

Chemical Kinetic Mechanism of Compression Ignition Derived from Intermediate Species for PRF and Toluene/ n-Heptane Fuel Systems

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ABSTRACT

Intermediate species formed in the cool ignition stage of autoignition were evaluated by exhaust gas analysis with FT-IR in a test engine at hot ignition suppressed conditions. PRF (iso-octane/ n-heptane) and NTF (toluene/ n-heptane) were used as the fuels. The fuel consumption rate decreases with increasing iso-octane content in PRF and toluene content in NTF. HCHO generation rate increases with increasing iso-octane content in PRF but the opposite trend was found in NTF. These tendencies correspond to the difference in the detail reaction mechanism for PRF and NTF oxidation.

INTRODUCTION

The process of compression ignition is composed of low and high temperature oxidation stages. Ignition timing of the high temperature oxidation is influenced by heat release and composition change in the low temperature oxidation (LTO). While high temperature oxidation mechanism is common to most hydrocarbons, LTO property depends strongly on molecular structure of hydrocarbons. Straight-chain alkanes like n-heptane have distinct LTO and hence they are readily to ignite, low octane number fuels. On the other hand, branched alkanes like iso-octane and aromatics like toluene exhibit little or no LTO, resultantly they are hard to ignite, high octane number fuels.

According to the demand for better control of combustion engines and application to alternative fuels, further detailed knowledge on ignition of various fuels and their mixtures is desired. As a movement toward this direction, recent progress in chemical mechanistic modeling study is outstanding [1]. The number of detailed and reduced models for various types of fuels has been phenomenally increased in this decade. On the other hand, there have been a number of experimental studies validating the models in shock tubes, jet stirred reactors, rapid compression machines

and internal combustion engines. Many experiments, however, measure only physical properties of ignition such as ignition delay time and pressure history, which is indirect information from a chemical mechanistic point of view. Studies looking into chemical composition are not so abundant except jet stirred reactor experiments.

Our group has conducted two different experimental methodologies to measure transient chemical composition in reciprocal engines operated with homogeneous charge compression mode. One is crank angle resolved gas sampling with our own direct mass-spectrometric detection, and the other is exhaust gas analysis at hot ignition suppressed conditions. The former is better to know real time composition change in ignition, but the number of detectable species is limited. This study adopts the latter, and it can detect variety of species although it uses impractical ignition conditions. This method originated from a study of Leppard et al. [2] and we applied it to DME/air compression [3] and n-heptane/air compression [4], finding the role of formaldehyde terminating the LTO chain reaction.

In this paper, we applied the experimental method to PRF (primary reference fuel; n-heptane and iso-octane mixture) and NTF (n-heptane and toluene mixture). Iso-octane and toluene are typical high octane number fuels that reduce ignition activity of n-heptane when mixed, but some different behaviors on the ignition control were reported by Shibata et al. [5]. In the following chapters, we present data of chemical composition in the course of compression ignition contrasting PRF and NTF, and discuss relevant chemical kinetic mechanism.

EXPERIMENTAL MEHOD

The experimental engine system is schematically shown in Fig. 1. A single cylinder, 4 cycle engine (displacement 541 cm³, compression ratio 8.0) is externally driven by an electric motor for constant

speed operation regardless of internal power generation, where the standard speed is 600 rpm. Liquid fuel is injected into the intake port, evaporated and mixed with preheated air to form combustible mixture gas. Crank angle resolved cylinder pressure is measured by a mounted pressure gauge and recorded at every crank angle degree indicated by a rotary encoder.

A part of exhaust gas is introduced in an optical cell of 3 m path length at the pressure of 10 kPa, and the chemical composition is analyzed by a Fourier transform infrared spectrometer (FT-IR, Shimadzu IR Prestige-21). Tubing to the cell is heated to 70 °C to avoid condensation.

Fuel mixtures are prepared prior to experiments. The mixing composition is defined by liquid volume ratio and indicated by the percentage of iso-octane for PRF or that of toluene for NTF; for example, NTF10 is 10% toluene + 90% n-heptane mixture. For quantitative determination of species concentration, standard samples of known concentration were prepared by diluting commercial chemicals.

Non dimensional numerical simulation of compression ignition was carried out on CHEMKIN IV platform with existing detailed oxidation reaction models of Curran et al. for PRF [6] and Sakai et al. for NTF [7].

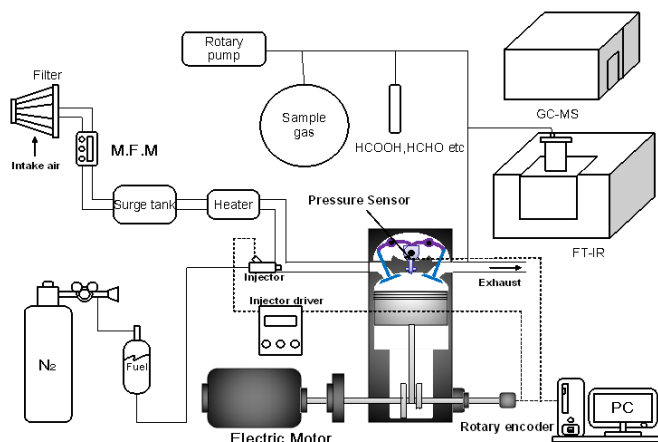


Fig.1 Experimental apparatus.

PRINCIPLE OF ANALYSIS

In the analysis of FT-IR spectrum containing absorption of a number of species, concentration of some species can be determined straightforwardly by the absorbance of a characteristic peak, when the peak is independently detected. Species having similar molecular structure, however, tend to overlap in the same range of wavenumbers. Combination of original fuel components, i.e., n-heptane, iso-octane and toluene, is a typical case of this kind. In such a case, a least-square analysis is conducted to distinguish individual contribution in the overlapped spectrum. An example of the least square analysis of IR spectrum is shown in Fig. 2.

The basic formula of the least square method is

$$Y_{(i)} = C_1 X_{i1} + C_2 X_{i2} + \dots + C_j X_{ij} + \dots + C_m X_{im} \quad (1)$$

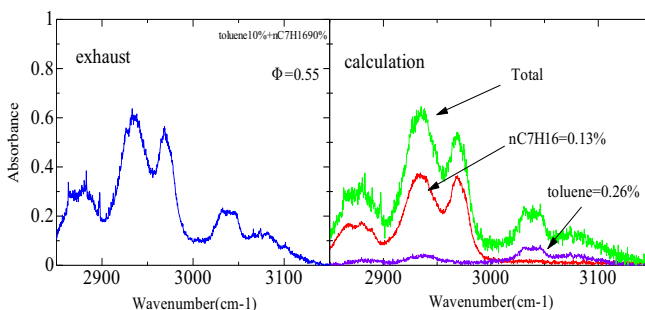


Fig.2 Spectrum analysis by least-square method

where $Y_{(i)}$ is the calculated spectrum as function of wavenumber i , X_{ij} is the spectrum of species j of known concentration N_{sj} and C_j is the coefficient of contribution for species j . the square sum of difference between observed and calculated spectra is

$$S = \sum_i (Z_{(i)} - Y_{(i)})^2 = \sum_i \left(Z_{(i)} - \sum_j C_j X_{ij} \right)^2 \quad (2)$$

Equations for coefficients C_j to minimize S is

$$dS/dC_j = 0 \quad (3)$$

The solution is

$$\begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_m \end{bmatrix} = \begin{bmatrix} B_{11} & B_{12} & \dots & B_{1m} \\ B_{21} & B_{22} & \dots & B_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ B_{m1} & B_{m2} & \dots & B_{mm} \end{bmatrix}^{-1} \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_m \end{bmatrix} \quad (4)$$

$$b_j = \sum_i X_{ij} Z_i \quad B_{jj'} = \sum_i X_{ij} X_{ij'} \quad (5)$$

Concentration of species j in the observed spectrum is $C_j \cdot N_{sj}$.

EXPERIMENTAL RESULTS

PRF0

Results of PRF0 (n-heptane) has been already reported [4], where CO, CO₂, HCHO, C₂H₄, and CH₃OH were observed as products at low temperature stage of ignition. In this study, CH₃CHO and C₂H₃CHO were additionally confirmed in the reexamination. Fuel consumption and intermediate production yield were measured at various equivalence ratios. The results are shown in Fig. 3. Here, "fuel consumption" means the consumed amount relative to the initial fuel charge, and "product yield" means the molar ratio of a product relative to the consumed amount of total fuel. Fuel consumption is ca. 80% through the range of equivalence ratio. On the product yields, dependence on equivalence ratio is generally weak, but HCHO yield tend to decrease with increasing equivalence ratio, This trend was judged as statistically significant, that is, the estimated error of the least square slope is 1/10 of the absolute value of the slope. While C₂H₄ and some other species tend to increase.