

Comparison of PRF and Toluene/n-Heptane Mixture Fuel in the Mechanism of Compression Ignition using CA Resolved Sampling

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ABSTRACT

Chemical kinetic mechanism of compression ignition with PRF (iso-octane/ n-heptane) and NTF (toluene/ n-heptane) is investigated according to crank angle resolved in-cylinder sampling experiments. Profiles of two-stage consumption of fuel components in accordance with the timings of heat releases have been obtained. As well, production and consumption of intermediate species were observed. It was found that toluene consumption at the first stage is considerably less than that of n-heptane, whereas iso-octane consumption is comparable to that of n-heptane, which is accounted for by the smaller rate constant of toluene with OH. N-heptane and iso-octane are considered to produce formaldehyde; however, toluene has no or little contribution.

INTRODUCTION

Requirement of investigating combustion chemical mechanisms of various fuel components is getting stronger, according to the demand for further improvement of engine thermal efficiency and development of new type fuels such as biofuels. While flame propagation mechanism is basically common to most hydrocarbons, auto-ignition property and mechanism differ among fuels. Especially, isomers of different molecular structure have their individual ignition properties, although they have similar thermal and physical properties. For example, straight-chain alkanes, represented by n-heptane, are low octane number fuels having strong ignitability, while branched alkanes and aromatics are high ON fuels. Iso-octane and toluene represent branched alkanes and aromatics, respectively.

Recently, considerable progress has been made for modeling work. So far detailed and reduced models open to public include those for most members of gasoline surrogate fuels, many

members of diesel surrogate fuels, and a couple of representative oxygenated and bio-fuels [1]. These models were constructed based on theoretical and empirical knowledge of elementary reactions, and validated by fundamental experiments such as shock tubes, jet stirred reactors and rapid compression machines. However, most shock tube and RCM experiments adopt only physical measurements such as ignition delay time and pressure history, which are indirect information from a stand point of chemical mechanistic analysis. Transient chemical composition is usually observed in jet stirred reactors; however, the reaction environment is different from that of internal combustion engines.

We have paid attention to changes in chemical composition during compression ignition processes as it provides more direct information on the chemical mechanism. By using our own sampling engine, transient composition during two-stage compression ignition of dimethyl ether and n-heptane has been measured. The distinctive feature of our sampling method is the millisecond time-resolution with small quantity of sampling volume, established by the non-storage, direct mass-spectrometric detection in a differential pumping system [2]. By the observation of formaldehyde (HCHO), its role inhibiting chain reaction of low temperature oxidation was confirmed [3]. This method also enabled detection of hydrogen peroxide (H₂O₂), which is another key intermediate species of ignition [4].

In this paper, we applied the established methodology to PRF (primary reference fuel; n-heptane and iso-octane mixture) and NTF (n-heptane and toluene mixture). Roughly speaking, the high ON fuels reduce the ignition activity of n-heptane when mixed, but the detailed mechanism ought to be different, as discussed by Shibata et al [5]. We aimed to further clarify the contrast between iso-octane and toluene on the effect to n-heptane

through the composition during ignition, which results and findings are described after introducing the experimental method. Finally the essential mechanism affecting the ignition property of n-heptane is discussed by developing a simplified model reproducing the experimental results.

EXPERIMENTAL MEHOD

The experimental setup used in this work is described in Fig. 1. A single cylinder, 4 cycle side valve type engine (displacement 383 cm³, compression ratio 8.0) is externally driven by an electric motor to maintain 600 rpm regardless of internal power generation. Liquid fuel is injected into the intake port to be dispersed in air preheated through an electric heater. The equivalence ratio is evaluated by air flow rate measured by a mass flow meter and the injection volume calibrated in advance. Temperatures of intake air and the engine head are separately controlled by each heater power. Cylinder pressure is measured by a mounted pressure gauge as a function of crank angle, which is monitored by a rotary encoder. Gas sampling is carried out through an electrically actuated pulse valve (General valve, 0.8 mm ϕ orifice) mounted on the engine head, and the valve is driven synchronously with the rotary encoder for the designated open and close timing. The sampled gas is introduced in a chamber of differential pumping system pumped by a mechanical booster pump and a part of reduced pressure arrives at the high vacuum chamber through an orifice and a control valve, finally detected by a Q-pole mass analyzer.

The pulse valve can be open and close within a short period of the order of 0.1 ms; however, operations less than 1 ms result in sampling from unreactive boundary layer at the wall only. Sufficient period for the core component to exceed 90% of the total sampled gas is longer than 10 ms, which is not tolerable on the requirement of time resolution. We then adopted a correction method obtaining core volume measurement with improved effective time resolution as follows. Taking raw data of two different open periods (t_a and t_b), and the signal is corrected by;

$$S_{\text{corr}} = \{S(b) - S(a)\} / \{V(b) - V(a)\} \quad (1)$$

where $S(a)$ and $S(b)$ are signal intensities of measuring gas component with open period of t_a and t_b , respectively, and $V(a)$ and $V(b)$ are total extracted gas quantities with open period of t_a and t_b , respectively. $V(a)$ and $V(b)$ are substituted by signal intensity of nitrogen (N_2), as it is the dominant component of the sampled gas. Through inspection of sampled gas composition as a function of open period, t_a and t_b are fixed to be 0.8 ms and 1.3 ms, respectively, in the current experiments. The effective crank angle resolution is 2° at 600 rpm operations.

DETECTION OF FUEL COMPONENT

The choice of mass number is important for selective detection of species in gas containing different

hydrocarbons and reaction products, since fragment ions generated by the electron impact ionization frequently overlap at the same mass and parent ions are not always sensible. Mass spectra showing fragment patterns of n-heptane and iso-octane are shown in Fig. 2. It is notable that iso-octane (C_8H_{18}) has no signal at the original mass number (m/e) of 114, whereas that of n-heptane (C_7H_{16}) at $m/e = 100$ is distinct. Mass signal at 114 is detected in oxidized PRF/air mixture; however, it is regarded as $C_7H_{14}O$ instead of C_8H_{18} . The fragment spectra are similar and most mass signals from the fuels overlap, but the fragment signal at $m/e = 99$ from iso-octane can be distinguished from the parent signal at $m/e = 100$ of n-heptane. Interference at $m/e = 99$ from n-heptane is neglected, since the intensity is less than 1/40 of that from iso-octane of the same concentration. On the other hand, iso-octane has a signal at $m/e = 100$ with the intensity about 1/15 of that from n-heptane. This is attributed to $C_7H_{15}^+$ having one ¹³C, whose isotope abundance is 1.07%. Hence the signal at $m/e = 100$ is corrected for pure n-heptane signal according to $S_h = S(100) - K \times S(99)$, where $S(100)$ and $S(99)$ are the raw signals at $m/e = 100$ and 99, respectively, and K is the intensity ratio $S(100)_o/S(99)_o$ from a standard sample of iso-octane.

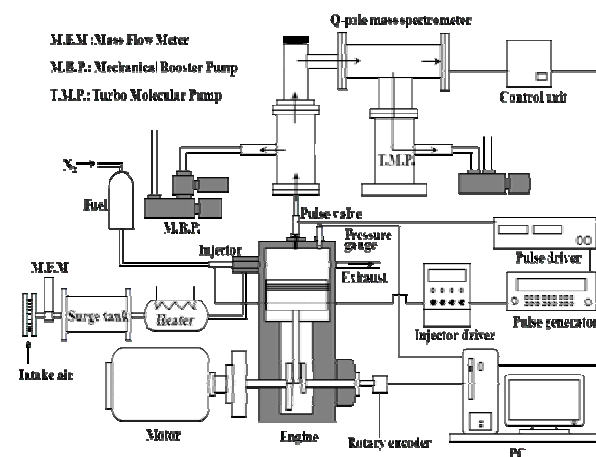


Fig.1 Experimental apparatus

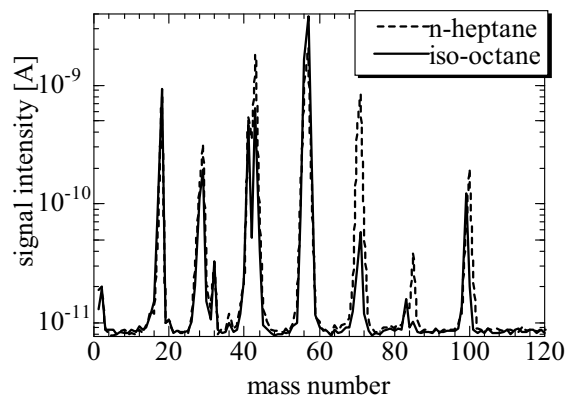


Fig.2 Fragment pattern of n-heptane and iso-octane in Q-pole mass-spectrometry.

DETECTION OF H₂O₂

Hydrogen peroxide is generated at the cool stage of ignition, causes a slow heat release of HCHO consuming loop reaction during the hot ignition preparation period, and finally triggers the hot ignition through its decomposition to OH radicals. Nevertheless it could not be detected by past sampling using storage bags, because of its low vapor pressure and chemical instability. Even in the current sampling of direct mass-spectrometric detection, the following procedure is needed for correct measurement of hydrogen peroxide.

The mass number of hydrogen peroxide is 34 and any interference from hydrocarbon species including fragments is unlikely at this mass; however, there found an overlap by isotopic molecular oxygen ¹⁶O¹⁸O, in which the natural abundance of ¹⁶O is 0.2%. Therefore the mass signal should be corrected for the H₂O₂ signal according to:

$$S(\text{H}_2\text{O}_2) = S(34) - C \times S(32) \quad (2)$$

where $S(34)$ and $S(32)$ are raw mass signal at $m/e = 34$ and 32 , respectively, and C is the intensity ratio $S_{\text{O}_2}(34)/S_{\text{O}_2}(32)$ obtained from gas without H₂O₂. In CA resolved sampling measurements, the constant C is determined from signals prior to the cool stage of ignition. The corrected value may shift to negative owing to raw signal fluctuation.

EXPERIMENTAL RESULTS

CA RESOLVED MEASUREMENTS OF TWO-STAGE IGNITION

Typical measurements in regular compression ignition events with PRF50 (50 vol% iso-octane + n-heptane) and NTF50 (50 vol% toluene + n-heptane) are shown in Figs. 3 and 4, respectively. Complete ignition was accomplished at equivalence ratios of 0.63 and 0.73 for PRF50 and NTF50, respectively, both with 140 °C of intake temperature. A small heat release of cool ignition and a large heat release of hot ignition are recognized from the pressure history, and stepwise fuel consumption occurs at the two stages. As well, formaldehyde is formed at the cool ignition, gradually increases, and finally disappears at the hot ignition. Hydrogen peroxide observed in the case of PRF50 behaves similarly. NTF shows lower peak pressure than PRF, in spite of the higher equivalence ratio. Probably this is because of the hot ignition property of toluene to ignite late and separately from that of mixed alkane, although it is not clear in the pressure profile.

CA RESOLVED MEASUREMENTS AT SINGLE COOL IGNITION CONDITIONS

Detailed measurements with various equivalence ratios and fuel mixture compositions have been conducted under moderate, hot ignition suppressed conditions in order to stably operate the engine and avoid damage to the pulse valve. Results of PRF30

and NTF30 are shown in Figs. 5 and 6, respectively. Partial fuel consumption and intermediate formation is observed at cool ignition, although the heat release is not clear in the ROHR chart derived from pressure profiles because of its weakness. The chemical composition at the cool ignition is maintained until the end of expansion stroke, therefore exhaust gas analysis at such engine operations is justified as a measurement for cool ignition composition.

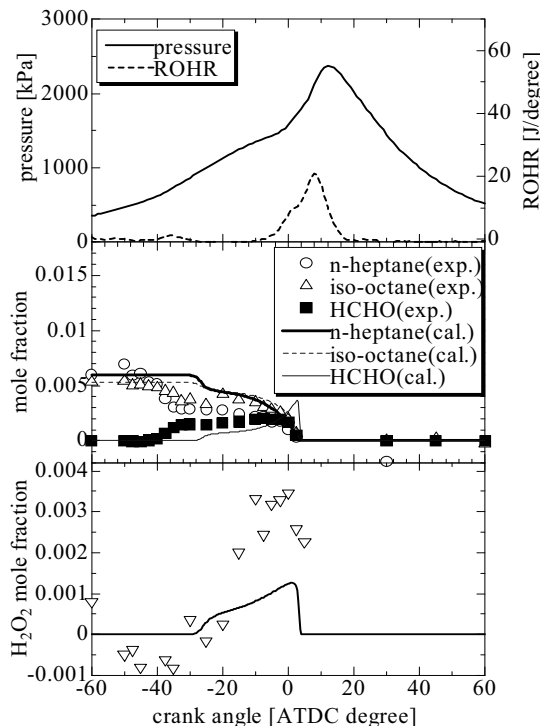


Fig.3 CA resolved profiles of pressure, ROHR and species mole fractions in PRF50/air compression. ($\phi = 0.63$, $T_{in} = 403\text{K}$)

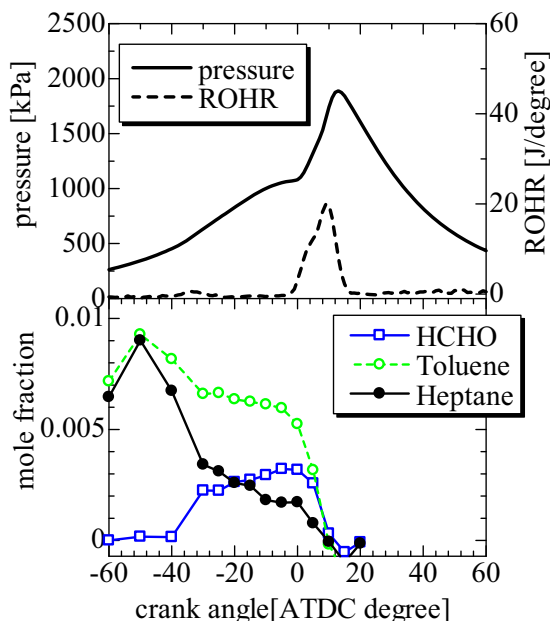


Fig.4 CA resolved profiles of pressure, ROHR and species mole fractions in NTF50/air compression. ($\phi = 0.73$, $T_{in} = 403\text{K}$)