

## Experimental measurement of ignition delay times of thermally cracked *n*-decane in shock tube

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### Abstract

The ignition characteristics of endothermic hydrocarbon fuels (with different pyrolysis degrees) were investigated in a shock tube using *n*-decane as model compound. Six component surrogates ( $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_6/\text{C}_3\text{H}_8/n\text{-C}_{10}\text{H}_{22}$ , marked as cracked *n*-decane) for thermally cracked *n*-decane were proposed based on the chemical compositions from the thermal stressing of *n*-decane on electrically heated tube under 5 MPa. Ignition delay times were measured behind reflected shock waves over temperature range of 1296-1915 K, pressure of 1-2atm and equivalence ratios of 0.5-2.0. *n*-Decane showed shorter ignition delay time than cracking gas at 1 atm, demonstrating higher reactivity. For cracked *n*-decane, it was found that thermal cracking could improve the ignitability at certain conditions with a limited degree, i.e. at  $T > 1480$  K for  $x = 37.97\%$  and  $x = 17.61\%$  and at  $T < 1480$  K for  $x = 62.15\%$  ( $x$  represents conversion of thermal cracking of *n*-decane) in this work. Unimolecular decomposition reactions of *n*-decane producing active radicals and H-atom would help chain initiation via H-abstraction reaction for unreacted fuels. This initial stage might accelerate ignition by activating cracking gas at these conditions. The empirical correlations for the ignition delay time of cracking gas and *n*-decane were also analyzed. Two models were also used to simulate the experimental data and showed good agreement with experimental results.

### 1 Introduction

Endothermic hydrocarbon fuels have been proposed to be used in the advanced aircraft as both propellants and coolants to solve thermal management by undergoing endothermic reactions. The fuel experiences thermal decomposition to produce smaller hydrocarbon species (such as methane, ethane and ethylene) and hydrogen in heat exchanger prior to combustion [1, 2]. Therefore, it's important to investigate the

ignition characteristics of cracked fuel for designing and developing the combustor in high-speed propulsion system.

There were several investigations focusing on the ignition of cracked fuels [3-6]. However, up to now the only experimental work by Colket and Spadaccini[4] has been reported but with very limited surrogate components ( $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ ). Therefore, it is still necessary to do more experimental study on the ignition behaviors of cracked fuel with suitable surrogate components for the further understanding the ignition and combustion of endothermic hydrocarbon fuel in the combustor.

In this paper, *n*-decane is selected as surrogate of endothermic hydrocarbon fuel to investigate the ignition characteristics of cracked fuels. High-pressure pyrolysis of *n*-decane was firstly carried out in an electrically heated tube reactor to get the detailed and thus the surrogate components. Then, a shock tube was used to measure the ignition delay time of *n*-decane, pyrolysis products, as well as the cracked fuel behind reflected shock waves in the temperature range of 1296-1915 K, pressure of 1-2atm and equivalence ratios of 0.5-2.0.

## 2 Materials and methods

*n*-Decane (mass fraction>99%) was obtained from Beijing Chemical Reagent Company, China. The cracking gas was obtained by mixing pure components including methane, ethane, ethylene, propane and propene with molar ratios of 23/19/32/7/18 (with the purity of 99.99% for each component, 75%  $\text{N}_2$  used as diluted gas) by Beijing AP BAIF Gases Industry Co., Ltd., with uncertainty of 1%.

Thermal cracking of *n*-decane was carried out in an electrically heated tube reactor, which has been introduced in detailed by our previous work [7].

Measurements of ignition delay time were carried out behind reflected shock waves using a helium-driven, stainless-steel aerosol shock tube apparatus at Tsinghua University [8, 9]. The shock tube with an internal diameter of 90 mm has a 3.46-m long driven section and a 3.79-m long driver section, separating by polycarbonate diaphragms. Helium (99.999%) worked as driver gas filling in the driver section. The ignition delay time  $\tau_{\text{ig}}$  in this work is defined as the time interval between the arrival of the reflected shock wave at the endwall and the time derived from back the extrapolation of the maximum slope of the whole chemiluminescence signal to the baseline, as illustrated in Figure 1. The uncertainty in the reflected shock temperatures is within 2.0%, while the uncertainty of ignition delay is time within 15%.

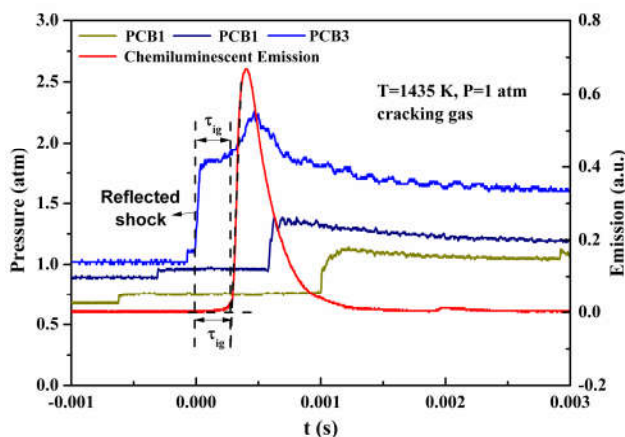


Figure 1. An example of oscilloscope traces illustrating definition of ignition delay time.

Simulations of ignition delay time were performed using Chemkin-pro [10] package assuming constant volume and adiabatic conditions in closed homogenous batch reactor. The calculated ignition delay time is defined as the time interval between the beginning of the simulation and the maximum rate of temperature rise ( $\max dT/dt$ ) [4, 11].

### 3. Results and discussion

#### 3.1 Pyrolysis of *n*-decane

There were more than 30 components produced by *n*-decane pyrolysis. It is difficult to investigate ignition delay time for all the pyrolysis products of cracked *n*-decane. So mixture of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> (with fixed molar ratio: 0.23CH<sub>4</sub>/0.19C<sub>2</sub>H<sub>6</sub>/0.32C<sub>2</sub>H<sub>4</sub>/0.07C<sub>3</sub>H<sub>8</sub>/0.19C<sub>3</sub>H<sub>6</sub>, marked as cracking gas) were proposed as surrogate for pyrolysis products to simplify this problem. Firstly, mixture of methane, ethane, ethylene, propane and propene, along with hydrogen, was always proposed as surrogate for cracked components of fuels [12, 8, 5]. Secondly, distribution of these major gaseous products showed in Figure 2, occupied 70%-85% of the whole products, and more than 92% of gaseous products in mole fractions under our interested conditions (conversion from 17.61% to 82.15%). Moreover, there was no dramatic change in concentration for this mixture at different conversions.

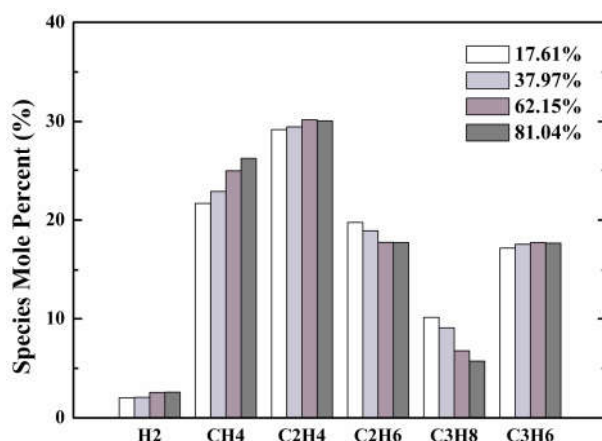


Figure 2. Thermally cracked components of *n*-decane at various conversions.

#### 3.2 Ignition delay time measurements of fuels

Ignition-delay experiments were conducted for *n*-decane in air over the range of pressure of 1-2 atm, temperature of 1310-1915 K, and equivalence ratio of 0.5 and 1.0. LLNL model [13] consisting of 693 species and 3249 reactions, was utilized to simulate for *n*-decane as shown in Figure 3. LLNL model achieved a reasonable agreement with the measured ignition delay times for the stoichiometric and fuel-lean mixtures at 1 and 2 atm within a factor of two.

For *n*-decane in current work, the ignition-delay correlation could be expressed as follows:

$$\tau_{ig} = 1.90 \times 10^{-13} \exp(41246/RT) [Fuel]^{0.77} [O_2]^{-1.41} \quad (1)$$

with an  $R^2$  correlation coefficient of 0.99505, where  $\tau_{ig}$  is the ignition delay time (in s),  $E_a$  is the global activation energy (in kcal/kmol),  $[Fuel]$ ,  $[O_2]$  are the fuel and oxygen concentrations (in mol/mL) in the combustible mixture, respectively (Although pressure is not specially included in the correlation for  $\tau_{ig}$ ,

the ignition-delay times are implicitly dependent on pressure through the concentration terms, hence,  $\tau_{ig} \propto p^{\alpha+\beta}$ .

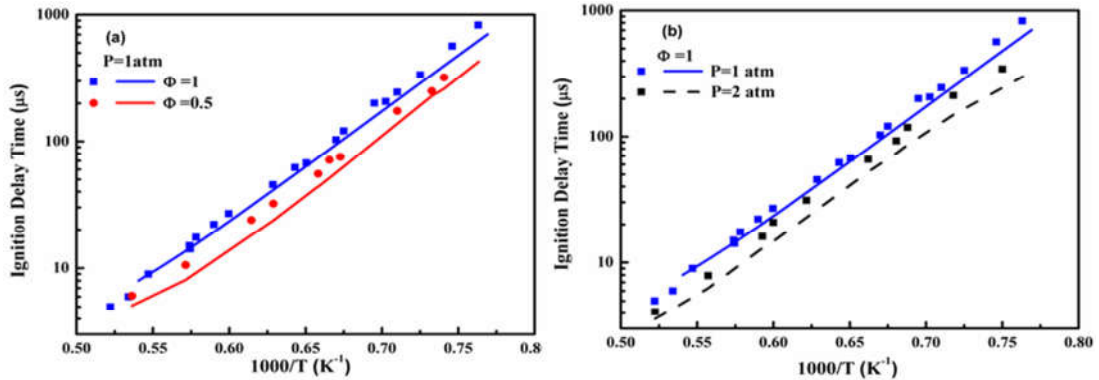


Figure 3. Comparison between experimental data and prediction by LLNL model for *n*-decane. (a) different equivalence ratio at 1 atm; (b) different pressure at  $\Phi=1$ . Symbols: experimental data; Lines: predicted data.

The ignition delay times for cracking gas/air mixtures were measured by aerosol shock tube at 1 and 2 atm, over the temperature range of 1296-1775 K with equivalence ratios of 0.5 to 2. AramcoMech2.0 [14] proposed by the Combustion Chemistry Centre at NUI Galway, is used as chemical kinetic mechanism for cracking gas, consisting of 493 species and 2716 reactions, as shown in Figure 4. AramcoMech2.0 predicted good agreement with the present work, except a distinct under-prediction for experimental data at  $\phi=2$ , over 1300-1650 K within a factor of two.

The empirical correlation of experimental data in this work could be expressed as follows:

$$\tau_{ig} = 1.55 \times 10^{-15} \exp(43215/RT) [Fuel]^{0.44} [O_2]^{-1.28} \quad (2)$$

with an  $R^2$  correlation coefficient of 0.98221.

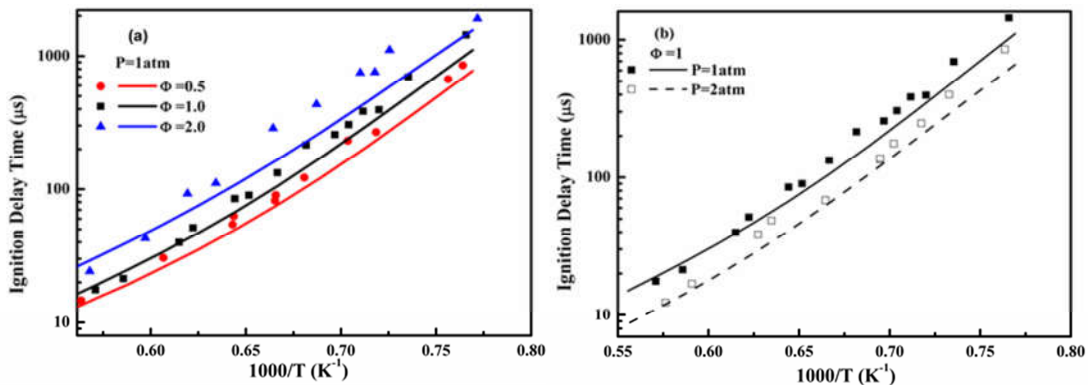


Figure 4. Measured and predicted ignition delay times for cracking gas: (a) different equivalence ratio (0.5-2.0) at 1 atm; (b) different pressure (1,2atm) at  $\Phi=1$ . Symbols: experimental data; Lines: calculated data.

Experiments on ignition delay time of cracked *n*-decane, added with *n*-decane with different proportions to represent different pyrolysis degrees (conversions of 17.61%, 37.97%, 62.15% and 81.04% to be investigated). Measurements for ignition delay times were conducted for stoichiometric cracked *n*-decane/air in the aerosol shock tube over the range of temperature 1305-1867K at 1 atm, which is shown in Figure 5 with linear regression, compared with ignition-delay data of *n*-decane and cracking gas. As

shown in Figure 5, cracking gas shows lower reactivity than pure *n*-decane, with longer ignition delay time at 1 atm. This result was consistent with conclusion drawn by Liao[8] that measured ignition delay time of pyrolysis gas was longer than kerosene.

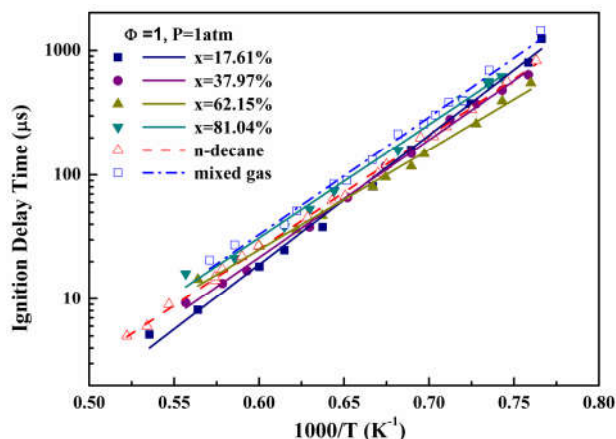


Figure 5. Comparison of measured ignition delay times of stoichiometric *n*-decane/air, cracking gas/air and cracked *n*-decane/air mixtures at 1 atm Symbols: experimental data, Lines: regression lines.

For cracked *n*-decane/air, it can be found that there exhibited specific features, but not simple enhancement or inhibition for cracked *n*-decane compared with *n*-decane. Cracked *n*-decane/air at  $x=81.04\%$  ignited most slowly than the other mixtures except cracking gas over the temperature range. Furthermore, thermal cracking of *n*-decane accelerated ignition at specific conditions: cracked *n*-decane with  $x=17.61\%$  and  $x=37.97\%$  at  $T > 1480$  K and  $x=62.15\%$  at  $T < 1480$  K, with a limited degree.

Colket and Spadaccini[4] focused on the effects of thermal and catalytic cracking of *n*-heptane with  $0.3\text{CH}_4/0.6\text{C}_2\text{H}_4/0.1\text{C}_7\text{H}_{16}$  as surrogate of endothermic reaction products. The results supported that fuel cracking improved ignition but with small enhancement at temperature of 1201K-1455K. Starik et al.[15] studied how the addition of hydrogen affected the ignition delay time of *n*-decane theoretically simulating by an especially built reduced reaction mechanism and got specific features with different hydrogen addition. They concluded that blending of small amount of *n*-decane could improve ignition compared with pure hydrogen-air mixture at some boundary temperature. The experimental results in present work also could support that thermal cracking could enhance ignition of pure fuels.

The possible reasons to these results could be explained as follows. For 81.04% cracked mixture, cracking gas dominated the ignition delay time with occupying almost 93.5% mole proportion in mixture. Hence, 81.04% cracked mixture showed similar and limited shorter ignition delay time with cracking gas. For cracked *n*-decane at  $x=17.61\%$ ,  $x=37.97\%$  at  $T > 1480$  K and  $x=62.15\%$  at  $T < 1480$  K, the initial step was unimolecular decomposition reactions of *n*-decane producing active radicals and H-atom, which would help chain initiation via H-abstraction reaction for unreacted fuels and participate chain propagation reactions<sup>35</sup>. This initial stage might accelerate the ignition delay time by activating cracking gas at these conditions. Further efforts should be focused on more experiments on ignition delay time of cracked fuel at a wider range of conditions and the explanations to the results.

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