Comparison of PRF and Toluene/n-heptane Mixture in the Mechanism of Compression Ignition Using Transient Species Measurements and Simplified Model Analysis

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ABSTRACT

Intermediate species formed in the low temperature heat release (LTR) of autoignition were evaluated in test engines by crank angle resolved in-cylinder sampling and exhaust gas analysis with FT-IR at hot ignition suppressed conditions. PRF (iso-octane/n-heptane) and NTF (toluene/n-heptane) were used as the fuels. The LTR fuel consumption decreases with increasing iso-octane content in PRF, whereas the effect of toluene in NTF is weaker. Formaldehyde generation yield increases with increasing iso-octane content in PRF but the opposite trend was found in NTF. The chain reaction mechanism of LTR accounts for the observations; i.e., the chain carrier OH reproduced by n-heptane is consumed by iso-octane, toluene and intermediates such as formaldehyde. Reaction pathways for product species characteristic to each fuel component are also discussed.

INTRODUCTION

Further detailed knowledge on ignition chemistry of various fuels and their mixtures is desired for better control of combustion engines and application to alternative fuels. As an activity 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 increased dramatically in this decade. On the other hand, many engine experiments 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.

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.

Our group has conducted two different experimental methodologies to measure transient chemical composition in reciprocal engines operated with homogeneous charge compression mode [2, 3]. 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. The latter, which is originated from a study of Leppard et al. [4], can detect variety of species present after LTO.

In this paper, we applied the methodologies 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. We aimed to further clarify the contrast between iso-octane and toluene on the effect to n-heptane through the composition during ignition. Finally the essential mechanism affecting the ignition property of n-heptane is discussed by developing a simplified model reproducing the experimental results.

EXPERIMENTAL SETUP

CA RESOLVED SAMPLING SYSTEM
The system is shown in Fig. 1. A single cylinder, 4-stroke side valve type engine (displacement 383 cm$^3$, compression ratio 8.0) is externally driven by an electric motor to maintain 600 rpm regardless of internal power generation. Gas sampling is carried out through an electrically actuated pulse valve (General valve, 0.8 mm$\phi$ 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 non reactive 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 signals of two different open periods ($t_1$ and $t_b$), a corrected data is obtained by differentiating these signals. Normalization was also conducted by dividing the signal of a species with a nitrogen signal of the same sampling condition. Through inspection of sampled gas composition as a function of open period, $t_1$ 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 $2^\circ$ at 600 rpm operations.

EXHAUST GAS ANALYSIS

The experimental engine is a single cylinder, 4-stroke overhead valve engine (displacement 541 cm$^3$, compression ratio 8.0). It is also motorized with the standard speed of 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.

For Exhaust Gas Analysis, 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.

For quantitative determination of species concentration, standard samples of known concentration were prepared by diluting commercial chemicals.

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.

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].

RESULTS AND DISCUSSION

CA RESOLVED SAMPLING PROFILES

(1) HOT IGNITION CONDITION

Typical measurements in regular compression ignition events with NTF50 (50 vol% toluene + n-heptane) are shown in Figs. 2 and 3. Complete ignition was accomplished at equivalence ratio of 0.73 with 140°C 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.

![Fig. 1 Experimental apparatus for sampling Method](image)

![Fig. 2 CA resolved profiles of pressure, ROHR and species mole fractions in NTF50/air compression. (φ = 0.73, $T_{in} = 403K$)](image)

(2) COOL IGNITION CONDITION

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 motored engine and avoid damage to the pulse valve. Results of NTF30 are shown in Figs. 3. 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.

![Graph showing pressure and ROHR as a function of crank angle.]

Fig.3 Profiles of pressure, ROHR and species mole fractions in NTF30 as a function of crank angle. (\(\phi = 0.33\), \(T_m = 404K\))

**EXHAUST GAS ANALYSIS**

1. **DETECTED SPECIES**
   From FT-IR spectra, intermediate products, as well as fuel components from the exhaust gas can be analyzed as shown in Fig. 4. Species detected in PRF0 (100% n-heptane) are HCHO, HCOOCH, CO, CO2, CH3OH, C2H6, CH2CHO, and C3H7CHO. All of them were also confirmed in other PRFs and NTFs. iC4H9 (isobutene) was detected in PRF except PRF0, and C3H7CHO (benzaldehyde) was detected in NTF, which are described in detail in the following sections.

2. **DETECTION OF ISO-BUTENE FROM PRF**
   Isobutene was actually confirmed by the absorption peak at 870 cm\(^{-1}\), as shown in the lowest panel in Fig.4. As a branched alkane, iso-octane is expected to produce C3-C4 olefins including isobutene. In PRF oxidation, iC4H9 is considered to be produced from iC3H7\(_2\) as shown in the following reaction pathways:

   \[\text{C}_3\text{H}_7^+ \rightarrow \text{iC}_4\text{H}_9 + \text{iC}_3\text{H}_7^+ \quad (1)\]
   \[\text{iC}_3\text{H}_7 + \text{O}_2 \rightarrow \text{iC}_4\text{H}_8\text{OO} \quad (2)\]
   \[\text{iC}_4\text{H}_9\text{OO} \rightarrow \text{iC}_4\text{H}_8\text{OOH}^- \quad (3)\]
   \[\text{tC}_4\text{H}_9\text{OH} \rightarrow \text{tC}_4\text{H}_9\text{OOO}^- \quad (4)\]
   \[\text{tC}_4\text{H}_9\text{OO} \rightarrow \text{tC}_4\text{H}_9\text{OOH}^- \quad (5)\]
   \[\text{iC}_4\text{H}_9\text{OOH}^- \rightarrow \text{iC}_4\text{H}_9\text{H} + \text{HO}_2 \quad (6)\]
   \[\text{tC}_4\text{H}_9\text{OH}^- \rightarrow \text{tC}_4\text{H}_9\text{H} + \text{HO}_2 \quad (7)\]
   \[\text{iC}_4\text{H}_9\text{H} + \text{HO}_2 \rightarrow \text{iC}_4\text{H}_9\text{H} + \text{HO}_2 \quad (8)\]

where a denotes a radical site at a methyl group of (CH\(_3\))\(_2\)-C, c denotes a radical site at a methyl group of (CH\(_3\))\(_2\)-CH, i denotes CH\(_3\), CH\(_2\), and t denotes CH\(_2\)-C\(_3\). Namely, iC4H9 is mainly generated from \(\beta\) -scission of C\(_3\)H\(_7\)-x and C\(_3\)H\(_7\)OOH-x-y, the latter of which is also a product of C\(_3\)H\(_7\) \(\beta\) -scission. The plenty of \(\beta\) -scission products is a reflection of the iso-octane property being inactive on branching chain reactions through isomerization of ROO radicals.

![Graph showing FT-IR spectra of exhaust from PRF50 compression (\(\phi = 0.25\), \(T_m = 403.5K\)) and standard samples.]

Fig. 4 FT-IR spectra of exhaust from PRF50 compression (\(\phi = 0.25\), \(T_m = 403.5K\)) and standard samples.

![Graph showing spectrum of reference C\(_3\)H\(_7\)CHO and exhaust spectrum of NTF70. Superimposed in (b) is a modified spectrum obtained by subtracting C1-C3 aldehyde contribution from the raw spectrum.]

Fig.5 (a) Spectrum of reference C\(_3\)H\(_7\)CHO and (b) Exhaust spectrum of NTF70. Superimposed in (b) is a modified spectrum obtained by subtracting C1-C3 aldehyde contribution from the raw spectrum.
(3) DETECTION OF BENZALDEHYDE FROM NTF

It was expected by the NTF oxidation model that C₆H₅CHO (benzaldehyde) and C₆H₅OH (phenol) are formed as products from toluene. In this study, C₆H₅CHO was detected by the characteristic absorption at 1710-1740 cm⁻¹ after a procedure eliminating superimposed absorption of other aldehydes from raw FT-IR spectrum. The concentration was calibrated with a standard sample of 0.1% C₆H₅CHO.

DEPENDENCE ON FUEL COMPOSITION

Octane Number (ON) dependence of fuel consumption and intermediate production yield in PRF are shown in Fig. 7. Here, the production yield is scaled relative to consumed quantity of fuel. Consumption of both fuel components decreases with increasing ON. HCHO yield increases with increasing ON, whereas those of HCOOH and CH₃OH are almost independent of ON. HCHO production pathways in PRF50 are shown as follows:

CH₃OH + O₂ \rightarrow CH₂O + H₂O

CH₃O(+) \rightarrow CH₂O + H₂O (+m)

CH₂CHO + O₂ \rightarrow CH₂O + CO + OH

CH₃OH + O₂ \rightarrow CH₂O + CH₂O

CH₃COCH₂O \rightarrow CH₂CO + CH₂O

CH₂O is formed through a variety of pathways and an example is [8]:

CH₃COC₂H₄ \rightarrow CH₃CO + C₂H₄

CH₃CO \rightarrow CH₂ + CO

CH₃ + O₂ \rightarrow CH₃OØ

CH₃OO + H₂O \rightarrow CH₃OØ + O₂

CH₃OØ \rightarrow CH₂O + OH

Ketonic radicals of different carbon numbers can be sources of CH₂O through similar pathways. CH₃ can also be formed via β-scission of alkyl radicals. n-heptane tends to form C₇ ketoalkylenperoxide through isomerization of RO₂ species, and finally contribute the HCHO forming process. In contrast, iso-octane tends to cause β-scission forming C₆H₈ + C₆H₄ or CH₃ + C₇ olefin. The fragment C₆H₄ also proceeds to the HCHO forming process.

Yield of C₆H₄ decreases with increasing ON, which means iso-octane produces less C₆H₄. Olefin species are products of β-scission of hydrocarbon radicals, but C₆H₄ is specific to straight chain alkane like n-heptane. Iso-octane, as a branched alkane, preferably produces C₃-C₄ olefins including isobutene.

In the case of NTF as shown in fig. 8, n-heptane consumption decreases when toluene content is over 40%, but the extent is less than that of PRF. Toluene consumption does not decrease until the maximum toluene content of the current experiments. On the other hand, HCHO yield decreases with increasing toluene content, probably because of fewer yield from toluene.

On C₆H₅CHO, the product yield increases with increasing toluene content in a quadratic manner. The production pathways of C₆H₅CHO extracted from the model are shown in fig. 6.

There is a self reaction of C₆H₅CH₂OO + C₆H₅CH₂OO in the main pathway forming C₆H₅CHO, which is the reason of the quadratic yield against toluene concentration. Possible causes for the disagreement of C₆H₅CHO yield is product branching of H abstraction from toluene for C₆H₅CH₂ vs. C₆H₅CH₃, rate and product branching of C₆H₅CH₂OO + C₆H₅CH₂OO, and product branching of C₆H₅CH₂O decomposition to C₆H₅CH₂OH vs. C₆H₅CHO.

DISCUSSION WITH A SIMPLIFIED MODEL

The low temperature oxidation mechanism of hydrocarbons consists of complicated reactions such as H-abstraction, O₂-addition, isomerization, second O₂-addition, decomposition and branching passes. Here, the oxidation mechanism of a mixture of n-heptane (base fuel) and iso-octane or toluene (second fuel) is expressed in a summarized manner as:

nC₆H₁₆ + OH \rightarrow αₙOH + βₙHCHO + other products

\[ \text{reaction 19} \]

iC₈H₁₈ (or C₆H₅CH₃) + OH \rightarrow αᵢOH + βᵢHCHO + other products

\[ \text{reaction 20} \]

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\[
\frac{d[	ext{nC}_7\text{H}_{16}]}{dt} = -k_b[\text{C}_7\text{H}_{16}][\text{OH}],
\]
(21)
\[
\frac{d[\text{subfuel}]}{dt} = -k_s[\text{subfuel}][\text{OH}],
\]
(22)
\[
\frac{d[\text{OH}]}{dt} = [(\alpha_b - 1)k_b[\text{C}_7\text{H}_{16}] + (\alpha_s - 1)k_s[\text{subfuel}]
- k_a[\text{HCHO}][\text{OH}],
\]
(23)
\[
\frac{d[\text{HCHO}]}{dt} = [\beta_b k_b[\text{C}_7\text{H}_{16}] + \beta_s k_s[\text{subfuel}]
- k_a[\text{HCHO}][\text{OH}],
\]
(24)

where \(k_i\) is the rate constant of species \(i\) with OH, and the subscript \(a\) denotes aldehyde.

Above equations can be translated into a form in which the independent variable is percentage consumption of base fuel \(x\) as:

\[
\frac{dy_b}{x} = -g_1y_b/(1-x)dx
\]
(25)
\[
\frac{dy_a}{x} = (\beta_b + \beta_s y_a/(1-x) - g_2y_a/(1-x))dx
\]
(26)
\[
\frac{dy_{OH}}{x} = [(\alpha_b - 1) + (\alpha_s - 1)g_1y_b/(1-x) -
\]
\[
\quad - g_2y_a/(1-x))dx
\]
(27)

where \(y_b\) is the remaining amount of second fuel (relative to initial amount of base fuel, and so forth), \(y_a\) is the accumulated amount of aldehyde, \(y_{OH}\) is the amount of OH, \(g_1 = k_b/k_s\) and \(g_2 = k_s/k_b\). \(a_b\) of low ON fuel is necessarily exceeding unity, but \(a_s\) may differ. When initial overall of OH recreation index is over unity, the OH concentration increases with repetition of the reaction chain. According to decrease in fuel and increase in the OH consuming aldehyde, the slope OH increase gradually reduces, turns into decrease, and finally the chain system is terminated. The point of termination is represented by the overall OH recreation index = 1.

The parameters used for PRF are \(k_b/k_s = 1.85, a_b = 2, a_s = 1.14, \beta_b = 1.6\) and \(\beta_s = 1.6\). They were obtained by analyzing the existing PRF mechanism [6,7]. Those for NTF are \(k_b/k_s = 5, a_b = 2, a_s = 0, \beta_b = 1.6, \beta_s = 0\), a part of which was assumed by overlooking the toluene oxidation mechanism [8]. The courses of integration for PRF50 and NTF50 are shown in Figs.9 and 10; respectively composition at the point of termination is summarized for PRF and NTF in Figs.11 and 12, respectively. These calculations successfully reproduce the experimentally observed tendency, i.e., toluene consumption is less than those of n-heptane and iso-octane, the effect of reducing n-heptane consumption is less in toluene than that in iso-octane, and aldehyde production reduces with increasing toluene content.

To summarize the mixing effect of high ON fuel to n-heptane ignition property, toluene acts as a simple dilution agent, since the toluene-OH reaction rate is slow and the OH recreation index is very low. In contrast, iso-octane takes considerable OH produced by n-heptane by the comparable rate constant with OH, but the deactivating effect is partly compensated with the OH recreation by iso-octane.

![Fig.7 Species mole fractions as a function of Octane rating of PRF (Φ = 0.33, \(T_{in} = 403.5K\))](image)

![Fig.8 Fuel consumptions and product yields as a function of toluene % in NTF (Φ = 0.5, \(T_{in} = 403.5K\))](image)

![Fig.9 Modeled evolution of chemical composition in LTO of PRF50.](image)
common to all investigated fuel mixtures, iC₄H₈ is a unique product from iso-octane, and C₆H₅CHO is a unique product from toluene. iC₄H₈ is formed by and after β-scission of iso-octyl radicals, which indicates weak tendency of iso-octane to chain branching pathways.

Production yield of HCHO increases with increasing iso-octane/n-heptane ratio, whereas it decreases with increasing toluene/n-heptane ratio. HCHO is a product of ketoalkylperoxide decomposition common to n-heptane and iso-octane. However, benzyl radical from toluene does not proceed such way because of the firmness of its aromatic ring.

Fuel consumption decreases with increasing iso-octane/n-heptane ratio, but the effect is weaker for toluene/n-heptane ratio. It is because toluene has lower rate constant with OH than that iso-octane, so that toluene barely interrupts the OH reproducing chain reaction of n-heptane.

**REFERENCES**


**CONCLUSIONS**

Combining the measurements of crank angle resolved sampling and exhaust gas analysis in homogeneous compression of iso-octane/n-heptane/air and toluene/n-heptane/air mixtures, low temperature oxidation mechanism of these fuel systems has been discussed as follows:

While most of detected intermediate species such as HCHO, HCOOH, C₂H₄ and C₂-C₃ aldehydes are