

Ignition Characteristics of Ethane and Its Roles in Natural Gas for HCCI Engine Operation

Hiroki Tanaka, Kazunobu Kobayashi, and Takahiro Sako
Osaka Gas Co., Ltd.

Yasuyuki Sakai
University of Fukui

Masahiro Furutani
Nagoya Institute of Technology

Kazunari Kuwahara
Osaka Institute of Technology

ABSTRACT

The ignition characteristics of each component of natural gas and the chemical kinetic factors determining those characteristics were investigated using detailed chemical kinetic calculations. Ethane (C_2H_6) showed a relatively short ignition delay time with high initial temperature; the heat release profile was slow in the early stage of the ignition process and rapid during the late stage. Furthermore, the ignition delay time of C_2H_6 showed very low dependence on O_2 concentration. In the ignition process of C_2H_6 , HO_2 is generated effectively by several reaction paths, and H_2O_2 is generated from HO_2 and accumulated with a higher concentration, which promotes the OH formation rate of $H_2O_2 (+M) = OH + OH (+M)$. The ignition characteristics for C_2H_6 can be explained by H_2O_2 decomposition governing OH formation at any initial temperature.

Furthermore, the relation between the operating characteristics of an HCCI engine and the ignition characteristics of C_2H_6 , and its roles in CH_4 -based blended fuels for HCCI engine operation were investigated through engine tests. The CH_4/C_2H_6 showed high ignition stability during the expansion stroke, high anti-knocking properties, and high EGR tolerance. These results revealed that C_2H_6 plays a significant role in expanding the operation range. Finally, engine operation tests at maximum loads, with and without EGR, indicated that CH_4/C_2H_6 provides greater indicated thermal efficiency compared to $CH_4/n-C_4H_{10}$, regardless of EGR rate and ignition timing. These results suggest that, in terms of thermal efficiency at the maximum load, anti-knocking properties are the most important ignition characteristics of C_2H_6 .

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INTRODUCTION

Homogeneous charge compression ignition (HCCI) is a technology that combines high efficiency with low NO_x emissions [1, 2, 3, 4, 5, 6]. However, HCCI engine operation is limited by knocking due to rapid combustion under high loads and cycle-to-cycle variation due to slow heat release under low loads [7, 8]. The former is caused by a steep rise in pressure due to bulk combustion, and the latter by the slow heat release during the thermal ignition preparation phase that is less than the decrease in internal energy due to expansion. With HCCI engines burning natural gas, high compression ratios must be used to achieve self-ignition in fuels with low ignitability, increasing the frequency of these problems. Many studies have examined ways to expand the operating range, such as supercharging, exhaust gas recirculation (EGR), and stratification [9, 10, 11, 12, 13, 14].

Controlling the combustion phase using EGR is a particularly effective approach to reducing the steep rise in pressure. However, excessive delay of ignition timing can lead to greater variation in combustion [15].

Ignition characteristics, such as the relation between initial temperature and ignition delay time, of methane, ethane, propane, and butane and blends of these small alkanes in air, have been examined using shock tubes, rapid compression machines, and flow reactors that can be used to simulate reactions of natural gas [16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28]. In many cases, experimental data have been compared with results from chemical kinetic modeling. Furutani *et al.* determined ignition delay times of methane, ethane, propane, normal butane, and dual-component

methane-based blends with ethane, propane, and normal butane in air using a rapid compression machine [18]. Huang *et al.* determined ignition delay times of dual-component methane-based blends with ethane and propane in air under engine-relevant conditions using a shock tube, and also conducted chemical kinetic analyses to understand interactions between methane and secondary fuels [19].

Kuwahara *et al.* analyzed the ignition process chemistry of *n*-heptane using a detailed chemical kinetic model and a contribution matrix method. They also proposed an approach that divides the hydrocarbon ignition process into five phases and seven reaction groups (listed below) [29, 30, 31, 32]. The thermal ignition preparation phase is the process in which relatively slow heat release by the H_2O_2 loop reaction increases the temperature to the thermal ignition point, at which the branching chain reactions of the hydrogen oxygen system become dominant.

The five phases of the hydrocarbon ignition process proposed by Kuwahara *et al.*:

- Low-temperature oxidation (LTO) preparation
- LTO
- Negative temperature coefficient (NTC)
- Thermal ignition preparation
- Thermal ignition

The seven reaction groups of the hydrocarbon ignition process proposed by Kuwahara *et al.*:

- Fuel series chemistry
- Fuel fragment chemistry
- H_2O_2 loop chemistry
- HO_2 chemistry
- Hydrogen oxygen system chemistry
- CO_2 chemistry
- H abstraction C_2H_2 addition (HACA) chemistry

Because HCCI combustion is controlled by chemical reactions without the help of forced ignition, such as spark discharge or diesel injection, ignition robustness against in-cylinder disturbances during the expansion stroke is low and cycle-to-cycle variation occurs easily because slow heat release during the thermal ignition preparation phase is less than the decrease in the internal energy due to expansion.

The ignition characteristics of the components of natural gas - methane (CH_4), ethane (C_2H_6), propane (C_3H_8), normal butane ($n-C_4H_{10}$), and isobutane ($i-C_4H_{10}$) - have been investigated using detailed chemical kinetic calculations, and results revealed that C_2H_6 exhibits unique ignition characteristics [33, 34]. In the present study, the reaction process of natural-gas components during the ignition delay was analyzed based on chemical kinetics, and the chemical kinetic factors determining the ignition characteristic of C_2H_6 were clarified. Furthermore, the roles of C_2H_6 in CH_4 -based blended fuels for HCCI engine operation were investigated through engine tests.

CHEMICAL KINETICS STUDY OF THE IGNITION PROCESS OF NATURAL GAS COMPONENTS

Computation Setup

A detailed chemical kinetic model for the oxidation of CH_4 , C_2H_6 , C_3H_8 , $n-C_4H_{10}$, $i-C_4H_{10}$, and blends of these was created using Knowledge-basing Utilities for Complex Reaction System (KUCRS). KUCRS is an automatic detailed chemical kinetic model generation software, developed by Miyoshi [35, 36, 37, 38, 39]. The model contained 145 chemical species and 658 elementary reactions and included H_2/O_2 reactions in the Leeds CH_4 model [40], and C_1 and C_2 reactions in the Lawrence Livermore National Laboratory (LLNL) isooctane model [41]. The unimolecular reactions of alkyl peroxy radicals (ROO), hydroperoxy alkyl radicals (QOOH), and hydroperoxy alkyl peroxy radicals (OOQOOH) were mentioned [38], and the molecular-size dependent fall-off rate constants of O_2 addition to alkyl radicals and thermal decomposition of hydroperoxy carbonyl compounds (HOOPO) were introduced [39]. Thermodynamic data were generated by THERM [37]. The computational ignition delay times of *n*-heptane and isooctane (2,2,4-trimethylpentane) in air using the model of primary reference fuels generated by KUCRS agreed well with experimental data in a shock tube [42] (Figure 1).

Using chemical kinetic computation software CHEMKIN-PRO, zero-dimensional calculations for the ignition of a mixture of a single-component fuel (CH_4 , C_2H_6 , C_3H_8 , $n-C_4H_{10}$, or $i-C_4H_{10}$) and air (O_2 : 21 vol%, N_2 : 79 vol%) in an adiabatic closed constant-volume vessel were conducted. The initial fuel molar concentration in each single-component fuel/air mixture was set at the equivalent of a calorific value of 32.20 MJ/m³, the initial O_2 molar concentration at 160.5 mol/m³, and the initial N_2 molar concentration at 603.7 mol/m³. These values correspond to the initial component molar concentrations in a CH_4 /air mixture at an equivalence ratio of 0.5, initial temperature of 1000 K and initial pressure of 6.687 MPa (Table 1). The calorific value of the fuel was defined as the heat of formation assuming complete oxidation. For each mixture, the initial temperature was varied, while the initial fuel, O_2 , and N_2 concentrations were kept constant to determine the relation between initial temperature and ignition delay time. The point at which the rate of reaction (R2) exceeded that of reaction (R1) was defined as the thermal ignition point, and ignition delay time was determined [32].

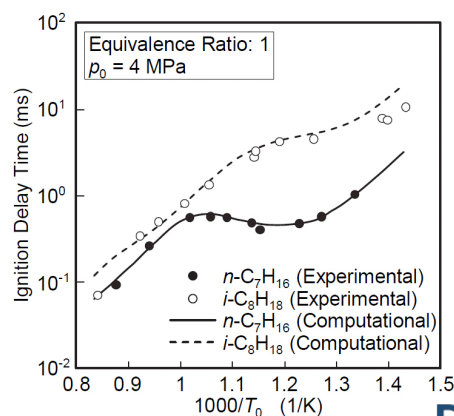
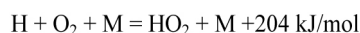


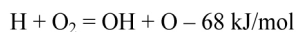
Figure 1. Ignition delay time for *n*-C₇H₁₆ and *i*-C₈H₁₈ in shock tube [42] and computed results using detailed chemical kinetic model [39].

Table 1. Initial conditions for single-component fuel/air mixtures in an adiabatic closed constant-volume vessel

	CH ₄ /Air	C ₂ H ₆ /Air	C ₃ H ₈ /Air	<i>n</i> -C ₄ H ₁₀ /Air	<i>i</i> -C ₄ H ₁₀ /Air
Initial O ₂	160.5 mol/m ³				
Initial N ₂	603.7 mol/m ³				
Initial Fuel	Equivalent to 32.20 MJ/m ³				
Equivalence Ratio	0.5	0.4915	0.4913	0.4909	0.4927
Initial Temperature	700 K to 1400 K				
Initial Press. at 1000 K	6.687 MPa	6.541 MPa	6.485 MPa	6.455 MPa	6.455 MPa



(R1)



(R2)

Ignition Delay Time

Figure 2 shows the relation between initial temperature and ignition delay time using the KUCRS model (upper). Ignition delay time was longest for CH₄ followed by C₂H₆, C₃H₈, *n*-C₄H₁₀, and *i*-C₄H₁₀ over a wide range of initial temperatures. The ignition delay time of CH₄ was much longer than those of C₃H₈, *n*-C₄H₁₀, and *i*-C₄H₁₀. The ignition delay time of *n*-C₄H₁₀ was clearly influenced by low-temperature OH chain branching at temperatures below about 950 K (black arrow), and was much shorter than those of C₃H₈ and *i*-C₄H₁₀ in this range. The ignition delay time of C₂H₆ was as long as that of CH₄ in the low-temperature range. However, it became closer to those of C₃H₈, *n*-C₄H₁₀, and *i*-C₄H₁₀ as the initial temperature increased, and was the shortest above about 1250 K (white arrow). The apparent activation energy of C₂H₆ was greater than those of the other small alkanes over a wide range of initial temperatures, which was noted in experimental studies using a flow reactor by Beerer *et al.* [26] and using a rapid compression machine by Furutani *et al.* [18]. However, the factors causing the high activation energy of C₂H₆ remain unknown.

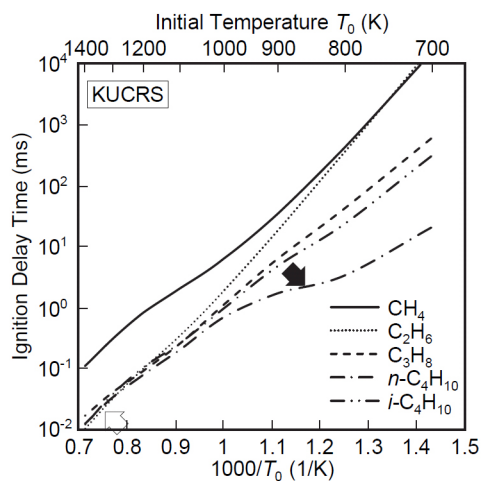


Figure 2.

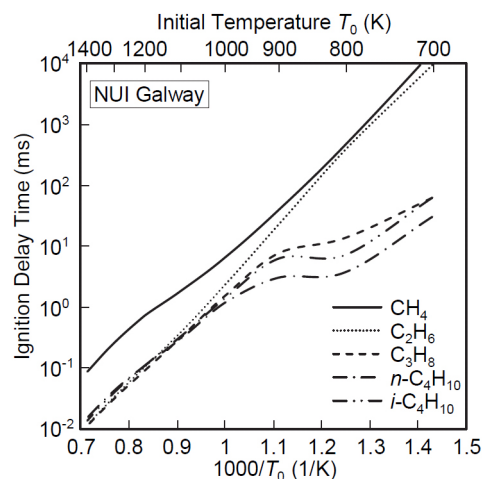


Figure 2. (cont.) Relation between initial temperature and ignition delay time for single-component fuels

Using the National University of Ireland (NUI) natural gas model (lower) [43], not only the ignition delay time of *n*-C₄H₁₀ but also those of C₃H₈ and *i*-C₄H₁₀ were clearly influenced by low-temperature OH chain branching, which was validated using a rapid compression machine by Gallagher *et al.* [20] and using both a rapid compression machine and a shock tube by Healy *et al.* [22, 23]. Excluding this difference in the low-temperature range, the relation between initial temperature and ignition delay time in the high-temperature range were similar to those using the KUCRS model. Accordingly, it is reliable to analyze ignition process in the high-temperature range using the KUCRS model.

Chemical Kinetic Factors Determining Ignition Delay Time

Chemical kinetic analyses were conducted using the contribution matrix method [29, 30, 31, 32], which could determine why the apparent activation energy of C₂H₆ was high. Significant reaction paths were determined, as shown in the Appendix.

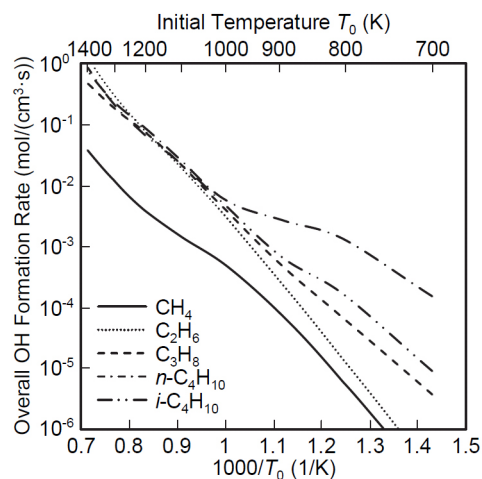


Figure 3. Relation between initial temperature and overall OH formation rate at the 5K increase point for single-component fuels

Figure 3 shows the relation between initial temperature and OH formation rate where temperature increased by 5 K from the initial temperature. The overall OH formation rate, which is the sum of

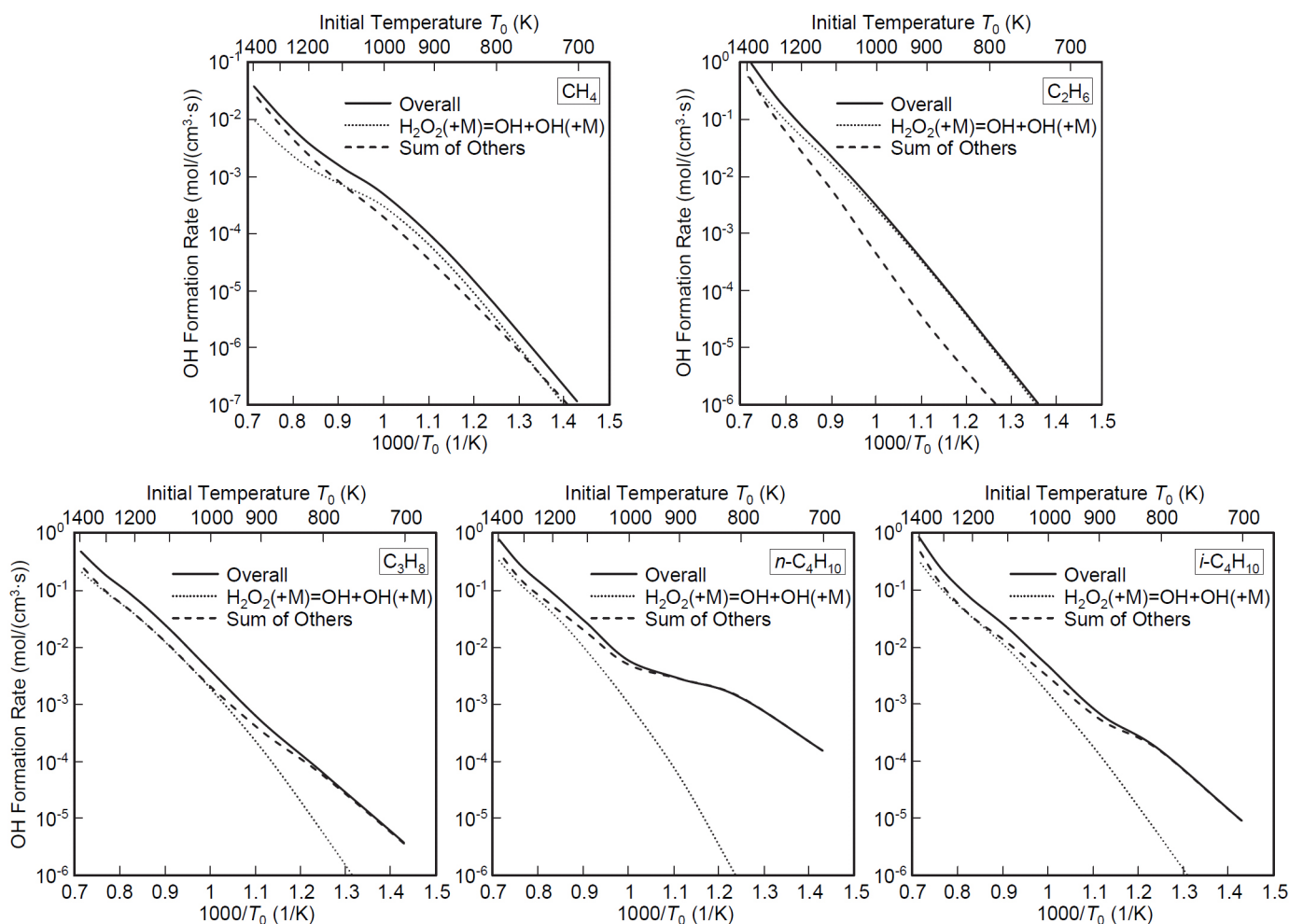
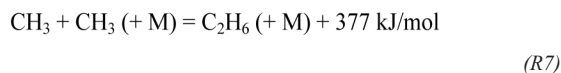
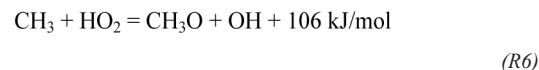
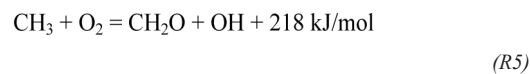
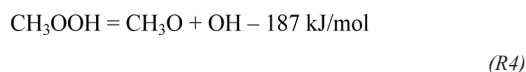
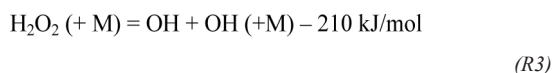


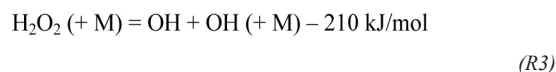
Figure 4. Relation between initial temperature and OH formation rate of R3 and the sum of OH formation rates for the other reactions

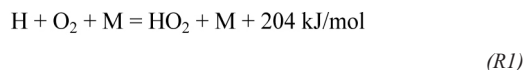
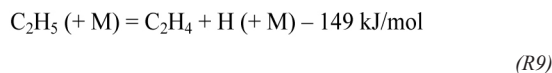
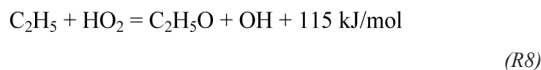
positive OH formation rates of all participating reactions, was plotted. These relations are reflected by initial temperature and ignition delay time plots shown in Figure 2. Overall activation energy of OH formation of C_2H_6 was greater than those of the other alkanes over a wide range of initial temperatures.

In Figure 4, overall OH formation rate at the 5 K increase point has been divided into the OH formation rate of (R3) and the sum of those of the other participating reactions. For CH_4 , the contribution ratios of (R3) and (R4) are high in the low-temperature range. However, the contribution ratio of (R3) decreased to less than 50%, while those of (R5) and (R6) increased with initial temperature. The contribution ratio of (R7) to CH_3 removal also increased with initial temperature, which interfered with OH formation. Therefore, overall activation energy of OH formation was low in the high-temperature range.

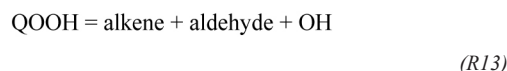
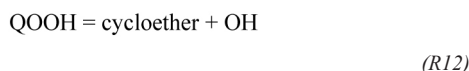
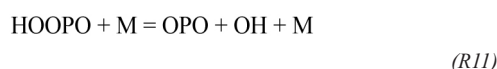
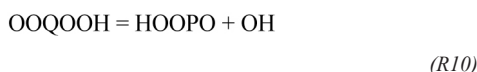
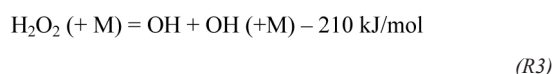


For C_2H_6 , the contribution ratio of (R3) was quite high in the low-temperature range. Although the contribution ratio of (R8) and the sum of those of the reactions with O and H increased with initial temperature, the contribution ratio of (R3) remained greater than 50% throughout the entire range of initial temperatures. The contribution ratio of (R9) to C_2H_5 removal also increased with initial temperature, which did not interfere with OH formation because (R9) is followed by (R1). Therefore, overall activation energy of OH formation was determined by (R3) over a wide range of initial temperatures.





For C_3H_8 , $n\text{-C}_4\text{H}_{10}$, and $i\text{-C}_4\text{H}_{10}$, the ignition delay time of $n\text{-C}_4\text{H}_{10}$ was clearly influenced by low-temperature OH chain branching, while those of C_3H_8 and $i\text{-C}_4\text{H}_{10}$ were not, as shown in Figure 3. However, the relation between initial temperature and OH formation rate was similar. The sum of the contribution ratios of (R10) and (R11) was quite high in the low-temperature range, and those of (R12) and (R13) increased initially and then decreased as initial temperature increased. The contribution ratio of (R3) was high, but was less than 50%, in the high-temperature range. Because of (R10), (R11), (R12), and (R13), which do not appear for CH_4 and C_2H_6 , the overall activation energy of OH formation was low in the low-temperature range.



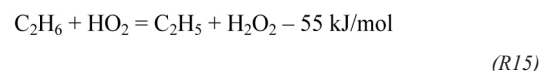
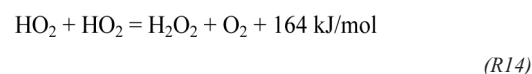
Heat Release Rate in the Late Stage of Ignition

Figure 5 shows the ignition delay time at an initial temperature of 1000 K, 1200 K, and 1400 K under the conditions shown in Table 1. A distinction in ignition delay time was made at the points where the temperature increased by 1 K, 10 K, and 100 K from the initial temperature. The ignition delay time of C_2H_6 became similar to those of C_3H_8 , $n\text{-C}_4\text{H}_{10}$, and $i\text{-C}_4\text{H}_{10}$ as initial temperature increased from 1000 K to 1200 K, particularly because the period of time from the beginning to the 10 K increase point (white and light gray bands) was relatively short. The period of time from the 10 K increase point to the ignition point (dark gray and black bands) of C_2H_6 was shorter than those of the other alkanes with initial temperatures of 1200 K and 1400 K.

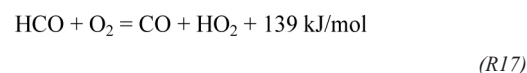
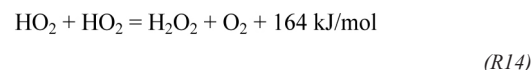
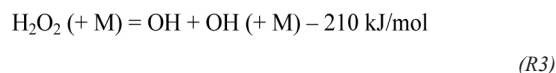
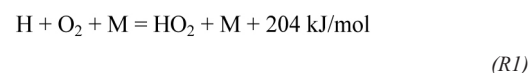
Figure 6 shows the profile for heat release rate during ignition delay time (shown in Figure 5). Overall heat release rate, which is the sum of heat release rates with both positive and negative values from all

reactions, was plotted against temperature increase during the ignition delay time. The heat release rate of C_2H_6 was lower than those of C_3H_8 , $n\text{-C}_4\text{H}_{10}$, and $i\text{-C}_4\text{H}_{10}$ until the temperature increased by 70 to 100 K from an initial temperature of 1000 K (white arrow). After that the heat release rate of C_2H_6 became greatest (black arrow). The heat release rate of C_2H_6 also became greatest after a temperature increase by approximately 10 K from an initial temperature of 1200 K and by several K from 1400 K. These profiles provided the breakdowns of ignition delay times shown in Figure 5.

Figure 7 shows overall OH formation rate, overall HO_2 formation rate, and H_2O_2 concentration plotted against temperature increase during the ignition delay time. Overall OH formation rate of C_2H_6 became greater than those of the other fuels after a certain increase in temperature. The greatest accumulation of H_2O_2 occurred during the ignition delay time of C_2H_6 . The overall HO_2 formation rate of C_2H_6 remained the greatest from the beginning of the temperature increase, resulting in the greatest H_2O_2 concentration because H_2O_2 is generated primarily by (R14) and reactions with fuel, such as (R15), until a small increase in temperature from the initial temperature, and then by (R14).



An H_2O_2 regeneration loop, composed of (R3), (R14), (R16), and (R17) and supported by (R1), plays a significant role in releasing heat during the ignition process after low-temperature OH chain branching, and also during the ignition process that bypasses the low-temperature OH chain branching [29, 30, 31, 32]. The loop operates when CH_2O and H_2O_2 accumulate to sufficient concentrations, recognized when the contribution ratio of (R14) increases to a specific level. During the ignition process of C_2H_6 , within the lower temperature range where fuel series chemistry is dominant, OH formation and heat release are both slow, but in the higher temperature range, once the H_2O_2 loop is activated, heat release is accelerated by the high H_2O_2 concentration.



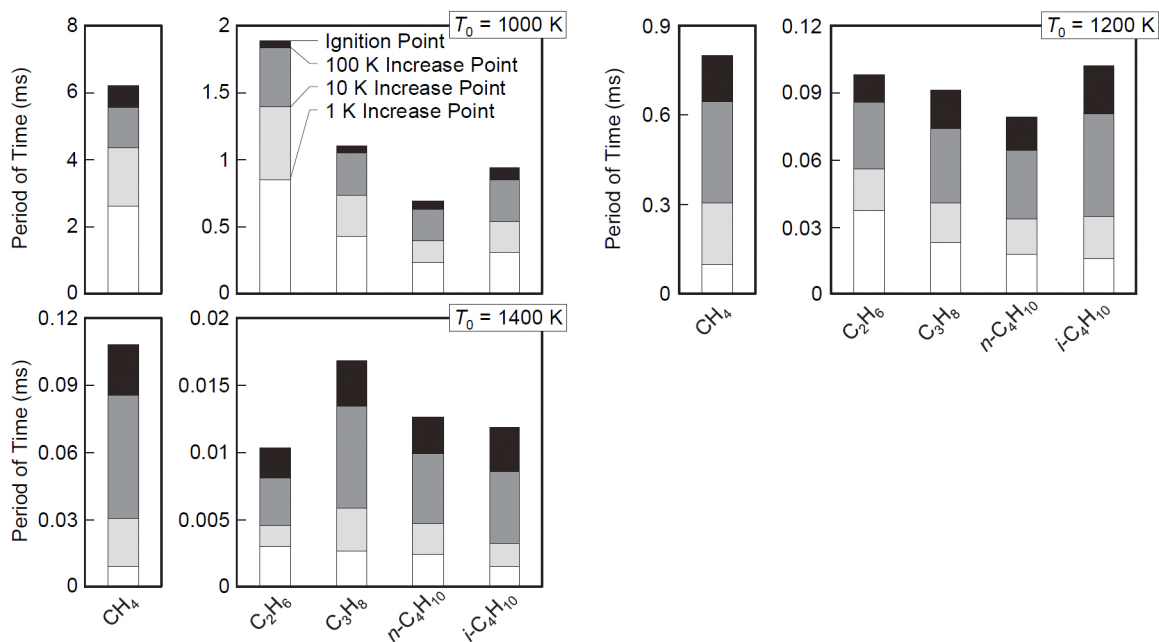


Figure 5. Breakdowns of ignition delay time for single-component fuels

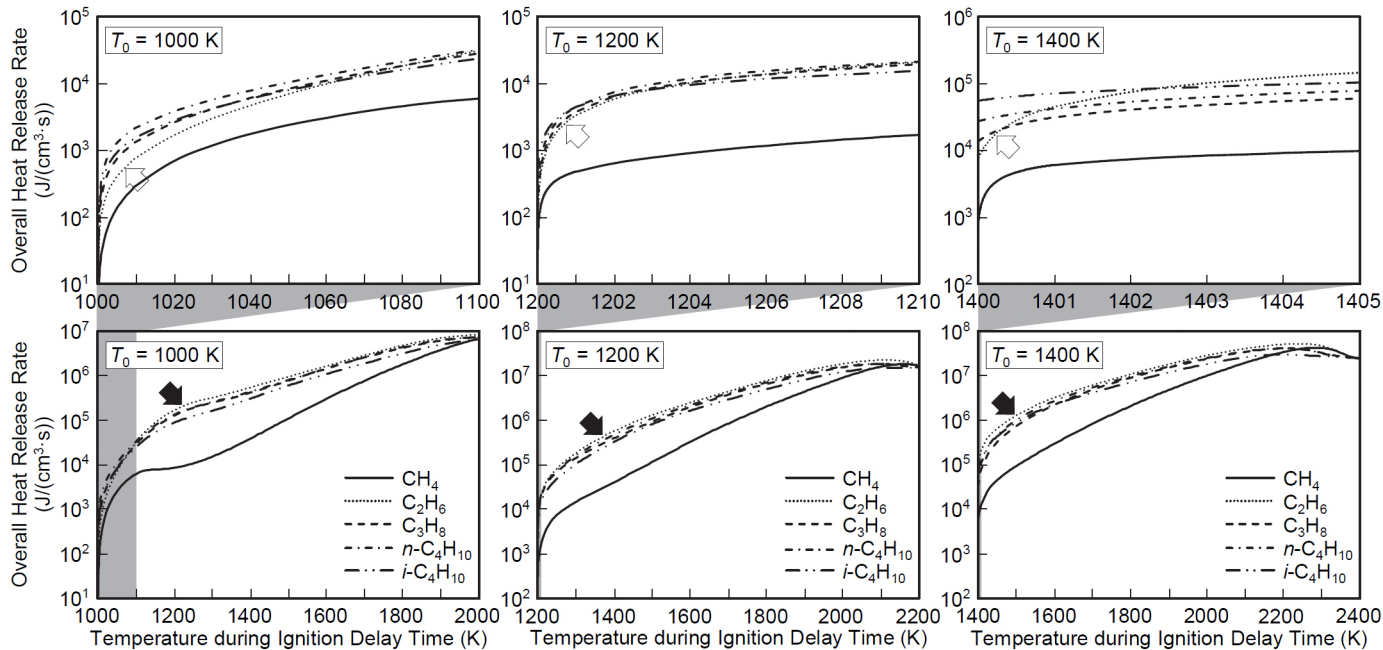


Figure 6. Profile of overall heat release rate against temperature increase during ignition delay times for single-component fuels

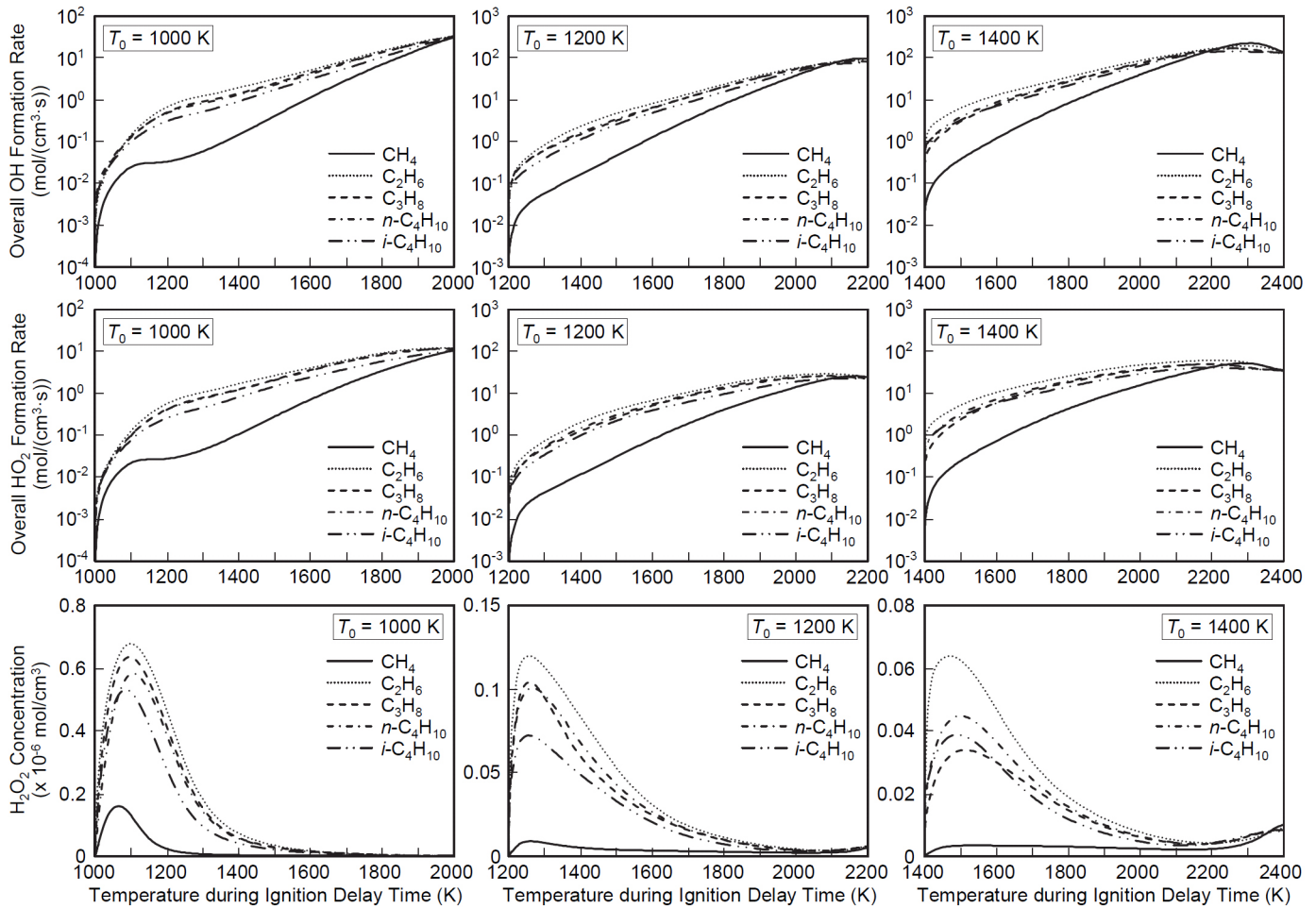


Figure 7. Profile of overall OH formation rate, overall HO₂ formation rate, and H₂O₂ concentration against temperature increase during ignition delay times for single-component fuels

Ignition During the Expansion Stroke in an HCCI Engine Model

C₂H₆ showed a relatively short ignition delay time when initial temperature was high, and the heat release profile was slow in the early stage of the ignition process and rapid during the late stage. If the early stage of an ignition process takes place during the compression stroke, this kind of heat release profile is desirable in an HCCI engine because it reduces cycle-to-cycle variation during the expansion stroke. In this respect, ignition stability against in-cylinder disturbances during the expansion stroke is likely to be greater for CH₄/C₂H₆ than for the other CH₄-based blended fuels such as natural gas.

Calculations for CH₄-based dual-component fuels, with CH₄ as the primary component and C₂H₆, C₃H₈, *n*-C₄H₁₀, or *i*-C₄H₁₀ as the secondary component, and for natural gas in an adiabatic rapid compression and expansion machine were conducted. First, the initial fuel, O₂ and N₂ molar concentrations for a mixture of air and natural gas (CH₄: 88 vol. %, C₂H₆: 6 vol. %, C₃H₈: 4 vol. %, *n*-C₄H₁₀: 1 vol. %, *i*-C₄H₁₀: 1 vol. %) were set at the equivalent of a calorific value of

1.643 MJ/m³, 8.107 mol/m³, and 30.69 mol/m³, respectively. These values correspond to the initial component molar concentrations in a natural gas/air mixture at an equivalence ratio of 0.5, initial temperature of 300 K, and initial pressure of 101.3 kPa. Next, the initial CH₄, O₂, and N₂ molar concentrations of each dual-component fuel/air mixture were set to the same values as those for the natural gas/air mixture, and the initial secondary fuel molar concentration was set to a value corresponding to an overall calorific value of 1.643 MJ/m³. The same calculations were performed for a CH₄/air mixture with the same calorific value and initial O₂ and N₂ molar concentrations. These mixtures were compressed and expanded with a 3:1 connecting-rod length:crank radius ratio and a compression ratio of 28:1, at rotation speeds of 900 min⁻¹ and 1800 min⁻¹ (Table 2). To keep 10% heat release timing at the same crank angle, the initial temperature was varied, keeping the initial fuel, O₂ and N₂ molar concentrations constant.

Figure 8 shows temperature plotted against crank angle. At a rotation speed of 900 min⁻¹, when the initial temperatures for CH₄/air, CH₄/C₂H₆/air, natural gas/air, CH₄/C₃H₈/air, CH₄/*n*-C₄H₁₀/air, and