A Comprehensive Chemical Kinetic Model of 2,6,10-trimethyl Dodecane

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1 Introduction

Global energy and environmental issues present new challenges for combustion equipment, while injecting tremendous momentum into the exploration of renewable fuels. Biomass-based synthetic liquid fuels have received extensive focus and development due to their reproducibility and environmental friendliness. One of the most commercially promising biofuels, 2,6,10-trimethyl dodecane can be used as an alternative fuel for aviation kerosene or diesel due to its lower freezing point and a higher cetane number [1, 2]. At the same time, 2,6,10-trimethyldodecane has been blended with conventional aviation kerosene for propulsion engines and commercialized in several countries.

In order to make better use of 2,6,10-trimethyldodecane, it is necessary to have a deep understanding of its kinetic properties. So far, the research on the combustion properties of 2,6,10-trimethyldodecane has mainly focused on experimental research. Won et al. [3] measured the ignition delay time of 2,6,10-trimethyl dodecane and analyzed the effect of functional groups. Osswald et al. [2] used a flow reactor to measure the effect of initial temperature on the intermediate species concentration at different equivalence ratios. Millo et al. [4] studied the effect of combustion on diesel engines after adding 2,6,10-trimethyl dodecane to diesel. Richter et al. [5] measured the ignition delay time and laminar flame speed of 2,6,10-trimethyl dodecane.

The combustion calculation simulation coupled with computational fluid dynamics and detailed reaction kinetics plays a very important role in the design and optimization of the combustion device. Since that, it is necessary to develop a detailed reaction mechanism. However, since 2,6,10-trimethyldodecane has a large molecular weight ($C_{15}H_{32}$) and its molecular structure is asymmetrical, it is difficult to obtain its precise chemical mechanism using only a conventional scheme suitable for small-molecule hydrocarbon fuels. Richter et al. [5] constructed a skeletal mechanism for 2,6,10-trimethyl dodecane, which can better predict the ignition delay time of fuel, but the ability to predict the laminar flame propagation speed under high pressure is poor. At present, a well-tested detailed 2,6,10-trimethyl dodecane kinetic mechanism is still not exist.

In this paper, we constructs a detailed chemical mechanism for 2,6,10-trimethyl dodecane, which provides a accurate model for the simulation study of aero-engine reaction flow to deeply understand of the its characteristics.

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2 Chemical Kinetic Mechanism Formation

Most of chemical reaction mechanisms of hydrocarbon follow a common path, that is, the macromolecular fuel is first decomposed into small molecular components, which are further oxidized to formaldehyde or formic acid, etc., and finally produce CO, CO_2 and water. Normally, a mechanism construction process of hydrocarbon fuel starts from small molecules and low-carbon mechanisms construction, then the chemical reaction mechanism of macromolecules is added step by step [6]. In this paper, the reaction mechanism of Curran [7, 8] and Sarathy [9] et al. was used to construct the chemical reaction mechanism of 2,6,10-trimethyl dodecane.

The first step in the mechanism construction is to select the "core mechanism" foe the low carbon, and the C_0-C_4 mechanism [10] named AramcoMech 2.0 of NUI Galway University was selected. On this basis, the mechanism of C_6-C_7 of Mehl et al. [11] was added to constitute a mechanism of small molecule components including C_0-C_7. The chemical reaction mechanism (C_{15}-C_8) was constructed using a reaction class-based method. The main idea of this method is to classify the combustion oxidation path of macromolecular fuel into 30 classes of reactions [9], as shown in Table 1. Among them, the first 1-10th classes are high temperature reactions, and the 11th to 30th ones are low temperature reactions.

These 30 classes of reactions constitute the main reaction path for hydrocarbon fuels, as shown in figure 1. After dehydrogenation of the fuel, an alkyl group R is formed, and R is first added with oxygen to form ROO, and then the same composition is formed into QOOH, and then oxygen is added for a second time to form OOQOOH. The OOQOOH is further decomposed to products with small molecule. Recently, a new reaction pathway, the formation and consumption of $P(OOH)_2$, has proven to be an important reaction pathway in the low-temperature oxidation of hydrocarbon fuels [12, 13]. Based on the previous 30 class of reactions, reference to Bugler et al. [14] is the chemical reaction mechanism of pentane construction, and the five classes of low temperature oxidation reactions are added to the chemical reaction of 2,6,10-trimethyl dodecane. In the mechanism, as shown in the reaction of the 31th to 35th classes in Table 1. The added reaction reactions describe the process of OOQOOH isomeric formation of $P(OOH)_2$, and $P(OOH)_2$ further generate the final products. The 35 class of reactions constructed a 2,6,10-trimethyl dodecane mechanism which consists 461 species and 3,559 reactions. The sub-mechanism of 2,6,10-trimethyl dodecane was added to the core mechanism to finally obtain a detailed chemical reaction mechanism containing 2443 species and 9490 reactions.

Table.1: Reaction classes of fuel

Number	Reaction class	Number	Reaction class
1	Fuel decomposition	19	$ROO + CH_3O_2 = RO + CH_3O + O_2$
2	H-atom abstraction from the fuel	20	$ROO + ROO = RO + RO + O_2$
3	Alkyl radical (R) decomposition	21	ROOH = RO + OH
4	Alkyl radical (R) isomerization	22	RO decomposition
5	H-atom abstraction from alkenes	23	QOOH = cyclic + OH
6	Addition of O and OH to alkenes	24	QOOH = alkene + HO_2
7	Addition of HO_2,,CH_3O_2 and $C_2H_5O_2$ to alkenyl radicals	25	QOOH = alkene +carbonyl + OH
8	Alkene decomposition	26	QOOH + O_2 = OOQOOH
9	Alkenyl radical decompostion	27	Isomerization of OOQOOH
10	Retroene decomposition	28	Decomposition of carbonyhydroperoxide
11	Addition of O_2 radicals (R + O_2 = ROO)	29	Cyclic ether reactions with OH and HO_2
12	R + ROO = RO + RO	30	Decomposition of carbonyl species and carbonyl radicals
13	R + HO_2 = RO + OH	31	OOQOOH = $P(OOH)_2$
14	R + CH_3O_2 = RO + CH_3O	32	$P(OOH)_2$ = Peroxide olefins + HO_2
15	ROO = QOOH	33	$P(OOH)_2$ = Cyclic ether peroxide + OH
16	Concerted elimination of RO_2	34	Cyclic ether peroxide = Cyclic ether alkyl + OH

17	ROO + HO_2 = ROOH + OH	35	Peroxy alkenes decompose
18	ROO + H_2O_2 = ROOH + HO_2		

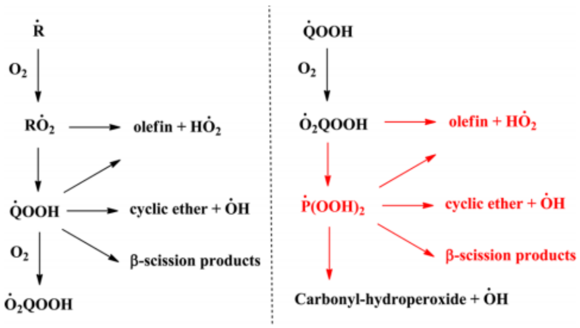

Figure 1. Schematic of pathways for 2,6,10-trimethyl dodecane combustion[14]

In the mechanism construction process, an analogy method is used to determine the reaction coefficients of the same class reaction. The reaction coefficient is mainly determined according to the position of the fuel breaking, the position of dehydrogenation or the spatial structure of the transition state [9]. After determining all chemical reactions of 2,6,10-trimethyl dodecane, the molecular structure of the intermediate species in all the mechanisms was introduced into the THERM [15] program to automatically generate then thermodynamic data and transport data for each species based on the group contribution method of Benson [16] and Bozzelli [17]. Finally, a optimized chemical mechanism of 2,6,10-trimethyl dodecane is obtained.

3 Chemical Kinetic Mechanism Verification

In order to verify the reliability of the constructed 2,6,10-trimethyl dodecane mechanism, the shock tube experimental data was used to compare the numerical data with CHEMKIN-PRO software [18] using the detailed mechanism. The concentration of important species and laminar flame speed were compared. First, in order to analyze the effect of the new low-temperature reaction path addition on the fuel ignition delay time, only the mechanism of the traditional 30-class reactions and the 2,6,10-trimethyl dodecane mechanism considering the 35-class reactions were used separately, and the results are shown in Figure 2. Compared with the experimental data [3], the 30-class reactions mechanism can only reproduce the high temperature ignition delay time, and the 35-class reactions one can reproduce the phenomenon in a wide temperature range.

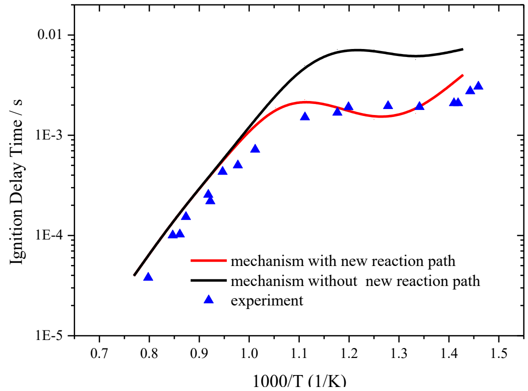

Figure 2. Ignition delay times of 2,6,10-trimethyl dodecane at the condition of 20 atm and equivalence ratio = 1.0

The ignition delay time sensitivity analysis results are shown in Figure 3. It can be seen that at the temperature of 800 K, the 2,6,10-trimethyl dodecane mechanism has two reaction paths. The first reaction path is R plus oxygen to form ROO, and then the same as the low temperature reaction path of QOOH; the other is the decomposition reaction of R, such as: C15H31-26X-5 = C11H22-37-1 + IC4H9. The competition of these two reaction paths causes the NTC phenomenon of the mechanism in the low temperature region. Comparing the sensitivity coefficients of the 30-class reactions mechanism of 2,6,10-trimethyl dodecane and the 35-class reactions one, it can be seen that the addition of the reactions make the sensitivity coefficient of the small molecule compounds significantly increased. This is because part of QOOH generates P(OOH)2, which is finally decomposed into small molecule hydrocarbon radicals, thereby increasing the activity of the entire low temperature reaction process.The comparison of numerical data and the flow reactor experimental data is shown in figure 4, and it can be seen that the predicted concentrations of the key species are in good agreement with the experimental data. The numerical laminar flame speeds also can be well reproduced compare with the experimental date from Richter et al. [5].

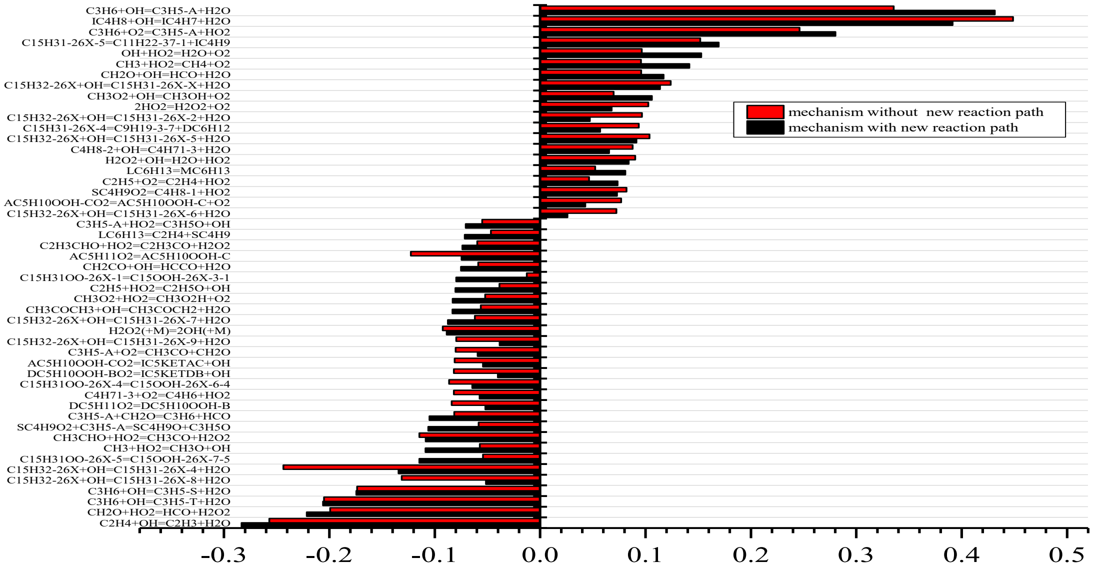

Figure 3. Sensitivity of total ignition delay time for 2,6,10-trimethyl dodecane at the condition of 20 atm, 800 K and phi = 1.0

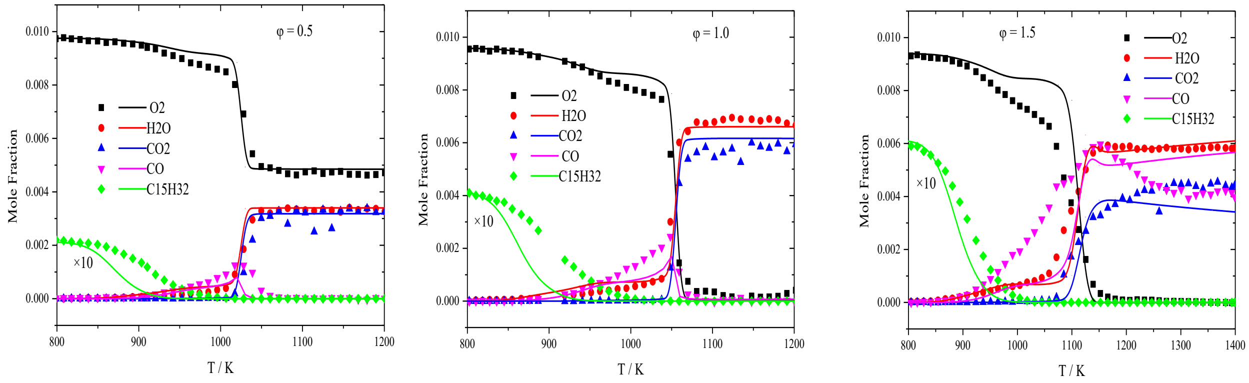

Figure 4. Mole fraction profiles for major species for various equivalence ratios of 2,6,10-trimethyl dodecane

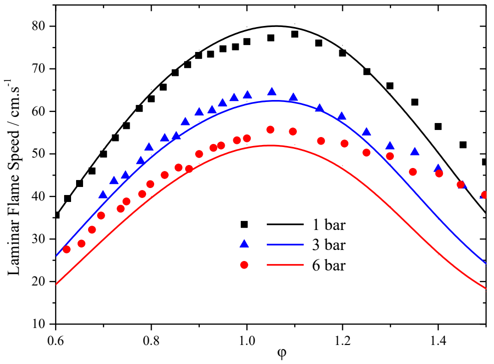

Figure 5. Comparison of measured burning velocities and simulated laminar flame speeds for 2,6,10-trimethyl dodecane

4 Conclusions

A detailed chemical kinetic mechanism of 2,6,10-trimethyl dodecane was proposted, based on the traditional 30-class reaction and the additional five class reactions. The verificating results show that the mechanism can predict the species concentration, ignition delay time and laminar flame speed well.

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