

## HIGH PRESSURE IGNITION BEHAVIORS OF METHANE/ETHANE/PROPANE-*n*-HEPTANE MIXTURES REPRESENTING NATURAL GAS-DIESEL DUAL FUEL

by

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*Considering that natural gas is the key transition fuel towards the carbon-neutral future, the objective of the present study is to gain insight into evolution features of natural gas-diesel dual fuel during ignition process. Firstly, new experimental data of ignition delay times for the stoichiometric methane/ethane/propane-*n*-heptane mixtures, which is of significance for validating and optimizing chemical kinetic models of the dual fuel at engine-relevant conditions, were acquired through a shock-tube facility at pressure of 40 atmopshere within temperature range of 1200-1600 K, and quantitative influences of components of the fuel mixtures on ignition were determined. Then importance of species including typical radicals and alkenes during ignition processes were identified. Besides, stage characteristics of the fuel mixtures during ignition processes were analyzed. The result shows that the ignition of real natural gas which contains some ethane and propane is greatly different from that of methane. It can be seen that the C2 substances are significant to control ignition of the mixtures. For methane-*n*-heptane and methane/ethane-*n*-heptane mixtures, the whole ignition process can be divided into decomposition and oxidation stages. While for the fuel mixtures containing propane and *n*-heptane, it seems to be more reasonable to divide the whole ignition process into three-stages, i.e., decomposition, mixed and oxidation stages.*

*Keywords: methane/ethane/propane-*n*-heptane mixtures, ignition, stage characteristics, natural gas-diesel dual fuel, conversion processes*

### Introduction

Natural gas is seen as the key transition fuel towards the zero-carbon energy future due to its potential to reduce the GHG emissions [1]. However, it is not easy to compress natural gas to ignite. Therefore, for the compression ignition engine fueled with natural gas (e.g., the marine liquefied natural gas engine), it is required to provide an additional ignition source. One method is to inject a certain quantity of pilot diesel fuel into the combustion chamber as an ignition source to ignite natural gas [2]. This type of engine is called as the natural gas-diesel dual fuel engine. Because of the difference in ignition between natural gas and diesel, understanding ignition characteristics of the natural gas-diesel dual fuel is of importance to clarify

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the complicated in-cylinder combustion process of the dual fuel engine [3]. Besides, as one of parameters to describe the ignition characteristics, the ignition delay time of the dual fuel is also necessary to comprehensively validate and improve the chemical kinetic schemes of the dual fuel, which is the indispensable part for the engine simulation based on the coupling model of fluid dynamics and chemical kinetics [4]. Thus the present study mainly concentrates on the ignition characteristics of the natural gas-diesel dual fuel.

It is known that both natural gas and diesel are complex mixtures, and their composition strongly depends on gas fields and production processes. Natural gas contains mainly methane, and a small quantity of ethane and propane can also be found in natural gas generally. The composition of diesel is much more complicated, which is composed of thousands of different species. Thus surrogate fuels of natural gas and diesel are basically necessary for the study on their combustion characteristics [5-15]. The typical candidate of natural gas surrogate fuel is methane due to its high content in real natural gas. Besides, ethane and propane are also contained. While for the diesel surrogate fuel, many schemes for it are proposed, and among them, *n*-heptane is often regarded as the surrogate fuel of diesel due to the approximate equality in cetane number between *n*-heptane and diesel [5, 16]. Thus in the present study on ignition characteristics of the natural gas-diesel dual fuel, methane/ethane/propane ( $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ ) and *n*-heptane are considered as the components of natural gas and diesel surrogate fuels, respectively.

The methane-*n*-heptane mixture was a typical surrogate fuel model of the natural gas-diesel dual fuel, and on this basis, ignition characteristics of the dual fuel was studied [5, 16], which mainly focus on exploring changes in ignition delay times and free radicals during ignition processes. However, as components of natural gas, ethane and propane also have remarkable influences on the ignition of methane, which has been indicated by studies in references [17-19]. To more comprehensively reveal ignition features of the natural gas-diesel dual fuel, it is quite necessary to introduce ethane and propane into the methane-*n*-heptane mixture. For the high pressure ignition of the dual fuel, less experimental data and information about the detailed conversion characteristics behind ignition such as decomposition and oxidation processes of the fuel components are available in the literature.

With regard to the chemical kinetic mechanisms, considering that methane, ethane and propane are indispensable intermediate species of combustion of *n*-heptane, the chemical kinetic schemes for combustion of *n*-heptane have to include the sub-mechanisms of methane, ethane, and propane. Thus theoretically, the detailed chemical mechanisms of *n*-heptane are capable of reproducing numerically the combustion processes of the mixtures composed of methane, ethane, propane, and *n*-heptane, but given the strong non-linearity of chemical processes, applicability of the chemical mechanisms to modelling accurately ignition processes of the aforementioned mixtures needs to be further verified. For *n*-heptane, Zhang *et al.* [20] proposed a chemical mechanism to describe its combustion process, which is called as the NUI 2016 mechanism in the present study. This mechanism consists of 1268 species and 5336 elementary reactions. Besides, Mehl *et al.* [21] also put forward a chemical kinetic scheme for combustion of *n*-heptane, which is denoted by the LLNL 3.1 mechanism here. This mechanism involves 654 species and 2827 elementary reactions. In the present study, these two mechanisms will be employed again to analyze their behaviors in reproducing numerically the ignition processes of methane/ethane/propane-*n*-heptane mixtures at high pressure.

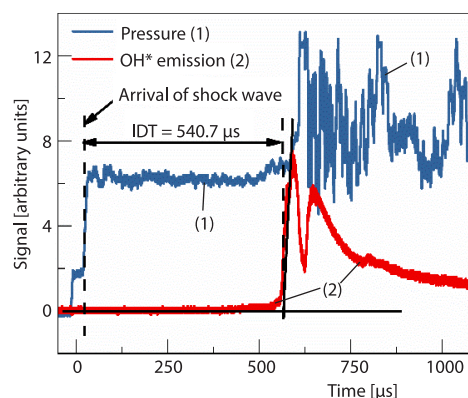
Therefore, the objective of the current study is to explore high pressure ignition characteristics of mixtures consisting of methane, ethane, propane, and *n*-heptane representing the natural gas-diesel dual fuel. New experimental data of ignition delay times of the fuel mixtures

will be obtained, and based on the analysis of behaviors of two detailed reaction mechanisms in producing the experimental data, quantitative effects of components of the fuel mixtures on ignition delay time will be determined. Influences of different intermediate species on the ignition will be studied in combination with the sensitivity of ignition delay time to elementary reactions. In addition, conversion and stage characteristics of components of the fuel mixtures at studied initial conditions will be analyzed.

## Methods

### Experimental method

In the present study, the desired ignition delay times were measured through a shock tube device. Regarding the construction of this shock tube, it consists of the low pressure driven section, the middle section and the high pressure driver section with lengths of 7 m, 0.2 m, and 3 m, respectively. The inner diameters of these sections are all 111.3 mm. A heating insulation jacket is installed outside the low pressure section ensure that the reactant in the tube is completely vaporized. Four pressure sensors are installed on the wall of the low pressure section to measure the pressure distributions accompanying the incident shock wave movement and then to obtain the incident shock wave velocity. According to the incident shock wave velocity and the initial conditions of reactant, values of temperature and pressure after the reflected shock wave are obtained using the GASEQ software [22]. An optical window and a pressure sensor are installed near the end of the low pressure section acquire signals of the emission spectrum and the pressure, respectively, of the test area after the reflected shock wave. When conducting the experiment, the target reactant is firstly injected into a mixing tank according to the Dalton's law of partial pressure, and this tank is left to stand for more than 12 hours to ensure that the different species of the reactant are uniformly mixed with each other. A heating insulation jacket is also installed outside the mixing tank. Then the reactant in the tank is transported into the low pressure section. More detailed information of this shock tube device can be found in our previous study [5]. Figure 1 presents the typical pressure and OH\* spectrum signals obtained. Here the start point of the ignition period is determined according to the pressure signal. The intersection of the baseline and the tangent line through the point which corresponds to the maximum slope of the OH\* spectrum signal defines the end point of the ignition period.



**Figure 1. Typical signals of pressure and OH\* spectrum during the ignition process of methane/propane-*n*-heptane-oxygen-argon mixture; initial pressure, temperature, equivalence ratio and argon dilution ratio are 40 atmosphere, 1340 K, 1.0, and 95%, respectively; IDT refers to the ignition delay time**

As mentioned previously, methane, ethane, and propane are selected to construct the natural gas surrogate fuel, and *n*-heptane is treated as the representative of diesel. For a natural gas-diesel dual fuel engine, natural gas dominates the heat release of the fuel, while diesel accounts for a relatively small proportion. Therefore, ignition characteristics of the mixtures of high content natural gas (methane/ethane/propane) and low content diesel, *n*-heptane, are investigated in the present study. In addition, as described in the introduction, methane is the main component of natural gas [23, 24], and consequently in the present study the content of

methane is set to be the highest. Natural gas also contains a small quantity of ethane and propane, and thus these two species are introduced into the natural gas surrogate fuel. Besides, to observe influences of ethane and propane additions on ignition of natural gas-diesel mixtures, perturbations are given to contents of ethane and propane in the mixtures. As a contrast, ignition delay times of pure *n*-heptane is also determined. Table 1 shows the detailed composition of the reactants studied. The method for calculating mole fraction of each component in reactants can be found in the related reference [5]. Considering the real combustion process of a dual fuel engine, the initial pressure, initial temperature range and the equivalence ratio in the present study are 40 atmosphere, 1200-1600 K, and 1.0, respectively.

**Table 1. Composition of the reactants at studied initial conditions; methane/ethane/propane, and *n*-heptane are components of surrogate fuels of natural gas and diesel, respectively**

Number	Natural gas/diesel [%]	CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub> [%]	Mole fractions of species in the mixtures					
			CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	<i>n</i> -C <sub>7</sub> H <sub>16</sub>	O <sub>2</sub>	Ar
1	0/100	0/0/0	0	0	0	0.417	4.5833	95
2	80/20	100/0/0	0.83	0	0	0.21	3.96	95
3	95/5	100/0/0	1.377	0	0	0.072	3.551	95
4	100/0	100/0/0	1.667	0	0	0	3.333	95
5	95/5	100/0/0	1.377	0	0	0.072	3.551	95
6		90/10/0	1.189	0.132	0	0.07	3.608	95
7		80/20/0	1.017	0.254	0	0.067	3.661	95
8		95/0/5	1.256	0	0.067	0.07	3.608	95
9		85/0/15	1.041	0	0.184	0.064	3.711	95
10	100/0	80/15/5	1.185	0.222	0.074	0	3.517	95
11	95/5		0.998	0.187	0.062	0.066	3.687	95
12	80/20		0.627	0.118	0.039	0.196	4.020	95

The uncertainty of temperature and pressure of the test zone after the reflected shock wave is mainly attributed to the non-ideal effect of the reactant and the error in measurement of velocity of the incident shock wave [25]. In combination with the shock wave theory and the method for error analysis, the error of the experimental data for the ignition measured in this work does not exceed 15% [26].

### Simulation method

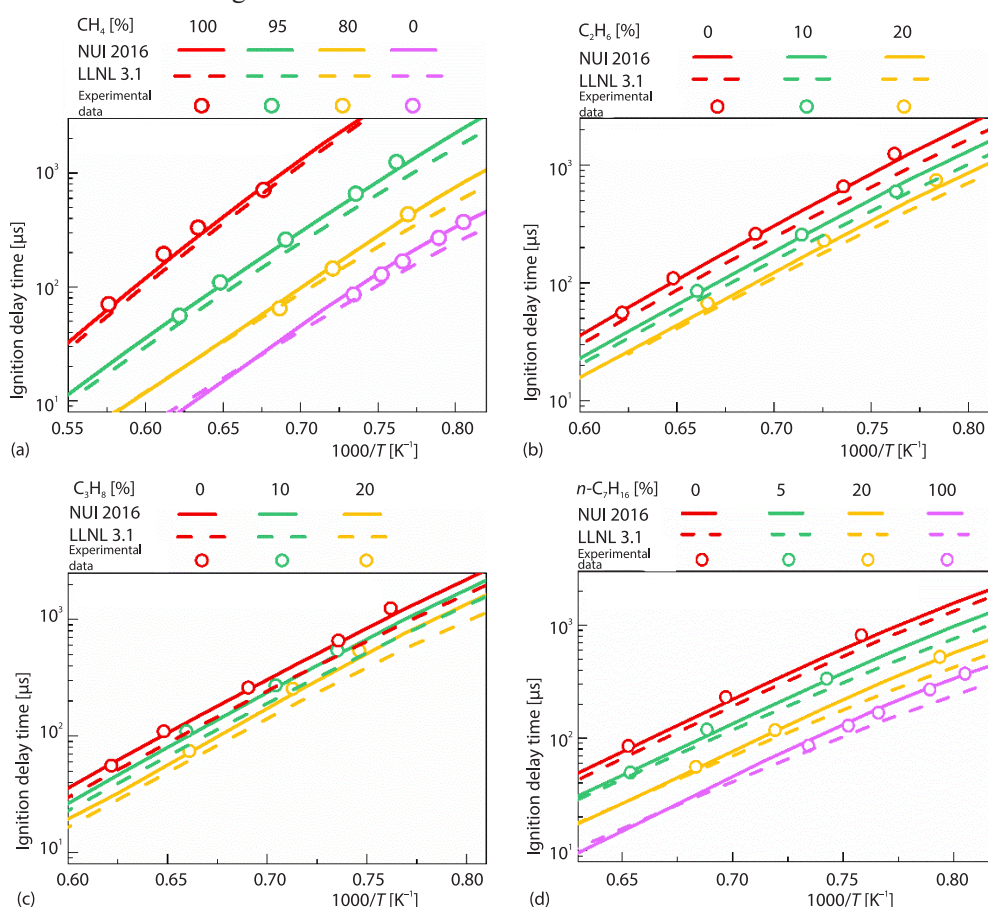
Ignition processes of mixtures involving methane, ethane, propane, and *n*-heptane under the conditions described previously, were modeled using the CHEMKIN-PRO software. Such processes are assumed to be zero-dimensional and adiabatic. The time corresponding to the maximum value of OH mole fraction is defined as the simulated ignition time point.

As mentioned in section *Introduction*, methane, ethane, and propane are generated during the combustion process of *n*-heptane, which means that the detailed *n*-heptane chemical kinetic mechanism includes the chemical kinetic sub-mechanisms of methane, ethane, and propane. Therefore, the mechanisms of NUI 2016 and LLNL 3.1 for describing combustion process of *n*-heptane were utilized to simulate the ignition processes of methane/ethane/propane-*n*-heptane mixtures. The accuracy of simulation of these two mechanisms will be discussed in section *Ignition delay times of mixtures involving methane, ethane, propane and n-heptane*.

## Results and discussion

### *Ignition delay times of mixtures involving methane, ethane, propane, and n-heptane*

Experimental values of ignition delay times of methane/ethane/propane-*n*-heptane mixtures under different initial conditions are presented in fig. 2. The NUI 2016 and LLNL 3.1 mechanisms were also employed to simulate ignition processes of the mixtures, and the result is shown in the same figure.



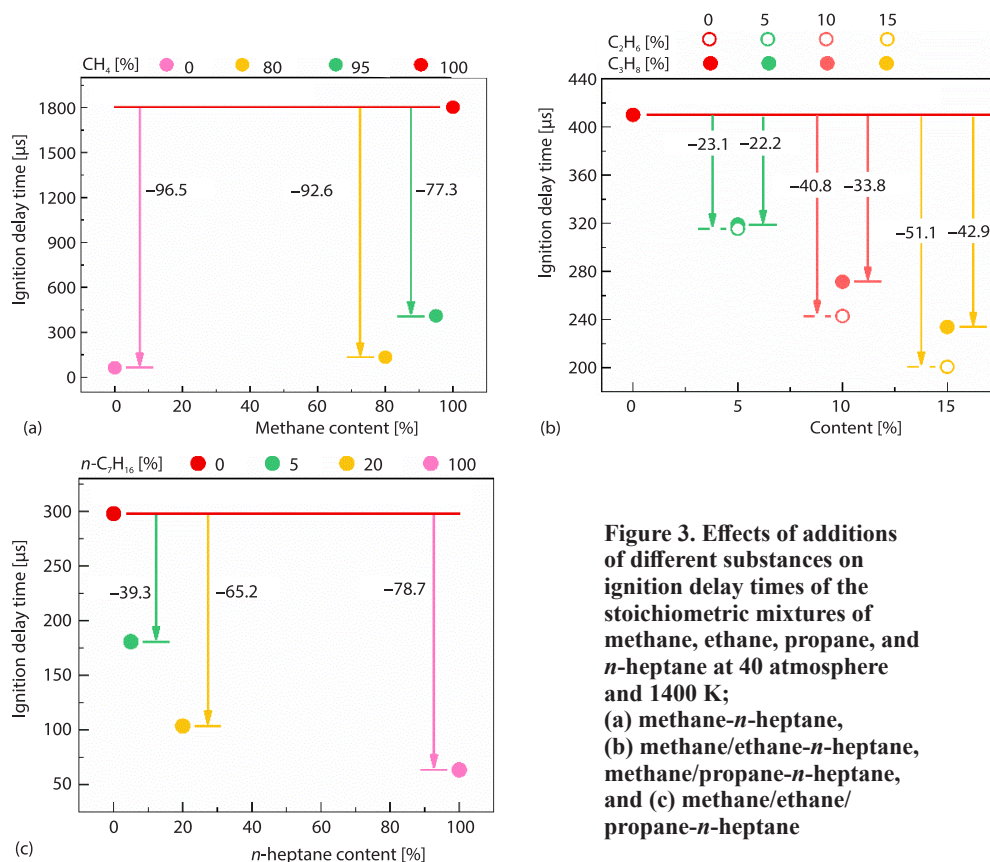
**Figure 2.** Ignition delay times for the stoichiometric methane/ethane/propane-*n*-heptane mixtures at 40 atmosphere within initial temperature range of 1200-1600 K; symbols are the experimental values of ignition delay times, and lines represent simulated values; (a) methane-*n*-heptane, (b) methane/ethane-*n*-heptane, (c) methane/propane-*n*-heptane, and (d) methane/ethane/propane-*n*-heptane

In fig. 2, it can be found that within the initial temperature range, the logarithm of ignition delay time of the several studied mixtures rises approximately linearly with the increasing reciprocal of the initial temperature. Considering changes in ignition delay times for the fuel mixtures composed of species with different contents, it is demonstrated that only the methane addition will suppress the ignition of the mixtures, and the incorporation of ethane, propane, and *n*-heptane have positive impact on the ignition. Besides, as shown in fig. 2, at initial pres-

sure of 40 atmosphere the NUI 2016 reaction mechanism predicts the ignition processes for all studied mixtures more accurately than the LLNL 3.1 mechanism, especially within the relatively lower temperature range. Considering such difference derived from the comparison between simulated and experimental data obtained, it seems that at higher pressures part of the LLNL 3.1 mechanism may need further improvement compared to the NUI 2016 mechanism. Thus for the following part, we choose the NUI 2016 mechanism to analyze ignition characteristics of methane/ethane/propane-*n*-heptane mixtures under given initial conditions.

Figure 2 shows the qualitative effects of additions of methane, ethane, propane, and *n*-heptane on ignition delay times of the mixtures in tab. 1 at the studied conditions, and in order to quantitatively determine such effects, we employed the NUI 2016 mechanism to predict the ignition delay times of these various mixtures under initial temperature of 1400 K, initial pressure of 40 atmosphere and equivalence ratio of 1.0, and then the changes in ignition delay times when altering the composition of the fuel mixtures were calculated. The result is given in fig. 3.

As shown in fig. 3(a), for methane-*n*-heptane mixtures at 40 atmosphere, comparing the difference in variation of the ignition delay time at *n*-heptane contents of 5% and 20% (*i.e.*, at methane contents of 95% and 80%, respectively), it can be seen that adding *n*-heptane into methane will have a strongly non-linear promotion for the ignition of methane at 40 atmosphere, and even introducing a small amount of *n*-heptane can impose a significant effect on the ignition of methane. In fig. 3(b), noticing the specific numbers for the reduction of the ignition delay time due to the inclusion of ethane and propane in methane-*n*-heptane mixtures under



**Figure 3. Effects of additions of different substances on ignition delay times of the stoichiometric mixtures of methane, ethane, propane, and *n*-heptane at 40 atmosphere and 1400 K; (a) methane-*n*-heptane, (b) methane/ethane-*n*-heptane, methane/propane-*n*-heptane, and (c) methane/ethane/propane-*n*-heptane**

the studied conditions, it can be found that the presence of ethane and propane also results in a non-linear promotion for ignition of mixtures of methane and *n*-heptane. But at lower ethane and propane contents of 5%, influences of ethane and propane additions on the ignition of methane-*n*-heptane mixtures are similar to each other. When continually raising the ethane and propane contents (from 5 to 10% and 15%), remarkable difference in promotion for the ignition between ethane and ethane occurs, and from fig. 3(b) the ethane addition will reduce the ignition delay time with a larger degree. From the point of the ignition, it can be concluded that ethane in natural gas is more important than propane to make natural gas spend less time igniting.

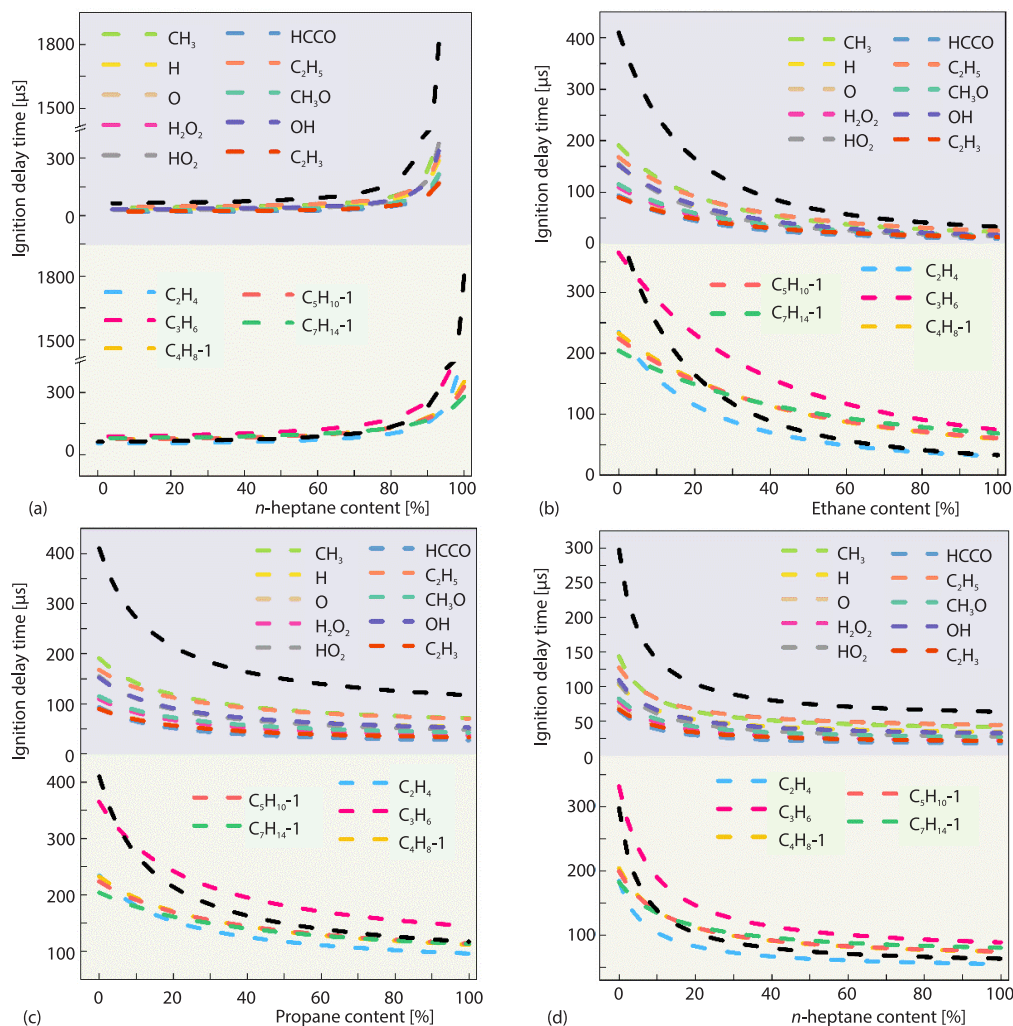
Comparing figs. 3(a) and 3(c), it is seen that value of the ignition delay time of the stoichiometric methane/ethane/propane mixture is only one sixth of that of pure methane at 40 atmosphere and 1400 K, suggesting that the ignition of methane is different from that of real natural gas which contains some ethane and propane. In addition, fig. 3(c) also shows that a small amount of *n*-heptane (5%) will remarkably alter ignition delay times of both pure methane and methane/ethane/propane mixture. Considering higher heating values and molecular weights of methane, ethane, propane and *n*-heptane [27], the *n*-heptane content defined by mole, mass and energy fractions, respectively, can be converted into each other. For the natural gas-diesel dual fuel engine, if the diesel content in the dual fuel by energy fraction is 1%, take *n*-heptane as the diesel surrogate fuel, and then the 1% diesel content by energy fraction corresponds to the 0.26% *n*-heptane content by mole fraction. From the point of regulating the ignition of natural gas with diesel, such *n*-heptane content just slightly affects the ignition delay time of methane/ethane/propane mixture, as shown in fig. 3(c).

#### *Influences of different species on ignition of methane/ethane/propane-n-heptane mixtures*

To understand ignition from the point of chemical kinetics for methane/ethane/propane-*n*-heptane mixtures, we first performed the sensitivity analysis of the ignition delay time of the mixtures shown in tab. 1 to the elementary reactions based on the NUI 2016 mechanism, and the result is shown in fig. S1 and tab. S1 in the supplementary material. From the sensitivity analysis result it can be found that under the studied conditions, reactions related to small species with carbon number of 2 or smaller play significant roles during the ignition processes. To quantitatively determine the effects of different species on the ignition of the mixtures, a certain quantity of target species was used to replace argon which is the dilution gas in the reactant, and then we calculated the ignition delay times of the mixtures using the NUI 2016 mechanism. Here the dilution ratio of argon is set to be 94.7%, and the content of the target species in the reactant, which consists of fuel, oxygen, argon and target species, is 0.3%. Other conditions including pressure, temperature and equivalence ratio are 40 atmosphere, 1400 K, and 1.0, respectively. The calculated result is shown in fig. 4.

In fig. 4, ignition delay times of the studied mixtures with additions of different radicals and alkenes were predicted. The  $C_2H_5$  and HCCO are closely related to  $C_2H_4$  and  $C_2H_3$ , which is shown in figs. S2 to S5 that present conversion pathways of components of the studied mixtures. The decomposition product of  $H_2O_2$  is mainly OH. Thus influences of  $C_2H_5$ , HCCO and  $H_2O_2$  on the ignition of the mixtures were also considered here. Figure S1 shows that the existences of  $C_2H_4$  has an effect on the ignition of the mixtures through the elementary reaction R248  $C_2H_4 + OH \rightleftharpoons C_2H_3 + H_2O$ , and to evaluate more comprehensively influences of alkenes on ignition, more different alkenes were included.

From fig. 4 it can be seen that the effect of each substance on the ignition of the methane/ethane/propane-*n*-heptane mixtures depends on the type of this substance, and such



**Figure 4. Effects of different species on ignition delay times of the stoichiometric mixtures of methane, ethane, propane and *n*-heptane at 40 atmosphere and 1400 K; (a) methane-*n*-heptane, (b) methane/ethane-*n*-heptane, (c) methane/propane-*n*-heptane, and (d) methane/ethane/propane-*n*-heptane**

result is consistent with the sensitivity of the ignition delay time to the reactions. Here take the elementary reaction R99:  $\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$  as the example. Based on fig. 4 it can be found that these four species in R99 affect the ignition of the mixtures in the order of  $\text{CH}_3 < \text{HO}_2 < \text{CH}_3\text{O} < \text{OH}$ . Therefore, the occurrence of R99 means a process where the substances with weak promotion on the ignition are converted into the substances which promote the ignition more strongly, thus resulting in the negative sensitivity coefficient of R99, as shown in fig. S1.

Furthermore, from fig. 4 it can also be seen that the radicals HCCO and C<sub>2</sub>H<sub>3</sub> have greater effects on ignition of methane/ethane/propane-*n*-heptane mixtures compared to the rest of free radicals, indicating that the abundant amount of HCCO and C<sub>2</sub>H<sub>3</sub> will trigger the ignition



faster. From the reaction pathway analysis shown in figs. S2-S5, it can be determined that both HCCO and  $C_2H_3$  are mainly produced from  $C_2H_6$ . Comprehensively considering the importance of HCCO and  $C_2H_3$  to the ignition and their origins, it can be concluded that the existence of  $C_2$  substances (including  $C_2H_6$ ,  $C_2H_5$ ,  $C_2H_4$  and  $C_2H_3$ ) is of importance for the ignition of the mixtures involving methane, ethane, propane, and *n*-heptane. In fact, when comparing the impacts of different alkenes on the ignition of the studied mixtures, the significant role of  $C_2H_4$  can be observed, as shown in fig. 4.

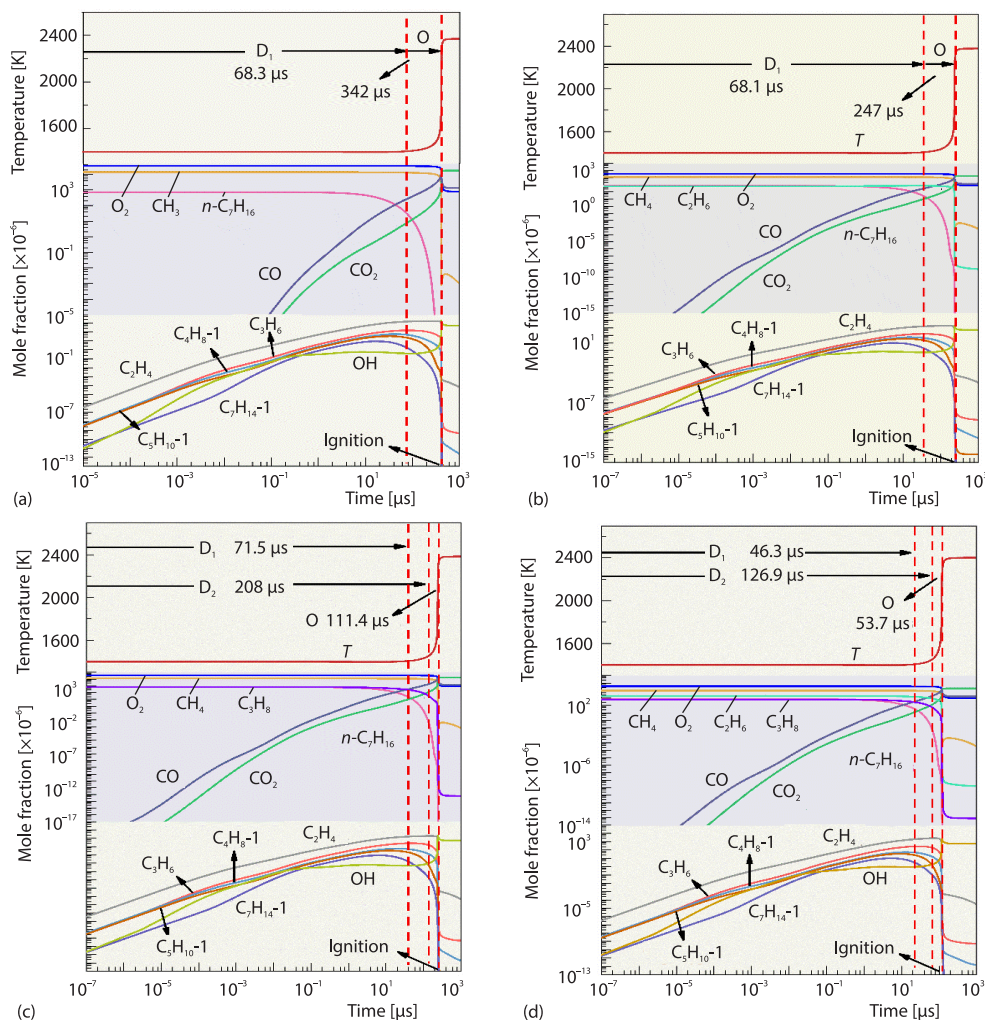
In addition, fig. 4 also presents the significance of O for the ignition of the studied mixtures, which is quite similar to influences of  $C_2H_3$  and HCCO. At the same time, other radicals such as  $H_2O_2$  and  $CH_3O$  also promote the ignition obviously. Influences of these oxygenated radicals on the ignition demonstrate the significance of oxygen in the combustion process. From fig. 4 the relatively lower reactivity of  $CH_3$  in the ignition process is also observed compared to other radicals.

#### *Conversion processes of components of methane/ethane/propane-n-heptane mixtures*

Based on reaction pathways, which are shown in figs. S2-S5, of components of methane/ethane/propane-*n*-heptane mixtures under 1400 K, 40 atmosphere and equivalence ratio of 1.0, it can be concluded that during ignition processes, conversion of methane and ethane are mainly through dehydrogenation and oxidation reactions. While propane and *n*-heptane will decompose directly or after dehydrogenation reactions, and their derivatives react to form final products through oxidation reactions. During such processes of propane and *n*-heptane, alkenes with different carbon numbers are produced. To gain in-depth understanding into stage characteristics of ignition processes of the fuel mixtures studied, we depicted mole fraction profiles of fuel components and main alkenes produced during ignition processes, and the result is shown in fig. 5. This figure also presents variations of temperature and mole fractions of  $O_2$ , CO,  $CO_2$ , and OH with the time, which are related to ignition processes.

In fig. 5 it can be clearly observed that propane and *n*-heptane mainly experience first the decomposition processes, and at the same time the oxidation processes are relatively weak. This is because when mole fractions of  $O_2$  still remain nearly unchanged, mole fractions *n*-heptane, figs. 5(a)-5(d), and propane, figs. 5(c) and 5(d), begin to reduce with the time. At this time, alkenes exhibit increase in their respective mole fractions, and mole fractions of CO and  $CO_2$  are still quite low. Changes in the temperature are also slight. Then it can be derived reasonably that the early stages of ignition processes feature the decomposition reactions for the fuel mixtures studied under the given conditions. Subsequently, in fig. 5 after the  $O_2$  concentrations start to decline near the ignition time points, mole fractions of all hydrocarbons shown in the figure reduce rapidly to very low values, and at the same time, CO and  $CO_2$  are produced on a large-scale, which indicates that after the initial decomposition reactions, the concerned ignition processes possess oxidation reactions as the main feature. In addition, it is noticed that during the whole processes,  $C_2H_4$  has a higher concentration than other alkenes. When the ignition occurs, remarkable changes to almost every parameter happen. For example, the temperature rises significantly, and  $C_2H_4$  is consumed rapidly. The radical OH achieves its maximum concentration.

Therefore, ignition processes of mixtures of methane, ethane, propane, and *n*-heptane at the given conditions involve two typical stages, *i.e.*, decomposition and oxidation stages. Here we quantitatively separated these two-stages from each other. Taking *n*-heptane as the example, defined the decomposition stage is defined as the period from the start to the time corresponding to consumption of 95% of *n*-heptane, and the rest of ignition period was called



**Figure 5.** Mole fraction profiles of reactants, related intermediate species and final products as well as profiles of temperature during ignition processes of the studied fuel mixtures under 40 atmosphere, 1400 K, and equivalence ratio of 1;  $D$  and  $O$  are the decomposition and oxidation stages, respectively; (a) 95% methane- $n$ -heptane, (b) methane/5% ethane- $n$ -heptane, (c) methane/5% propane- $n$ -heptane, and (d) methane/ethane/propane-5%- $n$ -heptane

as the oxidation stage [28]. Thus for ignition processes of methane- $n$ -heptane and methane/ethane- $n$ -heptane mixtures, as shown in figs. 5(a) and 5(b), decomposition and oxidation stages can be determined easily according to this definition. While as to ignition processes of methane/propane- $n$ -heptane and methane/ethane/propane- $n$ -heptane mixtures, because both propane and  $n$ -heptane can decompose, then for each case two different decomposition stages will be found corresponding to two different time points at which 95% of  $n$ -heptane and 95% of propane are consumed, respectively. Such results are illustrated in figs. 5(c) and 5(d).

For the fuel mixtures involved in fig. 5, the  $n$ -heptane content remains constant, *i.e.*, 5%. As shown in figs. 5(a) and 5(b), only  $n$ -heptane needs to decompose first, and methane and

ethane are consumed mainly during the oxidation stages. The time required for the oxidation stages (denoted by O) is greatly longer than that for the decomposition stages (denoted by  $D_1$ ). This difference means that the decomposition stages proceed faster than the oxidation stages. In addition, when adding ethane into methane-*n*-heptane mixtures, no remarkable changes happen in the decomposition stages. While for methane/propane-*n*-heptane and methane/ethane/propane-*n*-heptane mixtures, as shown in figs. 5(c) and 5(d), if using the time point corresponding to consumption of 95% of *n*-heptane to define the end point of the decomposition stage, the resulting conclusions are similar to those derived from figs. 5(a) and 5(b). Specifically, the corresponding decomposition ( $D_1$ ) and oxidation stages ( $D_2 + O - D_1$ ) in fig. 5(c) last for 71.5  $\mu\text{s}$  and 247.9  $\mu\text{s}$ , respectively, and in fig. 5(d) they are 46.3  $\mu\text{s}$  and 134.3  $\mu\text{s}$ , respectively. However, if the decomposition stage ends with the time point at which 95% of propane is consumed, relationships between the decomposition and oxidation stages become different. It is observed that the decomposition stages ( $D_2$ ) spend more time than the oxidation stages (O). But in figs. 5(c) and 5(d), during the stages ( $D_2 - D_1$ ) between  $D_1$  and O, the corresponding mole fraction of CO varies from  $\sim 0.03\%$  to  $\sim 0.2\%$ , thus suggesting that during these stages, the oxidation reactions occur on a certain scale. This means that the decomposition reactions of propane and the oxidation reactions proceed at the same time during the stages between  $D_1$  and O, and thus it can be derived that the boundaries between the decomposition and oxidation stages are not exactly distinct. As a result, for the ignition process of the fuel mixtures involving propane and *n*-heptane, it seems to be more reasonable to divide the whole process into three-stages, *i.e.*, decomposition, mixed and oxidation stages. The middle mixed stage just denotes the coexistence of the decomposition and oxidation reactions.

## Conclusions

In the present study, to understand evolution features of natural gas-diesel dual fuel during ignition process, ignition processes of methane/ethane/propane-*n*-heptane mixtures at 40 atmosphere and equivalence ratio of 1.0 were investigated within initial temperature range of 1200-1600 K. The main conclusions of the present study are summarized as follows.

- For the studied mixtures at given initial conditions, incorporation of ethane, propane and *n*-heptane enhances the ignition. Compared to propane, the ethane addition will reduce the ignition delay time more remarkably. The ignition of methane is significantly different from that of real natural gas which contains some ethane and propane.
- Free radicals HCCO and  $C_2H_3$  have greater effects on the ignition of the studied mixtures. Considering the origins of HCCO and  $C_2H_3$ , it can be derived reasonably that the existence of  $C_2$  substances is of importance for the ignition of the mixtures.
- For methane-*n*-heptane and methane/ethane-*n*-propane mixtures, the whole ignition process can be divided into decomposition and oxidation stages, and the later stage lasts for a longer time than the former one. While for the mixtures containing propane and *n*-heptane, it seems to be more reasonable to divide the whole ignition process into three-stages, *i.e.*, decomposition, mixed and oxidation stages.

## Acknowledgment

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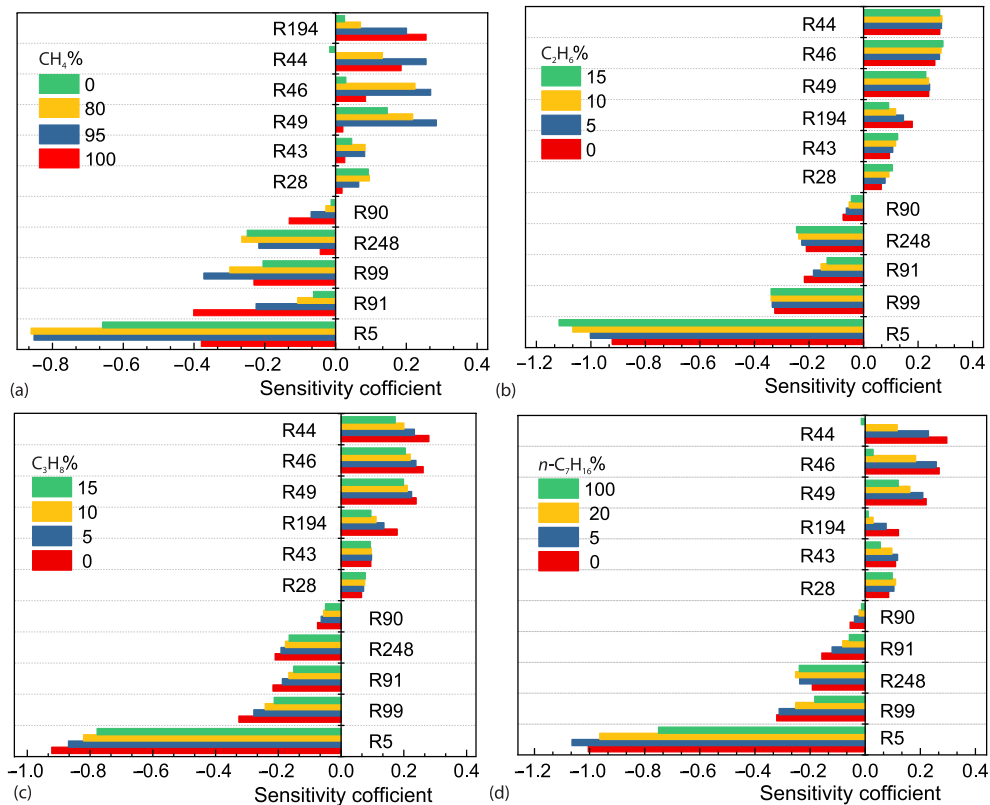
### Supplementary materials

#### Part 1: Sensitivity of the ignition delay time to elementary reactions

Notice: The sensitivity coefficient of ignition delay time to an elementary reaction is defined:

$$S = \frac{\tau(2.0k_i) - \tau(0.5k_i)}{1.5\tau(k_i)} \quad (1)$$

where  $\tau$  is the ignition delay time,  $k_i$  – the rate constant of the  $i^{\text{th}}$  elementary reaction, and  $S$  – the normalized sensitivity coefficient.



**Figure S1. Sensitivity coefficients of elementary reactions which influence significantly the ignition delay times of the stoichiometric mixtures of methane, ethane, propane and *n*-heptane at 40 atmosphere and 1400 K**

**Table S1. Detailed elementary reactions shown in fig. S1**

Number	Elementary reactions
R5	$O_2+H\rightleftharpoons O+OH$
R28	$HO_2+H\rightleftharpoons H_2+O_2$
R43	$CH_3+H(+M)\rightleftharpoons CH_4(+M)$
R44	$CH_4+H\rightleftharpoons CH_3+H_2$
R46	$CH_4+OH\rightleftharpoons CH_3+H_2O$
R49	$CH_3+HO_2\rightleftharpoons CH_4+O_2$
R90	$CH_3+O_2\rightleftharpoons CH_3O+O$
R91	$CH_3+O_2\rightleftharpoons CH_2O+OH$
R99	$CH_3+HO_2\rightleftharpoons CH_3O+OH$
R194	$2CH_3(+M)\rightleftharpoons C_2H_6(+M)$
R248	$C_2H_4+OH\rightleftharpoons C_2H_3+H_2O$

### Part 2: Reaction pathways of components of methane/ethane/propane-n-heptane mixtures

*Notice:* In the following figures, each line with an arrow refers to the direction for the conversion of a certain species, and each number represents the percentage of the amount of a species consumed through the corresponding path relative to its total consumption amount [1]. The forms of chemical formulas shown are based on the NUI 2016 mechanism. Besides, we also calculated the ratio of the total consumption amount for each species to the corresponding total production amount, which is called as the consumption ratio of the substance during ignition process. The consumption ratio  $CR_j$  for the  $j$ th species:

$$CR_j = \frac{\sum_{i=1}^m \int_0^{\tau} \text{ROP}_{j,i,t} \delta_{j,i} dt}{n_j + \sum_{i=1}^m \int_0^{\tau} \text{ROP}_{j,i,t} \delta'_{j,i} dt} \quad (2)$$

where  $i$  denotes the sequence number of each elementary reaction,  $m$  the total number of the elementary reactions,  $\tau$  the ignition delay time, and  $n_j$  the initial mole of the  $j$ th species in the reactant. The  $\text{ROP}_{j,i,t}$  refers to the net rate of production of the  $j$ th species at the time of  $t$  through the  $i$ th reaction. For  $\delta_{j,i}$ , its value is equal to  $-1$  when  $\text{ROP}_{j,i,t} < 0$ , or  $\delta_{j,i} = 0$ . As to  $\delta'_{j,i}$ , if  $\text{ROP}_{j,i,t} > 0$ ,  $\delta'_{j,i} = 1$ , or  $\delta'_{j,i} = 0$ . Thus the numerator of eq. (2) represents the total consumption amount of the  $j$ th species, and the denominator is the total production amount of the  $j$ th species. In figs. S2 to S5, heights of columns with different colors below formulas of the species denote the corresponding consumption ratios of these species.

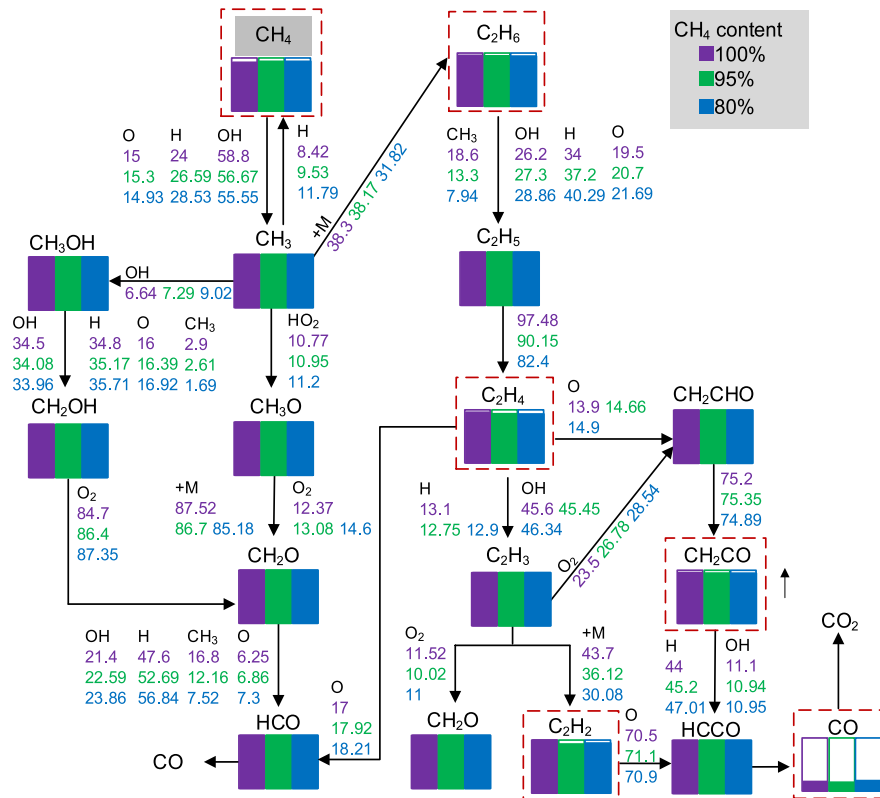
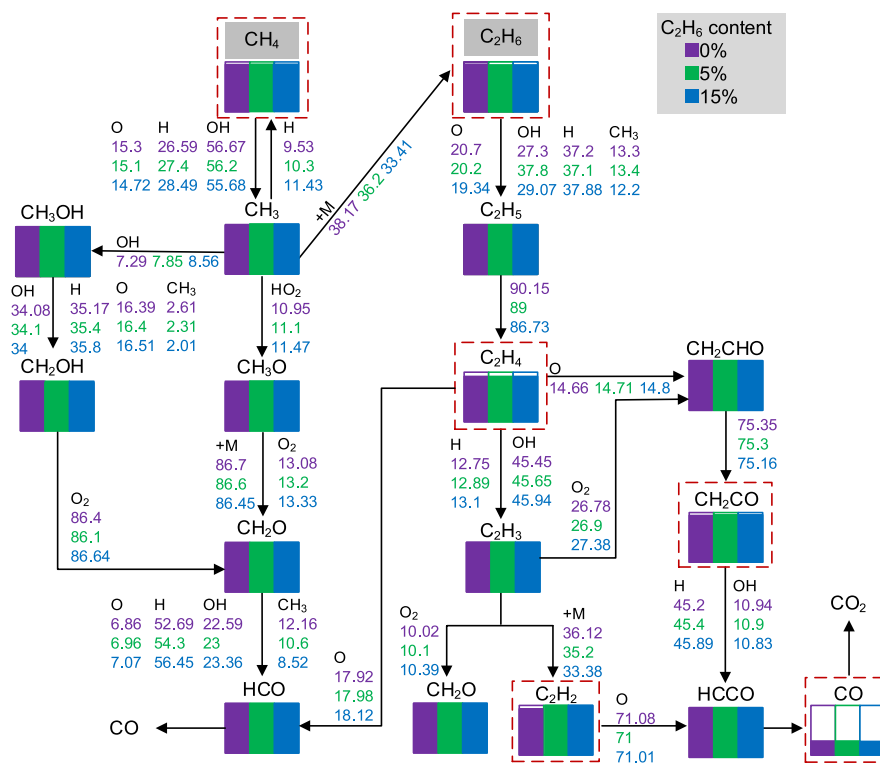
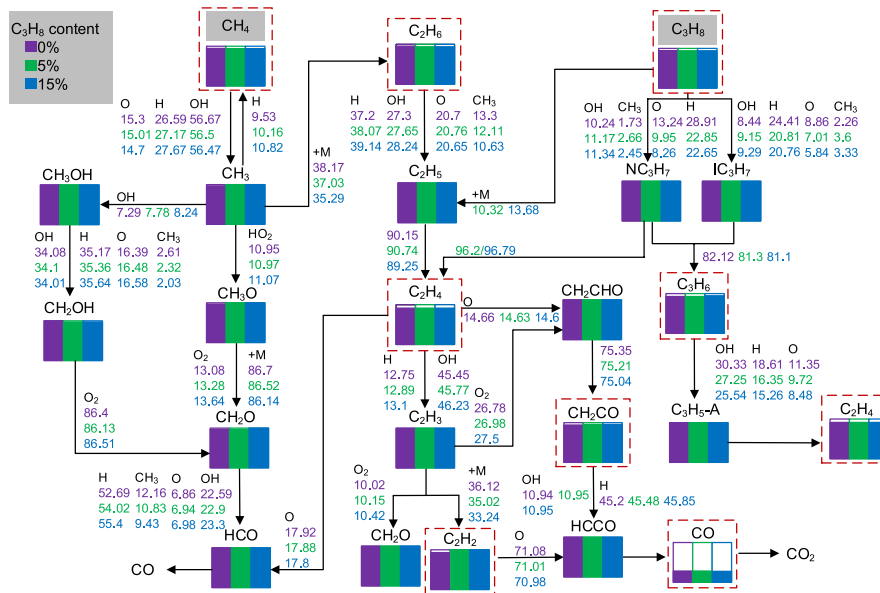


Figure S2. Reaction pathways of methane during ignition processes of the stoichiometric methane-*n*-heptane mixtures with various methane contents at 40 atmosphere and 1400 K. The boxes with red dashed lines highlight the substances with consumption ratios lower than 100%

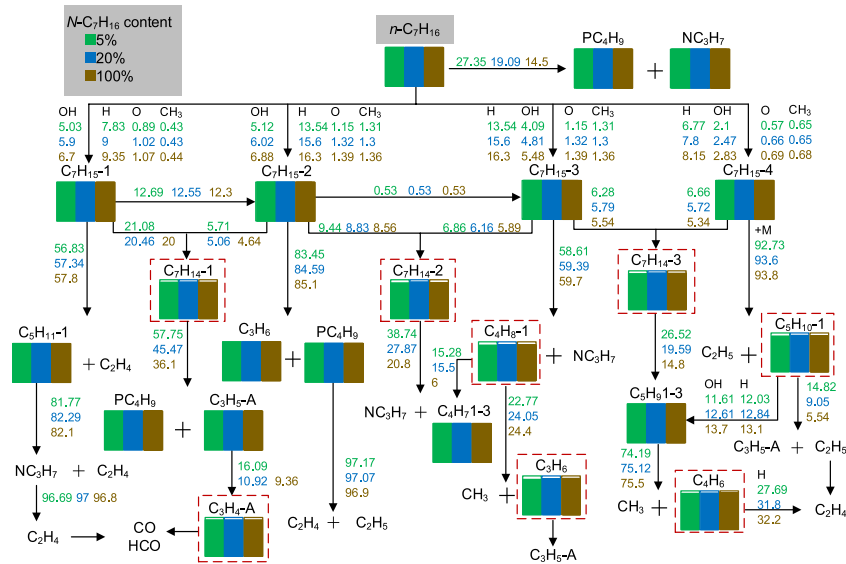


**Figure S3. Reaction pathways of methane and ethane during ignition processes of the stoichiometric methane/ethane-*n*-heptane mixtures with different ethane contents at 40 atmosphere and 1400 K; the boxes with red dashed lines highlight the substances with consumption ratios lower than 100%**





**Figure S4. Reaction pathways of methane and propane during ignition processes of the stoichiometric methane/propane-*n*-heptane mixtures with different propane contents at 40 atmosphere and 1400 K; the boxes with red dashed lines highlight the substances with consumption ratios lower than 100%**



**Figure S5.** Reaction pathways of  $n$ -heptane during ignition processes of the stoichiometric methane/ethane/propane- $n$ -heptane mixtures with different  $n$ -heptane contents at 40 atmosphere and 1400 K; the boxes with red dashed lines highlight the substances with consumption ratios lower than 100%

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