas temperature and density and the ratio of oxygen to fuel on IDT. Furthermore, the CO₂ volume fraction is divided into multiple group working conditions from 40% to 70%, and the multiple linear regression analysis methods are adopted to correlate the species data with the IDT. The final function converges by iterative calculation, and the goodness-of-fit \( (R^2) \) of the CDE model is 0.9482 with the coefficients shown in

\[
\tau_{CDE} = 0.221 C_{O2}^{-1.127} C_{fuel}^{0.050} \rho^{-4.512} \exp \left( \frac{5914}{T} \right) C_{CO2}^{1.762}
\]

(4)

The coefficients in Equation (4) are expressed as follows. The \( \tau_{CDE} \) decreases with increasing O₂ concentration in the mixture but increases with increasing CO₂ concentration, and they both influence each other coupling. The ignition delay time is inversely proportional to the mixture temperature, and the nature of this relationship can be expressed by the Arrhenius formula. The effect of density is more significant at higher fuel flow rates, as the spray may hit the wall at lower densities. The effect of fuel flow on ignition delay is relatively small but significant, with evaporation at higher fuel flow (richer mixture) causing pressure reduction and resulting in longer ignition delay.

The actual diesel engine has a different CO₂ concentration before and after autoignition as the working conditions change. More importantly, owing to the rapid and intense working process of the diesel engine, the in-cylinder temperature has strong transient characteristics, which affect the reactions of CO₂ and DSF. The CDE model has the advantage of better linking experimental data to actual diesel engines to quickly and accurately predict the IDT under CO₂/O₂ atmosphere, and the autoignition parameters of actual engines are further optimized to achieve the purpose of stable combustion. In addition, the density effect depends on the amount of fuel injected.

2.2. Chemical Model. The chemical model includes the n-heptane and toluene mechanisms from Lawrence Livermore National Laboratory. The adopted n-heptane mechanism is version 3.1 of the detailed chemical kinetics model developed by Mehl et al. [40], which is prominent in numerical research experiments in a wide temperature range and well characterizes the ignition. Besides, the adopted chemical kinetic model of toluene is developed by Nakamura et al. [41] to simulate a single aromatic hydrocarbon, which has outstanding performance in pioneering studies of reaction pathways and reaction rates. In addition, when the chemical reaction rate of the system reaches a high level, a large number of active molecules are clustered together at the autoignition moment, which accompanies by intense luminescence and heating. Among them, the OH radical determines the reaction activity in a low-temperature environment, so the autoignition moment is defined as the OH radical reaching the maximum [42], as shown in Figure 1.

2.3. Coupling and Reduction Processes of Mechanism. The n-heptane and toluene mechanisms need to be coupled and reduced by a directed relation graph with error propagation (DRGEP) [43] and SA [44] methods to reduce calculation time and cost. Firstly, according to the weight value, the larger elementary reactions are retained when the mechanisms are coupled. Secondly, the elementary reactions with fewer correlations with the coupling mechanism are eliminated according to the target parameter. Thirdly, the DRGEP method eliminates the error propagation caused by species reduction and further reduces the retained species through the SA method. Finally, the reduction process is controlled by setting the target parameters and error range to obtain the skeleton mechanism with different accuracy. However, if the target parameters are less and the error is large, the final obtained mechanism is simplified and if the error is small enough, the reduced mechanism converges to the detailed mechanism. The n-heptane/toluene mechanism with 273 components and 1544 elementary reactions is obtained by setting the IDT as the target parameter and the relative error is 10%. The reduced mechanism well simulates the diesel autoignition process thanks to the calculation errors of the simplified and detailed mechanism are
within 5%, and the mechanism coupling and reduction process are shown in Figure 2.

3. Experiment

In the experiment, the CVCC visualization platform is built to analyze the auto-ignition process of 70% n-heptane/30% toluene under the CO₂/O₂ atmosphere. As shown in Figure 3, the experiment platform divides into six parts, which are the CVCC device, cooling circulation system, intake and exhaust system, high-pressure fuel injection system, high-speed camera system, and electronic control unit (ECU), and the experimental parameters are shown in Table 1.

The shape of the CVCC device (product number: Y1403, produced by Beijing Institute of Technology) is similar to a cylinder with four fused quartz windows that are evenly distributed as shown in Figure 4. The CVCC device simulates the working environment of the actual diesel engine top dead center with an interior radius of 150 mm and an interior height of 560 mm. The electric heating wires maximum power is 11 kW, regulating the CVCC temperature by thermal convection, and its internal maximum temperature reaches 900 K, which meets the actual engine top dead center autoignition temperature. The quartz window diameter is 120 mm, and its effective observation diameter is 100 mm, which can achieve the high-speed camera to get the entire autoignition process. In addition, the cooling circulation system is composed of a condition control cabinet, a water tank, a water pump, temperature sensors, and cooling water channels. The CVCC outer wall is covered with cooling water channels that are monitored in real time by temperature sensors to regulate dynamically the temperature and avoid danger. The intake and exhaust system consists of the condition control cabinet, high-pressure gas cylinders, pressure regulator valves, pressure sensors and intake, and...
exhaust pipelines. During the intake process, the pressure regulator valve needs to be manually adjusted to feed evenly the mixture gas with a 0.02 MPa intake gradient. At the same time, the heating wires are cooperatively heated to ensure a steady rise in pressure and temperature in the CVCC until the initial values for the experiment are reached. When the first exhaust is completed, a certain amount of mixture gas needs to be charged again before continuing the exhaust to eliminate the disturbance of the previous cycle of combustion. Additionally, the high-pressure fuel injection system consists of the ECU, oil tank, oil pump and motor, battery, high-pressure oil rail, and injector (0.14 mm single-hole injector from BOSCH). The high-pressure oil pump driven by a variable-frequency motor enables the fuel to reach a maximum injection pressure of 175 MPa. The pressure is increased in 10 MPa gradients from 0 to 100 MPa and in 5 MPa gradient above 100 MPa to achieve precise regulation and protection of the high-pressure oil rail. A single-hole injector with a diameter of 0.12 mm is used for the experiment. The high-speed camera system is composed of a control computer, high-speed camera (FASTCAM SA5, Photron), digital delay generator (DG535), and the ECU. The maximum shooting speed is 10000 frames per second (FPS) of the high-speed camera, which is triggered by the digital delay generator. The digital delay generator is employed to adjust the time relationship between the fuel injection and the high-speed camera. At the same time, the autoignition process is recorded in real time by using the acquisition software matching with the high-speed camera.

The testing procedure of the CVCC visualization experiment platform is mainly divided into 4 steps. (a) Before the experiment starts, the high-speed camera needs to complete the focus and image size calibration, as shown in Figure 5. (b) The CVCC is charged with a specific ratio of CO\textsubscript{2}/O\textsubscript{2} mixture gas at a certain gradient pressure while the electric heating wires are adjusted to heat until reaching the initial temperature and pressure of the experiment. (c) When the high-pressure fuel injection system reaches the experimental injection pressure with a certain gradient, the control computer sends an electrical signal to the digital delay generator while the high-speed camera is triggered to work. (d) The first 60 images are sent back to the control computer for storage as a set of data since the combustion process is finished at 6 ms.

4. Results and Discussion

4.1. Ignition Delay Time. Figure 6(a) shows the key frames of the actual 70% n-heptane/30% toluene autoignition
Figure 5: Image calibration of the high-speed camera.

processes from the high-speed camera in four different conditions. The images are processed with pseudocolor to better highlight the autoignition moment and the flame shape as shown in Figure 6(b). Thus, the IDT obtained using the space integrated natural luminosity (SINL) [45, 46] method are 2.3 ms, 1.7 ms, 1.4 ms, and 1.1 ms in the four working conditions (air, 60% CO2/40% O2, 50% CO2/50% O2, and 40% CO2/60% O2). The IDT is reduced obviously by 52.17% in 40% CO2/60% O2 atmosphere than that in air. Besides, the flame front has an “umbrella” shape in air, while the flame is thinner and longer under CO2/O2 atmospheres. Due to the oxygen concentration increases, the collision chance between oxygen and fuel molecules becomes greater, resulting in shorter IDT and more complete combustion than that in air. Comparing the autoignition processes in the different CO2/O2 atmospheres, the IDTs in 40% CO2/60% O2 and 60% CO2/40% O2 atmospheres are 27.27% longer and 21.43% shorter than those in 50% CO2/50% O2 atmosphere, respectively. The result shows that the same O2 and CO2 volume fractions of change have different promotion and inhibition degrees of autoignition because the two have a coupling effect. Liu et al. [36] studied the effects of different CO2 concentrations on the diesel combustion characteristics in the CVCC experiment at an initial temperature and pressure of 850 K and 3.0 MPa, respectively. The result shows that with the increase of CO2 concentration, the flame length decreases and the IDT increases in the CO2/O2 atmosphere, and similar conclusions are drawn in the current experimental conditions.

The flame natural luminosity change processes of 70% n-heptane/30% toluene in the four working conditions are shown in Figure 7. The flame natural luminosity is obtained by converting the red (R), green (G), and blue (B) values of each pixel point on the image into the corresponding gray values and then superimposing them [47]. As shown in Figure 7, the flame natural luminosity in air is much smaller than that in the CO2/O2 atmospheres. On the one hand, the phenomenon is caused by a large amount of inert gas (N2) in air as well as the low oxygen concentration, which leads to insufficient combustion. On the other hand, N2 does not participate in the fuel oxidation reaction, while CO2 is involved in the reaction in localized high-temperature conditions [48]. In the 50% CO2/50% O2 atmosphere, the area enclosed by the flame natural luminosity curve and the time axis are the largest, indicating that the combustion is sufficient and lasts for a long time. However, the flame natural luminosity curves fluctuate strongly and even show flame breakage in the flame images in the different CO2/O2 atmospheres. What may explain the phenomenon is that CO2 is a triatomic gas, and its higher specific heat capacity and lower polytropic index disrupt the oxygen-rich conditions in CVCC, causing unstable combustion [49, 50]. Moreover, the diffusive combustion of gas entrained fuel during the fuel injection combustion process forms turbulence, which further leads to combustion fluctuations. The time from the beginning to the first slope of the flame natural luminosity curve also reflects the trend that the IDT gradually prolongs with increasing the CO2 volume fraction.

Figure 8 shows the simulation and experiment IDT in air and the three different CO2/O2 atmospheres and the CDE model reproduces negative temperature dependence. At the initial temperature and pressure of 700 K and 3.0 MPa, the IDT in air is much longer than that in CO2/O2 atmospheres, which all decrease gradually as the initial temperature increases from 700 K to 850 K. On the contrary, with the increase of the initial temperature from 850 K to 950 K, the IDT is prolonged, especially in air and 50% CO2/50% O2 atmospheres. The phenomenon shows that the oxidation of toluene in air and 50% CO2/50% O2 atmospheres consume a large amount of OH radical and the reaction heat release is much less than the heat loss, which eventually leads to a decrease in the system reactivity and a longer IDT. Overall, this is similar to the conclusion reached by Fu and Aggarwal [51], who explained the phenomenon of negative temperature coefficients for n-heptane/methane mixtures, where the reactions generating HO2 radical are preferred over those generating OH radical in this temperature interval, resulting in a smaller heat release than heat loss for low-temperature reactions. Subsequently, with increasing the initial temperature from 950 K to 1200 K, the IDT in the four atmospheres gradually shortens to zero. Because the higher initial temperature determines the progress of the reaction, the fuel spontaneously ignites immediately as soon as it is injected. The reasons for the error mainly include the simplification of the model and the experimental error, and the maximum error between the simulation and experiment is 16.96% in air. Moreover, the errors between the simulation and experiment IDT of 60% CO2/40% O2, 50% CO2/50% O2, and 40% CO2/60% O2 are 5.29%, 5.71%, and 8.18%, respectively, which verifies the CDE model applicability to predict the IDT in the O2/CO2 atmosphere.

4.2. The CO2 Effects. Figure 9 shows the correspondence between the IDT and temperature for different CO2 volume fraction working conditions at the initial temperature of
850 K and the pressure of 3.0 MPa. Under CO$_2$/O$_2$ atmosphere, the IDT prolongs with the increases of CO$_2$ volume fraction and the corresponding autoignition temperature gradually decreases, and the three effects of CO$_2$ show distinct changes. Then, when the CO$_2$ volume fraction changes from 40% to 60%, the IDT growth rate gradually increases, reaching a maximum of 18.75% between 55% and 60%. However, when the CO$_2$ volume fraction continues to increase, the growth rate drops instead, and the growth rate drops to 10.53% between 60% and 70%. Thus, the change in growth rate indicates that the way of CO$_2$ inhibiting autoignition has changed. The CO$_2$ thermal effect gradually increases and causes a significant decrease in temperature with increasing the CO$_2$ volume fraction from 40% to 60%, which is the
Figure 8: The IDT of simulation and experiment.

Figure 9: The IDT and temperature in the different working conditions.
main reason for the increase in the IDT growth rate. However, when the volume fraction of CO$_2$ reaches over 60%, the CO$_2$ third body collision efficiency is improved obviously, which promotes the occurrence of autoignition and reduces the IDT growth rate. Zhang et al. [10] and Sabia et al. [52] studied the autoignition process of n-heptane and propane. To study a certain CO$_2$ effect separately, virtual species were introduced to replace the thermal CO$_2$ effect, the CO$_2$ third body collision effect, and the CO$_2$ chemical effect through numerical simulation. The research results under a low-temperature environment are consistent with this paper that the CO$_2$ thermal effect is the most important factor affecting the IDT. Furthermore, when the CO$_2$ volume fraction reaches 60%, the third body effect of CO$_2$ is significantly enhanced.

4.3. Sensitivity Analysis. The oxidation process of the mechanism strongly depends on temperature, so it is important to identify the elementary reactions that are sensitive to the temperature for studying the autoignition. The temperature sensitivity of the n-heptane/toluene coupling mechanism is analyzed by the SA module in the kinetic software CHEMKIN-PRO [53] to determine the important elementary reactions affecting IDT, as shown in Figure 10. The initial ambient temperature and pressure for conducting SA are 850 K and 3.0 MPa, respectively, which are consistent with the CVCC experiment. Besides, Table 2 lists the ten most important elementary reactions affecting the IDT, including dehydrogenation of n-C$_7$H$_{16}$ chain branching, isomerization of C$_7$H$_{15}$OO radical, and chain termination reaction.

The sensitivity coefficients of R13 and R43 are negative for all four working conditions, implying the decrease in the system temperature and inhibition of auto-ignition with increasing the reaction rates, as shown in Figure 10. In addition, the R670, R852, R856, R861, and R864 are isomerization reactions of C$_7$H$_{15}$OO radical to form isomeric peroxyalkyl and the sensitivity coefficients are positive. The sensitivity coefficients increase with increasing the oxygen concentration, indicating that by increasing the reaction rate, the system temperature is increased and the autoignition is promoted. The elementary reaction R15 has the negative sensitivity coefficients in air and high CO$_2$ volume fraction ambient. However, the sensitivity coefficient of R15 is positive when the CO$_2$ volume fraction is reduced to 40%. On the one hand, it shows that the R15 is the H$_2$O$_2$ dehydrogenation reaction in high CO$_2$ volume fraction ambient, which absorbs a large amount of heat. On the other hand, when the oxygen concentration is high, the sensitivity coefficient is positive, which is explained by the Le Chatelier principle.

The elementary reaction R16 has the negative sensitivity coefficient in the 40% CO$_2$/60% O$_2$ atmosphere. Hence, when the oxygen concentration is high, the R15 takes precedence over the R16, resulting in an obvious decrease in the H$_2$O$_2$ concentration. However, the R16 sensitivity coefficients are positive in the other three working conditions because the reaction of H$_2$O$_2$ decomposition into two OH radical releases a lot of heat, which is often adopted as an autoignition sign. Also, the sensitivity coefficients are much higher in 60% CO$_2$/40% O$_2$ and 50% CO$_2$/50% O$_2$ atmospheres than in air under these three conditions. In fact, the high concentration of CO$_2$ enhances the CO$_2$ third body collision effect and increases the energy transfer efficiency, resulting in a faster reaction process. Moreover, among the ten elementary reactions with the greatest impact on IDT in Table 2, the CO$_2$ does not show a significant chemical effect in the experimental conditions. Zhang et al. [10] studied the CO$_2$ effects on the autoignition process of n-heptane by separating the CO$_2$ thermal effect and third body effect and got similar results that the thermal effect of CO$_2$ is the main reason for the autoignition delay.

According to Figure 10 and Table 2, R16 (H$_2$O$_2$ (+M)$\rightarrow$2OH (+M)) is sensitive to temperature also an important reaction that affects the IDT. Also, R16 is the major source of OH radical and the reaction most affected by the CO$_2$ third body collision effect [54]. With the progress of the elementary reaction, the reaction activity and temperature of the system are increased markedly. The R43 and R670 are dehydrogenation reactions through OH radical, while R120 is the chain termination reaction, and they all consume a certain number of OH radical. Besides, R15 (H$_2$O$_2$+O$_2$$\rightarrow$2H$_2$O) is dehydrogenated by O$_2$ to generate the HO$_2$ radical, and then, HO$_2$ radical is consumed by R13 (HO$_2$+OH$\rightarrow$H$_2$O+O$_2$). Except in the 40% CO$_2$/60% O$_2$ atmosphere, R15 consumes a large number of radicals in the other three working conditions and significantly reduces the reaction activity and temperature of the system. Additionally, the reactions R852, R856, R861, and R864 are isomerization reactions of C7H15OO radical, which release large amounts of heat and promote the autoignition occurrence. The above reactions are consistent with Wu et al. [55] using a zero-dimensional model to study the reaction of O$_2$ content to the low-temperature oxidation process of n-heptane.

The SA of temperature shows that H$_2$O$_2$, HO$_2$, and OH radicals have strong correlations with the autoignition of n-heptane/toluene mixtures. Therefore, it is necessary to analyze the total production of H$_2$O$_2$, HO$_2$, and OH radicals in four different CO$_2$ volume fractions, as shown in Figure 11. Comparing Figures 11(a)–11(d), we conclude that the production peaks of H$_2$O$_2$, HO$_2$, and OH radicals under the CO$_2$/O$_2$ atmosphere are obviously higher than those in air, and the time to reach the peaks is shorter obviously. Comparing Figures 11(a) and 11(b), the biggest difference is that the time required for H$_2$O$_2$ to reach the peak in Figure 11(b) is 16.67% shorter than Figure 11(a), but the peaks reached by both are almost the same. However, the HO$_2$ radical all first increase, then decrease, and finally reach their peak at the same time as the OH radical in all four working conditions. The first peak of the HO$_2$ radical is mainly produced by the n-heptane dehydrogenation reaction through oxygen in the low-temperature reaction stage, and the second peak is caused by the oxidation of hydrogen peroxide. Additionally, with the increase of the CO$_2$ volume fraction, the OH mole fraction change remarkably, reduced by 18.6%, and the time to reach the peak of the OH mole fraction is prolonged by 17.78%. The results show that the CO$_2$ high-concentration atmosphere prolongs
obviously the IDT, but the increase of the CO₂ volume fraction does not affect the formation of H₂O₂ and HO₂ radicals.

4.4. Rate of Production Analysis. OH radical has a strong relationship with IDT [56, 57], so further research on the ROP of OH radical is essential for autoignition. The four elementary reaction processes with the greatest influence on the OH radical ROP under the initial temperature of 850 K and pressure of 3.0 MPa in four working conditions are shown in Figure 12. What is most intuitive in Figure 12 are the rapid change processes of the R4 (O+H₂O→2OH) and R1 (H+O₂→O+OH), while the peaks of R12 (HO₂+O→OH+O₂) and R16 (H₂O₂ (+M)→2OH (+M)) have lower peaks. In addition, two peaks appear during the R16 reaction, which drops immediately after reaching the second peak and shows negative values under the CO₂/O₂ atmosphere. Due to the rapid increase in temperature at the moment of autoignition, the reaction R16 proceeds towards heat absorption.

Next, the change processes of OH radical ROP under four different working conditions are specifically analyzed. From Figures 12(a) and 12(b), the OH radical maximum ROP of reactions R4 and R16 increase by 138% and 94.2%, respectively. The results show that the increase of oxygen concentration significantly boosts the OH radical ROP, which is consistent with the conclusions drawn from the above analysis of OH production. Buras et al. [57] used convolutional neural networks to investigate the relationship between the onset time scale of spontaneous oxidation and the IDT of first-stage under stoichiometric engine-related conditions and concluded that a strong relationship between the ROP peak of radicals such as OH and IDT was derived. From Figures 12(b) and 12(c), the OH radical maximum ROP peaks of reactions R4 and R16 increase by 36.8% and 23.8%, respectively. Then, from Figures 12(c) and 12(d), the OH radical maximum ROP peaks of reactions R4 and R16 increase by 105% and 80%, respectively. Comparing the changes of R4 and R16 in Figures 12(b)–12(d), we obtain

<table>
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<tr>
<th>Reaction number</th>
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<tbody>
<tr>
<td>R13</td>
<td>HO₂+OH→H₂O+O₂</td>
<td>R670</td>
<td>nC₁₆H₁₆+OH→C₁₅H₁₅+H₂O</td>
</tr>
<tr>
<td>R15</td>
<td>H₂O₂+O₂→2HO₂</td>
<td>R852</td>
<td>C₇H₁₄O₂⁺→C₇H₁₄O₂⁻⁺</td>
</tr>
<tr>
<td>R16</td>
<td>H₂O₂ (+M)→2OH (+M)</td>
<td>R856</td>
<td>C₇H₁₅O₂⁻→C₇H₁₄O₂⁻⁺</td>
</tr>
<tr>
<td>R43</td>
<td>CH₂O+OH→HCO+H₂O</td>
<td>R861</td>
<td>C₇H₁₅O₂⁻→C₇H₁₄O₂⁻⁺</td>
</tr>
<tr>
<td>R120</td>
<td>CH₃O₂+OH→CH₃OH+O₂</td>
<td>R864</td>
<td>C₇H₁₅O₂⁻→C₇H₁₄O₂⁻⁺</td>
</tr>
</tbody>
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Figure 11: Continued.
that the ROP peaks of OH radical decrease significantly with an equal proportional increase of the CO₂ volume fraction and do not show a regular linear change. Hence, the result also indicates a change in the way CO₂ affects the ROP of OH radical as increasing the CO₂ volume fraction. In addition, with the increase of CO₂ volume fraction, the OH radical ROP peak shows a trend of rapid decline first and then slowly decline. When the CO₂ volume fraction is changed from 60% to 40%, the reaction R4 and R16 OH radical ROP peaks increase by 180%
Figure 12: Continued.
and 124%, respectively. The result shows that R16 has a greater contribution to the generation of OH radical in a high-concentration CO₂ atmosphere, while the R16 is an important reaction affecting IDT.

5. Conclusions

This work studies the IDT of 70% n-heptane/30% toluene in a high-concentration CO₂/O₂ atmosphere and establishes
the CDE model. Then, the CDE model is verified through experiment, and the relevant factors affecting the IDT are discussed. In summary, we draw the following conclusions:

(1) The CDE model is employed to predict well the IDT of 70% n-heptane/30% toluene under the CO₂/O₂ atmosphere, and the IDT average errors in 60% CO₂/40% O₂, 50% CO₂/50% O₂, and 40% CO₂/60% O₂ atmospheres are 5.29%, 5.71%, and 8.18%, respectively.

(2) With increasing the CO₂ volume fraction from 40% to 60%, the CO₂ thermal effect is the main reason for the prolongation of IDT, while the chemical effect has little effect. However, when the CO₂ volume fraction exceeds 60%, the CO₂ third body effect is significantly enhanced, reducing the growth rate of IDT.

(3) The CO₂ content significantly affected the OH radical ROP, and the OH radical ROP peak of R4 (O+H₂O→→2OH) decreases by 180% when the CO₂ volume fraction increases from 40% to 60%.

Limited by time and experimental conditions, there is still room for further research in this paper in the future:

(1) The initial conditions of the constant volume combustion chamber test in this paper are relatively simple, only 850 K and 3 MPa. In future research, tests can be carried out for n-heptane ignition at different temperatures and pressures to verify the CDE model.

(2) In this paper, the high-speed camera direct shooting method is used to photograph the ignition process of the flame. This test method cannot obtain the content and distribution of free radicals in the flame. Laser-induced fluorescence testing can be added in future research.

(3) The inclusion of quantum chemical calculations in the n-heptane/toluene mechanistic study to explore new reaction pathways and the impact of new pathways on ignition characteristics.

Data Availability
No data were used that are available upon request or included within the article.

Conflicts of Interest
There is no conflict of interest between all authors, and it does not influence the publication of this article.

Authors’ Contributions
Yongfeng Liu and Guijun Bi proposed the idea of a visualization experiment combined with the simulation experiment. Yuewei Zhang and Jinou Song designed the experiments. Ping Wei and Hua Sun performed the experiments and analyzed the data. Yuewei Zhang accomplished the numerical simulation. Shengzhuo Yao and Yuewei Zhang wrote the paper. Yongfeng Liu and Lu Zhang revised the paper.

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References


