Full Length Article

Experimental and kinetic studies of ignition processes of the methane–*n*-heptane mixtures

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ABSTRACT

Ignition delay times of methane–*n*-heptane mixtures at different methane contents were determined at various initial temperatures through a shock tube setup. Based on comparisons between the experimental and modeled values of ignition delay times of methane–*n*-heptane mixtures, the applicability of two reaction schemes to the simulation of the zero-dimensional constant-volume adiabatic ignition processes of the mixtures at the present conditions was validated. Then mole fractions of the species and main radicals involved and rates of the main elementary reactions for the formation and consumption of methane and *n*-heptane in the ignition processes were analyzed. The results show that a nonlinear relationship exists between the ignition delay time of methane–*n*-heptane mixtures and the methane content. The ignition delay time of methane will change significantly when even a little amount of *n*-heptane is mixed with methane. It is proved that the two reaction mechanisms studied can predict accurately the ignition delay times of the mixtures under the present initial conditions. Due to the existence of *n*-heptane, all methane will be reacted early, and the more *n*-heptane there exists, the earlier all methane is consumed. Different from HO_2, CH_3 and H_2O_2, concentrations of OH, H and O remain low during the ignition period, and only when approaching the ignition time points, their concentrations begin to rise. The formation and consumption reactions for methane occur mainly near the ignition time points. For *n*-heptane, it is consumed in a short time, and the decomposition reactions prevail at the start of the ignition period. Then the reactions between *n*-heptane and the radicals take the dominant positions. Compared to methane, *n*-heptane has a stronger competitiveness for the radicals.

1. Introduction

As a clean fuel candidate, natural gas has attracted much attention for its potentials such as reducing the dependence on the petroleum-based fuels including diesel and gasoline [1–3]. The engines fueled with natural gas tend to reach higher thermal efficiency and lower carbon dioxide emission due to the high octane number and low mole ratio of carbon to hydrogen of natural gas, respectively [4,5]. Natural gas is difficult to be ignited, and as a result, when natural gas is applied to the compression ignition engines, an additional ignition source is required. One of the solutions is to inject a small amount of diesel into the engine cylinder to ignite natural gas. For this type of dual-fuel engine, during the initial combustion period, the premixed natural gas-diesel mixture, which is formed mainly during the ignition delay period of diesel, is consumed first. The premixed combustion of the natural gas-diesel mixture has a prominent impact on the engine operation [6]. For

instance, it is during this period that the heat release rate and the in-cylinder pressure reach their individual peaks. Thus the attention is necessarily paid to the premixed combustion of the natural gas–diesel mixture.

As known, the contribution made by the numerical simulation to the design and optimization of the engines has been increasing continually, and to couple the chemical kinetic mechanism and the fluid mechanics when conducting the numerical simulation is conducive to reducing the dependence on the engine tests and to predicting more accurately the performances and emissions of the engines. To achieve this target, chemical kinetic mechanisms for the fuels are required. As one of important characteristic parameters for the fuel combustion, the ignition delay time plays a significant role for development and validation of chemical kinetic mechanisms of the fuels.

As to natural gas and diesel, they are both complex mixtures, and thus studies on ignition delay times of natural gas and diesel are mainly

related to their surrogate fuels. Methane is generally treated as the representative of natural gas due to the high methane content of natural gas [7]. The cetane number of *n*-heptane is close to that of diesel, and thus in previous related studies *n*-heptane is taken as the single-component surrogate fuel of diesel [8]. For methane and *n*-heptane, their respective ignition delay times were investigated experimentally and numerically [9–18]. Methane is a relatively stable species [19], showing a certain inertia. While for *n*-heptane, the chemical bonds in the *n*-heptane molecule structure are easier to break [20], leading to *n*-heptane exhibiting a stronger activity. Due to the different activities between methane and *n*-heptane and the strong nonlinearity of the chemical reaction processes, it is somewhat difficult to determine accurately the ignition characteristics of methane–*n*-heptane mixtures based on their respective ones. Within the literature published, few studies on the ignition characteristics of premixed methane–*n*-heptane mixtures have been performed except the one by Aggarwal et al. [21]. Aggarwal and the coworkers [21] investigated the ignition delay times of methane–*n*-heptane mixtures through the modeling based on a reduced reaction mechanism. In order to determine more accurately the ignition characteristics of methane–*n*-heptane mixtures and also to provide the required data for the reaction mechanism validation which is the premise of conducting a more convincing chemical kinetic analysis of the ignition processes, it is necessary to carry out an experimental study on the ignition processes of methane–*n*-heptane mixtures.

Methane is one of intermediate species in the *n*-heptane oxidation process, and the reaction mechanism for methane is also part of that for *n*-heptane. With regard to methane, several chemical schemes including USC Mech II [22], AramcoMech 2.0 [23] and GRI-Mech 3.0 [24] have been proposed to simulate its oxidation process. In the aspect of *n*-heptane decomposition and oxidation processes, several reaction mechanisms including the NUI scheme by Zhang et al. [25] and the LLNL 3.1 scheme by Mehl et al. [26] can be used to describe the details of them. Theoretically speaking, the *n*-heptane reaction mechanism is capable of modeling the premixed combustion of methane–*n*-heptane mixtures based on the relationship between the methane and *n*-heptane reaction mechanisms. For the ignition processes of methane–*n*-heptane mixtures, the influence of *n*-heptane on the ignition delay time of the mixtures was numerically studied by Aggarwal et al. [21] based on a reduced mechanism named the Chalmers mechanism, as mentioned above. However, less information about the chemical kinetic characteristics of the ignition stages of premixed methane–*n*-heptane mixtures such as the detailed fuel consumption processes is available.

The objective of the present study is to investigate the ignition characteristics of premixed methane–*n*-heptane mixtures experimentally and numerically. The experiments are conducted through a shock tube setup, and then ignition delay times obtained experimentally are compared with those from other researchers and the corresponding modeled results to validate the applicability of the reaction mechanism to the prediction of the ignition processes of methane–*n*-heptane mixtures. On this basis, the chemical kinetic analysis is conducted to gain some understanding of the ignition processes of premixed methane–*n*-heptane mixtures from the point of the fuel consumption.

2. Experimental method

The schematic of the shock tube setup used in the present study is shown in Fig. 1. The experimental setup consists of a shock tube with the inner diameter of 111.3 mm, a system for preparing the initial reactants, a data acquisition system and heating systems. The shock tube is made of stainless steel, and it is mainly divided into three sections by two diaphragms, i.e., the high-pressure driver section, the middle section and the low-pressure driven section. The lengths of the high-pressure driver section and the low-pressure driven section are 3 and 7 m, respectively. A mixing tank is employed to prepare the homogeneous reactants, and the initial pressure in the driven section (i.e., the pressure of the gas mixture before the incident shock wave) is

monitored through a vacuum gauge. Heating systems are mounted outside the driven section and the mixing tank to ensure that the components of the mixtures in these two vessels are fully vaporized. The driver gas is injected directly into the driver section from the high-pressure gas bottle.

Near the end wall of the driven section of the shock tube four piezoelectric pressure sensors (made by PCB Piezotronics, Inc., type 113B26) are mounted on the sidewall to measure the shock wave speed. The distance between two adjacent sensors is 300 mm. A piezoelectric pressure sensor (made by Kislter, type 603B) is mounted at the end wall of the driven section to record the pressure history during the ignition period. In addition, a quartz optical window is fixed at the end wall to provide the channel for recording the emission spectrum through a monochromator. All pressure and optical signals are transmitted to two four-channel oscilloscopes (made by Tektronix, type MDO 3024), which are connected to a computer. The typical signals obtained from the present shock tube setup are shown in Fig. 2. In the present study, the pressure signal is used to determine the start point of the ignition period, and the time at which the slope of the CH^* emission signal reaches its maximum defines the end point of the ignition period [27].

When conducting experiments, it is necessary to figure out the desired compositions of the mixtures in the driven section of the shock tube at first. For the ignition processes of methane–*n*-heptane mixtures in the oxygen, the equivalence ratio ϕ is defined as follows:

$$\phi = \frac{(\text{F/O})}{(\text{F/O})_{stoic}} = \frac{\frac{n_{CH_4} + n_{nC_7H_{16}}}{n_{O_2}}}{\left(\frac{n_{CH_4} + n_{nC_7H_{16}}}{n_{O_2}}\right)_{stoic}} = \frac{\frac{n_{CH_4} + n_{nC_7H_{16}}}{n_{O_2}}}{\left(\frac{n_{CH_4} + n_{nC_7H_{16}}}{2n_{CH_4} + 11n_{nC_7H_{16}}}\right)_{stoic}} \quad (1)$$

where (F/O) and (F/O)$_{stoic}$ denote the mole ratios of the fuel to the oxidizer at actual and stoichiometric conditions, respectively. n_{CH_4}, $n_{nC_7H_{16}}$ and n_{O_2} are the moles of methane, *n*-heptane and oxygen, respectively. At stoichiometric conditions, the mole ratio of methane to oxygen is 1:2, while for *n*-heptane, the mole ratio between it and oxygen is 1:11. In the present study, the methane content X_{CH_4} is equal to the mole fraction of methane in methane–*n*-heptane mixtures, i.e.,

$$X_{CH_4} = \frac{n_{CH_4}}{n_{CH_4} + n_{nC_7H_{16}}} \quad (2)$$

When X_{CH_4} is not equal to 0, substitute Eq. (2) into (1), and the relationship between ϕ and X_{CH_4} can be expressed as follows:

$$\phi = \frac{\frac{X_{CH_4}n_{CH_4} + (1 - X_{CH_4})n_{CH_4}}{X_{CH_4}n_{O_2}}}{\left(\frac{X_{CH_4}n_{CH_4} + (1 - X_{CH_4})n_{CH_4}}{2X_{CH_4}n_{CH_4} + 11(1 - X_{CH_4})n_{CH_4}}\right)_{stoic}} = \frac{\frac{n_{CH_4}}{X_{CH_4}n_{O_2}}}{\frac{1}{11 - 9X_{CH_4}}} = \frac{(11 - 9X_{CH_4})n_{CH_4}}{X_{CH_4}n_{O_2}} \quad (3)$$

When X_{CH_4} is equal to 0, the equivalence ratio ϕ is

$$\phi = \frac{11n_{nC_7H_{16}}}{n_{O_2}} \quad (4)$$

Based on Eqs. (2)–(4), when ϕ and X_{CH_4} are determined, the mole ratio of methane to oxygen and then the compositions of methane–*n*-heptane–oxygen mixtures can be derived. In the present study, ignition delay times of the stoichiometric methane–*n*-heptane mixtures were experimentally determined at methane contents of 0%, 50%, 70%, 90%, 96%, 98% and 100%. During the experimental processes, the dilution gas is argon (Ar), and the corresponding dilution ratio is 95%, which is defined as the mole fraction of argon in methane–*n*-heptane–oxygen–argon mixtures. Table 1 shows the detailed compositions of methane–*n*-heptane–oxygen–argon mixtures at the above experimental conditions.

When conducting the experiments, based on the respective desired partial pressures of oxygen, argon, methane and *n*-heptane, they were injected into the mixing tank in order at first. The partial pressure of the *n*-heptane was kept less than 50% of its saturated vapor pressure to avoid potential condensation [28]. The mixtures in the mixing tank