

Chemical Kinetics Study on Two-Stage Main Heat Release in Ignition Process of Highly Diluted Mixtures

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ABSTRACT

Some experimental data indicate that an HCCI process of a highly diluted mixture is characterized with a two-stage profile of heat release after the heat release by low-temperature oxidation, and with slow CO oxidation into CO₂ at a low temperature. In the present paper, these characteristics are discussed using a detailed chemical kinetic model of normal heptane, and based on an authors' idea that an ignition process can be divided into five phases.

The H₂O₂ loop reactions mainly contribute to heat release in a low-temperature region of the TI (thermal ignition) preparation phase. However, H+O₂+M=HO₂+M becomes the main contributor to heat release in a high-temperature region of the TI preparation phase. H₂O₂ is accumulated during the LTO (low-temperature oxidation) and NTC (negative temperature oxidation) phases, and drives the H₂O₂ loop reactions to increase the temperature during the TI preparation phase. When the heat capacity of a mixture increases by dilution, H₂O₂ is consumed in a lower-temperature region. Thus, the heat release by the H₂O₂ loop reactions stagnates at a lower temperature, causing a gap of heat release between the low-temperature and high-temperature regions of the TI preparation phase.

When a mixture is diluted to a considerable extent, the rate of a branching chain reaction, H+O₂=OH+O, cannot overtake the rate of H+O₂+M=HO₂+M to the end of an ignition process. Thus, the CO oxidation into CO₂, CO+OH=CO₂+H, slowly proceeds along with H+O₂+M=HO₂+M rather than with the branching chain reaction. Conventional combustion control ways cannot be useful for activating low-temperature combustion.

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INTRODUCTION

Low-temperature combustion such as ultra-lean HCCI (homogeneous charge compression ignition) [1,2,3,4,5,6] and high-EGR diesel combustion [7,8,9] was proposed and has been widely investigated as a potential way for operating an internal combustion engine with a higher thermal efficiency and lower NO_x emissions. Difficulties in operating an HCCI engine are how to moderate the rate of heat release at a high load, and how to reduce the cycle-to-cycle variation in heat release at a low load. Thus, controlling the phase and profile of heat release is required for expanding the limits of HCCI engine operation. Dual fuel which is a combination of one

fuel with a high ignitability and the other fuel with a low ignitability, is one of strategies for controlling the phase and profile of heat release. Shibata et al. investigated engine operation by dual-fuel HCCI using normal heptane and toluene [10, 11], and Iijima et al. did using dimethyl ether and methane [12]. Both of them reported that a two-stage profile of heat release can be observed after the heat release by low-temperature oxidation on some conditions. Machrafi et al. investigated HCCI engine operation using gasoline, a primary reference fuel (a mixture of normal heptane and isooctane) or a gasoline surrogate (a mixture of normal heptane, isooctane and toluene), and reported a two-stage profile of heat release excluding the heat release by low-temperature oxidation in

cases of gasoline and a gasoline surrogate [13]. However, the authors have experienced that such a two-stage profile of the main heat release can be observed even using a single-component fuel, as shown in Figure 1 (see a circle), although it might be caused by the unexpected heterogeneity of the local fuel concentration or temperature.

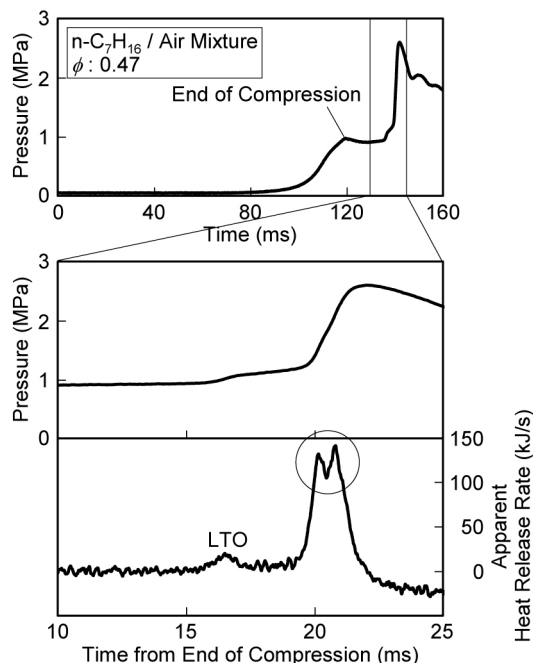


Figure 1. Histories of Pressure and Heat Release Rate in Rapid Compression Machine (The pressure and temperature at the end of compression were set at 1.0 MPa and 624 K.)

Miyoshi developed a utility software library for the automatic generation of detailed chemical kinetic models of various hydrocarbons, KUCRS (knowledge-basing utilities for complex reaction systems) [14], and has opened it on his Web site [15]. The latest version can generate detailed models of any non-cyclic alkanes, single-ring (5- to 7-membered) cyclic alkanes, any non-cyclic alkenes (mono-ens) and any non-cyclic alcohols. In non-cyclic alkane models, the unimolecular reaction mechanisms of RO_2 , R'OOH and $\text{O}_2\text{R'OOH}$ have been discussed on the basis of quantum chemical calculations [16]. The molecular-size dependent fall-off rate constants of the O_2 addition to alkyl radicals and the thermal decomposition of hydroperoxy carbonyl compounds have been also introduced [17]. As shown in Figure 2, there is a good agreement between computational ignition delays of normal heptane and isooctane using a detailed model of primary reference fuels and experimental ones in a shock tube [18].

The authors analyzed ignition process chemistry using a detailed chemical kinetic model of normal heptane released by Lawrence Livermore National Laboratory [19] or KUCRS, and by means of the contribution matrix [20,21,22,23]. They proposed an idea that an ignition process

can be divided into the following five phases, and these phases are characterized with the following seven reaction groups, as shown in Figure 3-(a) [23].

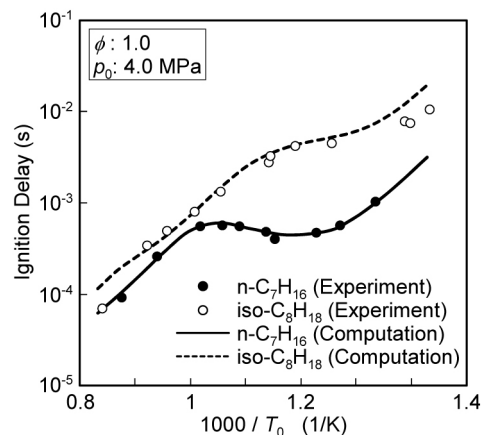


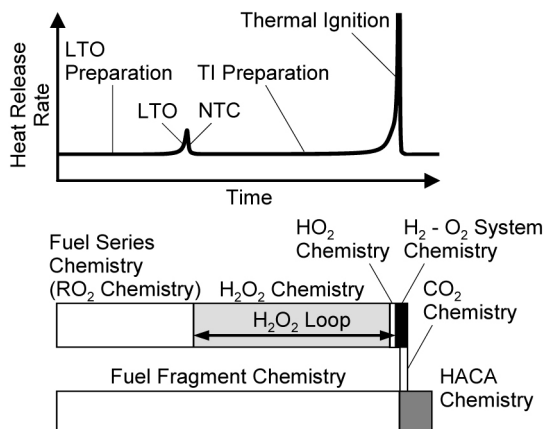
Figure 2. Experimental and Computational Ignition Delays of Normal Heptane / Air and Isooctane / Air Mixtures (Experimental data refer to those in a shock tube [18], and computations were conducted using a KUCRS PRF model.)

- LTO preparation phase
- LTO (low-temperature oxidation) phase
- NTC (negative temperature coefficient) phase
- TI (thermal ignition) preparation phase
- Thermal ignition phase
- Fuel series chemistry (RO₂ chemistry) whose reactions include species with the same number of C atoms as that of the fuel molecule.
- Fuel fragment chemistry which integrates all the other reactions.
- H₂O₂ loop chemistry which consists of reactions (R1), (R2), (R3), (R4) constructing an H₂O₂ regeneration loop as shown in Figure 3-(b), and reactions (R6), (R7), (R8), (R9) involved in the loop. The reactions (R2), (R3), (R4) are the main contributors to heat release during the TI preparation phase. The loop is not a branching chain process, but a heat release process by its overall reaction (R5).
- HO₂ chemistry which consists of the same reactions as the H₂O₂ loop chemistry does. However, the reaction (R6) becomes the main contributor to heat release. The H₂O₂ loop and HO₂ chemistry plays a role in increasing the temperature up to the thermal ignition point.
- Hydrogen oxygen system chemistry which consists of reactions with all the elements generated only from H and O atoms such as reactions (R10), (R11), (R12), (R13), except

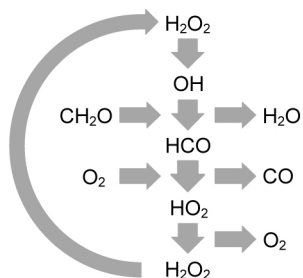
for the H_2O_2 loop chemistry. A thermal ignition point is defined as a point when the rate of a branching chain reaction (R10) overtakes the rate of the reaction (R6). This definition is chemical-kinetically reasonable because branching chain reactions in the hydrogen oxygen system chemistry become dominant above a temperature of this point.

- CO_2 chemistry which is CO oxidation into CO_2 mainly by a reaction (R14).

- HACA (H abstraction C_2H_2 addition) chemistry which describes the formation of soot precursors.

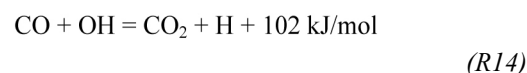
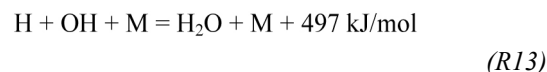
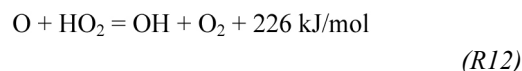
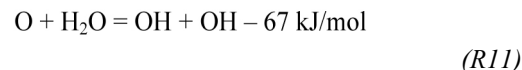
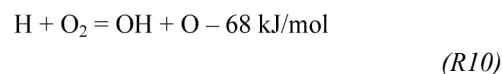
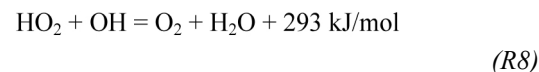
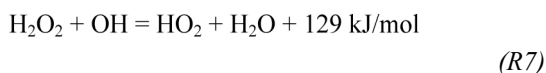
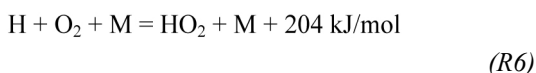
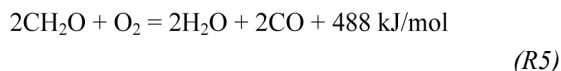
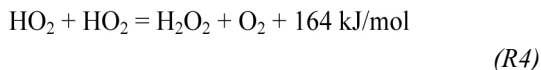
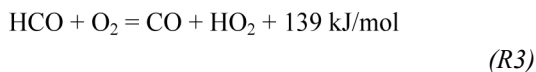
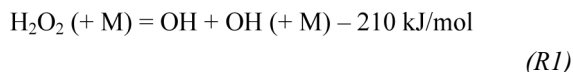


(a). Five Phases and Seven Reaction Groups



(b). H_2O_2 Regeneration Loop

Figure 3. Hydrocarbon Ignition Process Chemistry [23]



The authors also analyzed effects of the fuel, O_2 and N_2 concentrations on each phase of an ignition process, and separated these effects into chemical kinetic and thermodynamic factors [23].

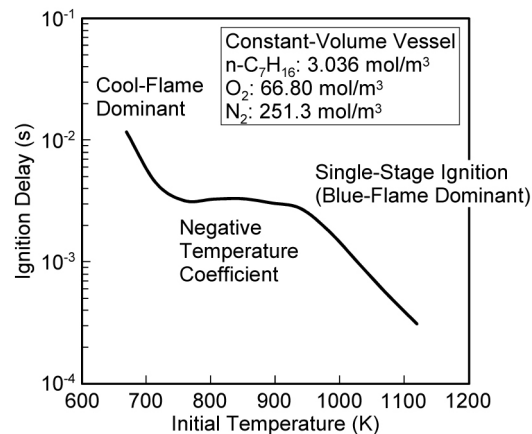


Figure 4. Relationship between Initial Temperature and Ignition Delay (The initial $n\text{-C}_7\text{H}_{16}$, O_2 and N_2 concentrations are equivalent to those in a mixture with an equivalence ratio of 0.5 at an initial temperature and pressure of 759 K and 2.027 MPa.)

In the present paper, ignition process chemistry of a highly diluted or ultra-lean mixture will be analyzed using a detailed model of normal heptane generated by KUCRS. Effects of an increase in the N_2 concentration and a decrease in the fuel concentration on the profile of heat release will be separated into chemical kinetic and thermodynamic factors. A mechanism of a two-stage profile of the main heat release will be elucidated. It will be presented that CO oxidation into CO_2 at a low temperature is different from that in a conventional ignition process.

COMPUTATIONAL CONDITIONS

A detailed chemical kinetic model of n-C₇H₁₆ (normal heptane) generated by KUCRS, consists of 372 chemical species and 1071 elementary reactions. CHEMKIN-PRO was used as a solver. Computations were conducted using various mixtures of n-C₇H₁₆, O₂ and N₂ in an adiabatic closed constant-volume vessel for simplification. On the assumption of a condition at TDC in a reciprocating engine with a compression ratio of 10:1, base values of the initial n-C₇H₁₆, O₂ and N₂ molar concentrations were set at 3.036, 66.80 and 251.3 mol/m³ which are equivalent to those in a mixture of n-C₇H₁₆ and the air (O₂: 21 vol.%, N₂: 79 vol.%) with an equivalence ratio of 0.5 at an initial temperature and pressure of 759 K and 2.027 MPa. The initial N₂ concentration increased while the initial n-C₇H₁₆ and O₂ concentrations were kept at those base values, which represented a diluted mixture. Also, the initial n-C₇H₁₆ concentration decreased while the initial O₂ and N₂ concentrations were kept at those base values, which represented a leaner mixture. The initial temperature was set at 669, 759, 849 or 1029 K with the same initial concentrations as those at 759 K. [Figure 4](#) shows a relationship between the initial temperature and the ignition delay with all the base values of the fuel, O₂ and N₂ concentrations (equivalence ratio of 0.5). An initial temperature of 669 K is located in a cool-flame dominant region [24, 25]. 759 and 849 K are located on the low-temperature boundary of a negative temperature coefficient region and in the middle of the region, respectively. 1029 K is located in a single-stage ignition region which is known as blue-flame dominant region [24, 25].

RESULTS AND DISCUSSION

Profile of Heat Release with Dilution

[Figure 5](#) shows histories of the temperature and the overall heat release rate during an ignition process when the N₂ concentration increases to double or quadruple of the base value, or when the fuel concentration decreases to half or quarter of the base value (the equivalence ratio changed from 0.5 to 0.25 or 0.125). A history of the overall heat release rate with a decrease in the fuel concentration to quarter was shown by quintuple of its true value. [Figure 6](#) shows a noticeable profile of heat release with an increase in the N₂ concentration. When a mixture is diluted or leaner with an initial temperature $T_0 = 669, 759$ or 849 K, a profile of heat release indicates double peaks excluding a peak by low-temperature oxidation. When a mixture is diluted or leaner further, the second one of the double peaks shrinks and finally disappears, and extremely slow heat release continues for a considerably long time after the remaining first peak. As a matter of course, a diluted or leaner mixture indicates a longer ignition process than a mixture with all the base values does.

An ignition process bypasses the LTO phase with $T_0 = 1029$ K. When a mixture is diluted or leaner on this condition, a profile of heat release remains as it indicates the single peak with all the base values. When a mixture is diluted or leaner further, extremely slow heat release continues for a long time after the single peak in the same way as shown with the LTO phase.

Effect of Dilution on Low-Temperature Oxidation

Effect of dilution on LTO beginning point

[Figure 7](#) shows histories of the temperature during the LTO and NTC phases with $T_0 = 759$ K. According to the top and middle graphs, even when the N₂ concentration increases or the fuel concentration decreases to a considerable extent, the beginning point of the LTO phase appears to stay constant. However, a closer look notifies that the LTO beginning point is just slightly advanced by an increase in the N₂ concentration.

The bottom graph shows those when the O₂ concentration decreases while the N₂ concentration increases so that the third body concentration stays constant. When the O₂ concentration decreases, the LTO beginning point is undoubtedly retarded.

These effects of the fuel, O₂ and N₂ concentrations on the LTO beginning point can be explained in the following way. The fuel series chemistry of n-C₇H₁₆ is represented by reactions (R15), (R16), (R17), (R18), (R19), (R20), (R21), (R22). Several values of the heat of a reaction correspond to those with several isomeric reactants. The LTO initiation is controlled by a branch of C₇H₁₄OOH removal during the LTO preparation phase into the second O₂ addition (R19) for generating two OH's or the thermal decomposition (R20) for generating one OH. The branching ratio into a third body reaction with O₂ (R19) or a unimolecular reaction (R20) is determined by the O₂ and third body concentrations, especially by the O₂ concentration, as well as by the temperature. Therefore, the branching ratio into the second O₂ addition (R19) decreases by a decrease in the O₂ concentration, causing a retarded LTO beginning point. The branching ratio into the second O₂ addition (R19) slightly increases by an increase in the N₂ concentration, causing a slightly advanced LTO beginning point.

