

Chemical Kinetics Study on Small-Alkane Ignition Process to Design Optimum Methane-Based Blend for HCCI

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ABSTRACT

The ignition delay times and heat release profiles of CH_4 , C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ and dual-component CH_4 -based blends with these alkanes in air were determined using a detailed chemical kinetic model. The apparent activation energy of C_2H_6 in the relationship between initial temperature and ignition delay time is higher than those of the other alkanes because OH formation is dominated by $\text{H}_2\text{O}_2(+\text{M})=\text{OH}+\text{OH}(+\text{M})$ from the beginning over a wide range of initial temperatures. The heat release rate of C_2H_6 is higher than those of the other alkanes in the late stage of ignition delay time because H_2O_2 is accumulated with a higher concentration and promotes the OH formation rate of $\text{H}_2\text{O}_2(+\text{M})=\text{OH}+\text{OH}(+\text{M})$. These ignition characteristics are reflected in those of $\text{CH}_4/\text{C}_2\text{H}_6$.

In an HCCI engine, misfire and partial combustion occur easily because the heat release rate during the ignition process after low-temperature OH chain branching and also during the ignition process bypassing low-temperature OH chain branching, becomes lower than the rate of decrease in internal energy during the expansion stroke. Partial combustion causes cycle-to-cycle variation in combustion as well as high HC emissions. Therefore, the heat release profile, which is slow in the early stage of ignition process, but more rapid than those of other fuels in the late stage, can reduce cycle-to-cycle variation in combustion. This type of profile is similar to that of $\text{CH}_4/\text{C}_2\text{H}_6$ for an HCCI engine targeting CH_4 -based fuels.

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INTRODUCTION

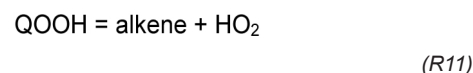
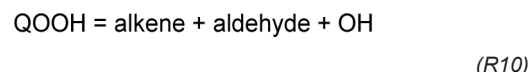
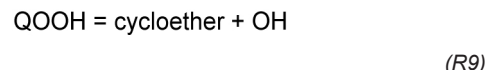
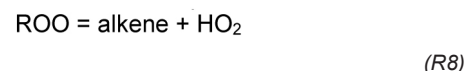
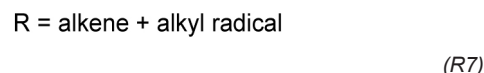
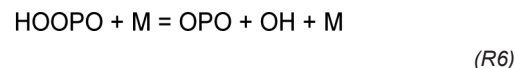
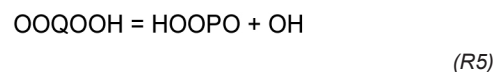
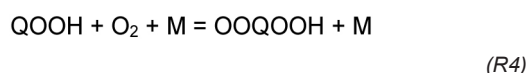
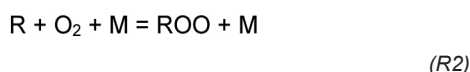
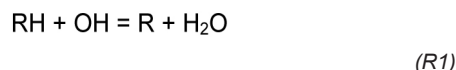
Natural gas is an abundant and low-carbon fuel. Homogeneous charge compression ignition (HCCI) is a combustion mode for operating an internal combustion engine with both high thermal efficiency and low NO_x emissions [1, 2, 3, 4]. Therefore, an HCCI engine fueled with natural gas is expected to be a clean, efficient, and sustainable energy conversion technology. However, HCCI engine operation using natural gas is limited by knocking at high loads and by cycle-to-cycle variation in combustion at low loads. Various methods to expand the narrow operation range, such as external EGR, internal EGR, and intake air charging, have been investigated [5, 6, 7]. In contrast, ignition characteristics, such as the relationship

between initial temperature and ignition delay time, of methane, ethane, propane, and butane, typical components of natural gas, and blends of these small alkanes in air have been examined using shock tubes, rapid compression machines, and flow reactors to simulate those of natural gas [8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. In many cases, experimental data have been compared with results from chemical kinetic modeling. Furutani et al. determined the ignition delay times of methane, ethane, propane, and normal butane and dual-component methane-based blends with ethane, propane, and normal butane in air using a rapid compression machine [10]. Huang et al. determined the ignition delay times of dual-component methane-based blends with ethane and propane

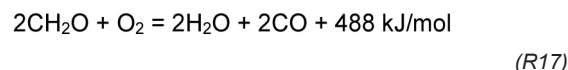
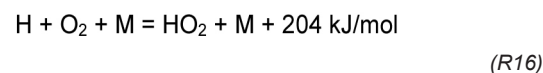
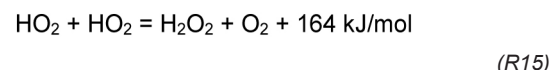
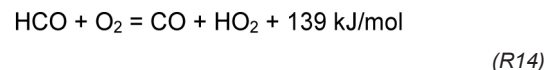
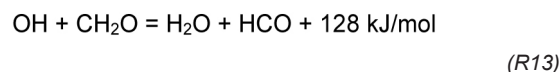
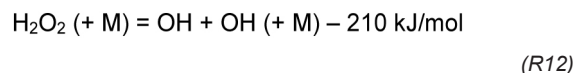
air under engine-relevant conditions using a shock tube, and also conducted chemical kinetic analyses to understand interactions between methane and the secondary fuels [11].

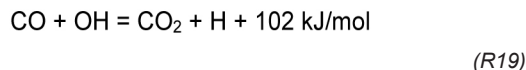
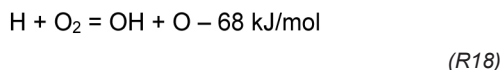
Miyoshi developed a software framework, called KUCRS (knowledge-basing utilities for complex reaction systems) [21], for the automatic generation of detailed chemical kinetic models for oxidation of various hydrocarbons, and posted it on a web site [22]. The latest version of KUCRS can model any non-cyclic alkane, single-ring (5- to 7-membered) cyclic alkane, non-cyclic alkene (monoene), and non-cyclic alcohol. For non-cyclic alkanes, the unimolecular reaction mechanisms of alkyl peroxy radicals (ROO), hydroperoxy alkyl radicals (QOOH), and hydroperoxy alkyl peroxy radicals (OOQOOH) were discussed on the basis of quantum chemical calculations [23], and the molecular-size dependent fall-off rate constants of O₂ addition to alkyl radicals and thermal decomposition of hydroperoxy carbonyl compounds (HOOPO) were introduced [24]. As shown in Figure 1, the computed ignition delay times of normal heptane and isooctane (2,2,4-trimethylpentane) in air using the model for blends of normal heptane and isooctane agree well with experimental data in a shock tube [25].

Ignition mechanisms of various alkanes in air were comprehensively analyzed using detailed chemical kinetic models generated by KUCRS and using the contribution matrix method [26, 27, 28, 29, 30]. Kuwahara et al. computed the ignition delay time of normal heptane with various initial fuel, O₂, and N₂ concentrations in an adiabatic closed constant-volume vessel, and discussed the chemical kinetic factors of initial pressure and fuel, O₂, and N₂ concentrations affecting ignition delay time [29]. Ando et al. computed the ignition delay times of normal alkanes of propane to octane and all the isomers of octane with air in an adiabatic closed constant-volume vessel, and discussed the chemical kinetic factors determining the octane numbers of the alkanes [30], a standard measure of the antiknocking tendencies of fuels in a spark ignition engine. The low-temperature oxidation of an alkane is described as (R1), (R2), (R3), (R4), (R5), (R6), (R7), (R8), (R9), (R10), (R11). The OH chain branching path is (R1), (R2), (R3), (R4), (R5), (R6), and its inhibition reactions are (R7), (R8), (R9), (R10), (R11). In the above studies, the effects of fuel, O₂, and N₂ concentrations and the molecular structure of alkanes as well as temperature on branch ratios of the OH chain branching path and its inhibition reactions were analyzed.



After low-temperature OH chain branching (R1), (R2), (R3), (R4), (R5), (R6), temperature slowly increases by an H₂O₂ regeneration loop [26, 27, 28, 29]. The loop is composed of four reactions (R12), (R13), (R14), (R15) and supported by (R16). The overall reaction of (R12), (R13), (R14), (R15) is (R17), which means that the loop is not an OH chain branching path, but merely a heat release path through oxidation of CH₂O into CO and H₂O. During a slow increase in temperature after low-temperature OH chain branching, the heat release rate of the loop accounts for about one-third of the sum of those of all reactions. When temperature increases to the ignition point at which the rate of (R18) becomes higher than the rate of (R16), branching chain reactions in H₂/O₂ reactions become dominant, and CO oxidation into CO₂ by (R19) becomes active. In an HCCI engine, misfire and partial combustion occur easily because the low heat release rate after low-temperature OH chain branching becomes lower than the rate of decrease in internal energy during the expansion stroke.





In contrast, Huang et al. analyzed the ignition mechanism of methane in air, and noted that (R12), (R13), (R14), (R15) and (R20) can be approximated by a one-step reaction (R21) [11].

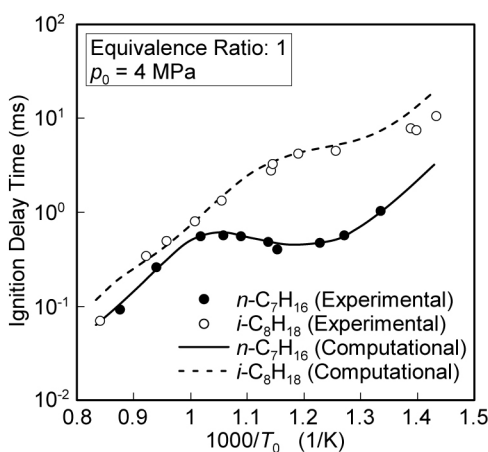
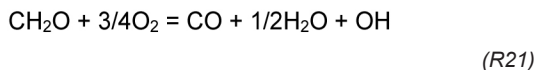
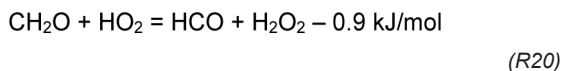


Figure 1. Ignition Delay Times of $n\text{-C}_7\text{H}_{16}$ and $i\text{-C}_8\text{H}_{18}$ with Air in Shock Tube [22] and Computed Results Using Detailed Chemical Kinetic Model Generated by KUCRS

In the present study, the ignition delay times of methane, ethane, propane, isobutane, and normal butane with air in an adiabatic closed constant-volume vessel are computed using a detailed chemical kinetic model generated by KUCRS. Differences in the temperature dependence of ignition delay time and in the profile of heat release rate during ignition delay time are determined, and the chemical kinetic factors affecting these differences are analyzed. In addition, the ignition delay times and profiles of heat release rate of dual-component blends of methane as the primary fuel and ethane, propane, isobutane, and normal butane as secondary fuels in air are computed to optimize a methane-based blend for stable combustion in an HCCI engine.

IGNITION CHARACTERISTICS OF SMALL ALKANES

Computational Conditions

A detailed chemical kinetic model for the oxidation of blends of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), isobutane ($i\text{-C}_4\text{H}_{10}$), and normal butane ($n\text{-C}_4\text{H}_{10}$) was generated by KUCRS, which contains 145 chemical species and 658 elementary reactions. The model includes H_2/O_2 reactions in

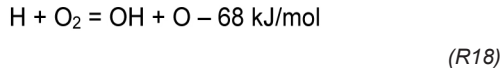
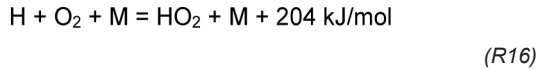
the Leeds CH_4 model [31], and C_1 and C_2 reactions in the LLNL isooctane model [32]. The unimolecular reactions of alkyl peroxy radicals (ROO), hydroperoxy alkyl radicals (QOOH), and hydroperoxy alkyl peroxy radicals (OOQOOH) were discussed [23], and the molecular-size dependent fall-off rate constants of O_2 addition to alkyl radicals and thermal decomposition of hydroperoxy carbonyl compounds (HOPO) were introduced [24]. Thermodynamic data were generated by THERM [33]. Elementary reactions are expressed along with heats of reactions at 298.15 K in the following sections.

CHEMKIN-PRO was employed as a solver. Zero-dimensional computations were conducted for the ignition delay times of CH_4 , C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ in air with O_2 and N_2 molar fractions of 21 % and 79 % in an adiabatic closed constant-volume vessel. Table 1 shows the initial conditions of CH_4/air , $\text{C}_2\text{H}_6/\text{air}$, $\text{C}_3\text{H}_8/\text{air}$, $i\text{-C}_4\text{H}_{10}/\text{air}$, and $n\text{-C}_4\text{H}_{10}/\text{air}$ mixtures. Initial O_2 and N_2 concentrations were set at 160.5 mol/m³ and 603.7 mol/m³. Initial fuel concentrations were chosen to release a quantity of heat of 32.20 MJ/m³ with complete oxidation of fuel into CO_2 and H_2O . The values of heat and O_2 and N_2 concentrations are equivalent to those in the CH_4/air mixture with an equivalence ratio of 0.5 and an initial pressure and temperature of 6.687 MPa and 1000 K. Initial temperature was varied from 700 K to 1400 K, while initial fuel, O_2 and N_2 concentrations were kept constant at the above values. The pressure and temperature values were determined with the assumption of in-cylinder conditions with a compression ratio of 28:1.

Table 1. Initial Conditions of Fuel/Air Mixtures

	CH_4/Air	$\text{C}_2\text{H}_6/\text{Air}$	$\text{C}_3\text{H}_8/\text{Air}$	$i\text{-C}_4\text{H}_{10}/\text{Air}$	$n\text{-C}_4\text{H}_{10}/\text{Air}$
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	0.4927	0.4909
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

Ignition delay time was determined as the period of time from the beginning to the ignition point, defined as the point at which the rate of (R18) becomes higher than the rate of (R16). This definition of ignition point is chemical kinetically reasonable because, at this point, branching chain reactions in H_2/O_2 reactions become dominant. However, this ignition point is about 2000 K, which is much higher than some experimental ignition points. However, the ignition delay time is consistent with that determined by the threshold of a lower temperature because temperature increases rapidly in the final step of computed ignition process.



Ignition Delay Time and Profile of Heat Release Rate

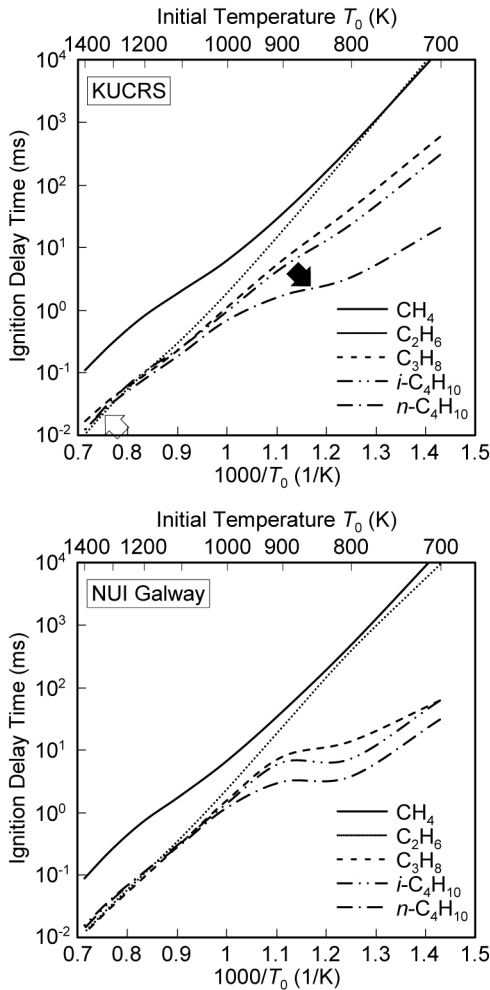


Figure 2. Relationships between Initial Temperature and Ignition Delay Times of Single-Component Fuels

Figure 2 shows the relationships between initial temperature and ignition delay time using the KUCRS model (upper). Ignition delay time is longer in the order of $\text{CH}_4 > \text{C}_2\text{H}_6 > \text{C}_3\text{H}_8 > i\text{-C}_4\text{H}_{10} > n\text{-C}_4\text{H}_{10}$ over a wide range of initial temperatures. The ignition delay time of CH_4 is much longer than those of C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$. The ignition delay time of $n\text{-C}_4\text{H}_{10}$ is clearly influenced by low-temperature OH chain branching in the range below about 950 K (black arrow), and is much shorter than those of C_3H_8 and $i\text{-C}_4\text{H}_{10}$ in this range. The ignition delay time of C_2H_6 is as long as that of CH_4 in the low-temperature range. However, it becomes closer to those of C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ as initial temperature increases, and is the shortest above about 1250 K (white arrow). The

apparent activation energy of C_2H_6 is higher 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. [18] and using a rapid compression machine by Furutani et al. [10]. However, the factors causing the high activation energy of C_2H_6 are unknown.

Using the NUI natural gas model (lower) [34], not only the ignition delay time of $n\text{-C}_4\text{H}_{10}$ but also those of C_3H_8 and $i\text{-C}_4\text{H}_{10}$ are clearly influenced by low-temperature OH chain branching, which was validated using a rapid compression machine by Gallagher et al. [12] and using both a rapid compression machine and a shock tube by Healy et al. [14, 15]. Excluding this difference in the low-temperature range, the relationships between initial temperature and ignition delay time in the high-temperature range are similar to those using the KUCRS model. Accordingly, it is reliable to analyze ignition process in the high-temperature range using the KUCRS model.

Figure 3 shows ignition delay times with initial temperatures of 1000 K, 1200 K, and 1400 K using the KUCRS model. Ignition delay time is divided at the points when temperature increases by 1 K, 10 K, and 100 K from the initial temperature. The ignition delay time of C_2H_6 becomes similar to those of C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ as initial temperature increases 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) is relatively shortened. The period of time from the 10 K increase point to the ignition point (dark gray and black bands) of C_2H_6 is shorter than those of the other alkanes with initial temperatures of 1200 K and 1400 K.

Figure 4 shows the profiles of heat release rate during the ignition delay times shown in Figure 3. The overall heat release rate, which is the sum of heat release rates with both positive and negative values of all reactions, has been plotted against temperature increase during ignition delay time. The heat release rate of C_2H_6 is lower than those of C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ until temperature increases by about 70 to 100 K from an initial temperature of 1000 K (white arrow). Thereafter, the heat release rate of C_2H_6 becomes the highest (black arrow). The heat release rate of C_2H_6 also becomes the highest after a temperature increase by ten and several K from an initial temperature of 1200 K and by several K from 1400 K. These profiles provide the breakdowns of ignition delay times shown in Figure 3.

Chemical kinetic analyses were conducted using the contribution matrix method [26, 27, 28, 29], which can answer why the activation energy of C_2H_6 is high and why the heat release rate of C_2H_6 is high in the late stage of ignition delay time. Significant reaction paths were determined, as shown in Appendix.

Chemical Kinetic Factors Causing Ignition Characteristics of Ethane

Why is Activation Energy High?

Figure 5 shows the relationships between initial temperature and OH formation rate at the point when temperature increases by 5 K from initial temperature. The overall OH formation rate, which is the sum of positive OH formation rates of all participating reactions, has been plotted. These relationships are reflected in the relationships between initial temperature and ignition delay time shown in Figure 2 (upper). The overall activation energy of OH formation of C₂H₆ is higher than those of the other alkanes over a wide range of initial temperatures.

In Figures 6 and 7, the overall OH formation rate at the 5 K increase point has been divided into the OH formation rate of (R12) and the sum of those of the other participating reactions. In addition, the contribution ratios of significant reactions to overall OH formation rate at the 5 K increase point have been plotted. For CH₄ (Figure 6, left), the contribution ratios of (R12) and (R27) are high in the low-temperature range where the primary OH formation path is described as (R22), (R23), (R24), (R25), (R26), (R27), (R28), (R29), (R20), and (R12), (R13), (R14), (R15), (R16). However, the contribution ratio of (R12) decreases below 50 % while those of (R30) and (R31) increase with initial temperature. The contribution ratio of (R32) to CH₃ removal also increases with initial temperature, which interferes with OH formation. Therefore, the overall activation energy of OH formation is low in the high-temperature range.

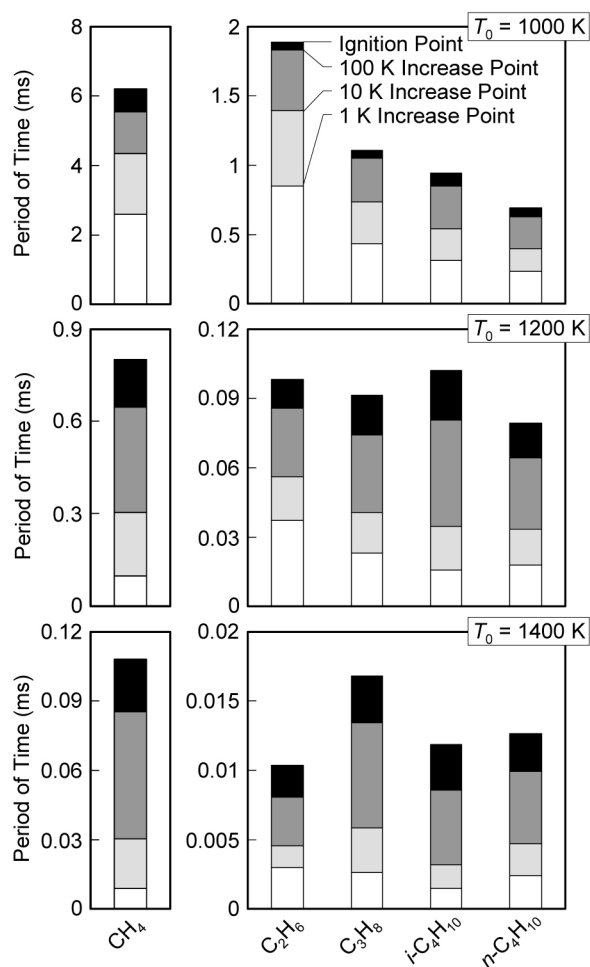
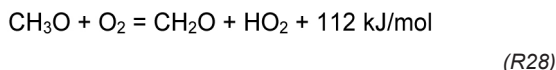
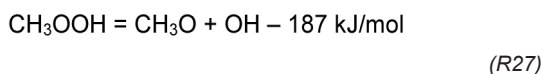
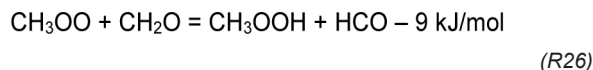
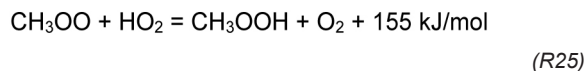
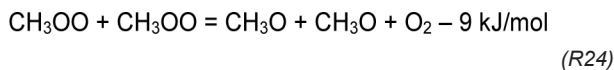
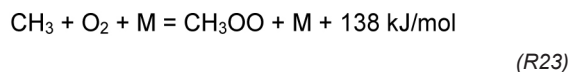
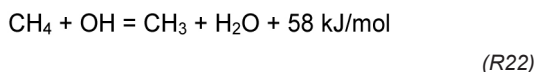
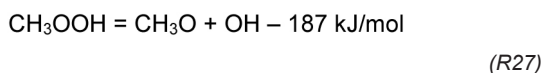
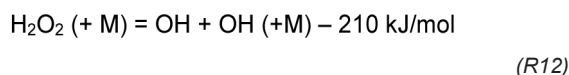
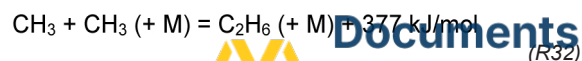
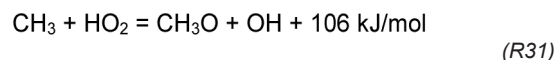
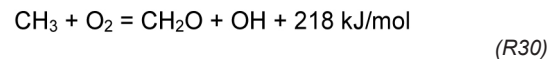
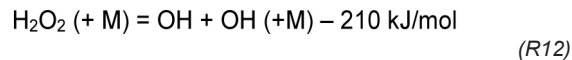
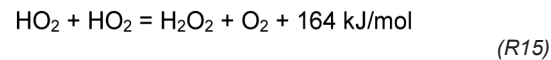
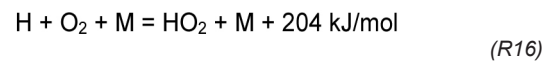
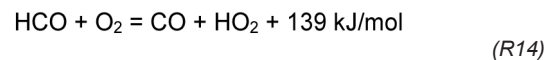
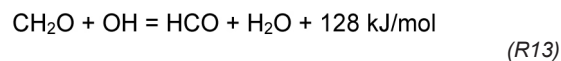
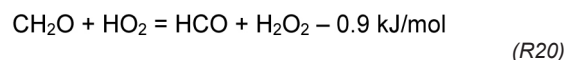
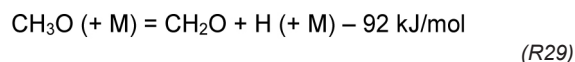


Figure 3. Breakdowns of Ignition Delay Times of Single-Component Fuels Using KUCRS Model



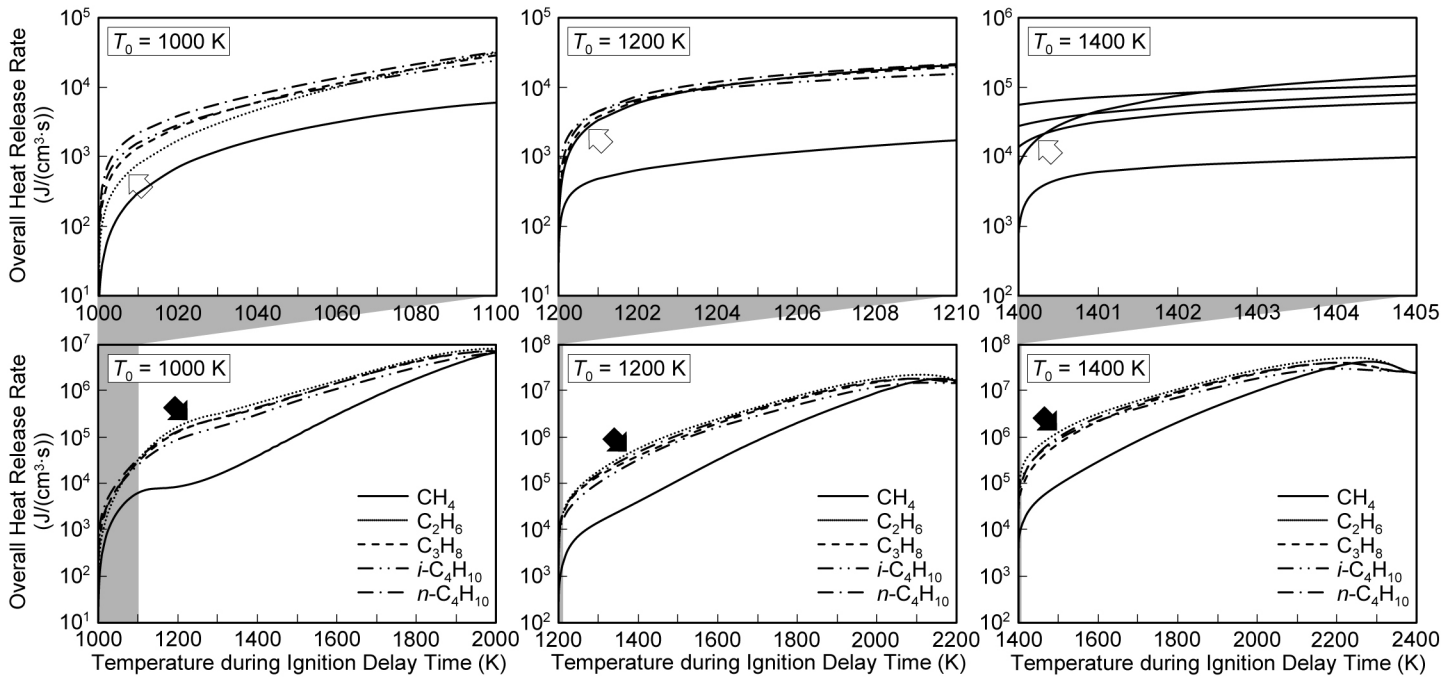
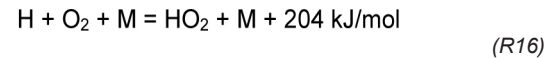
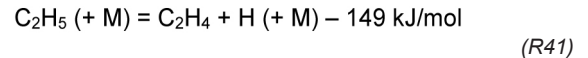
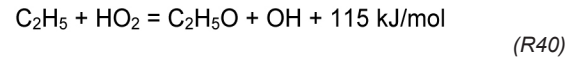
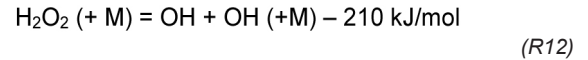
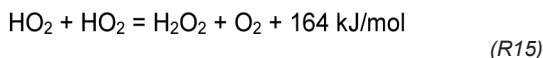
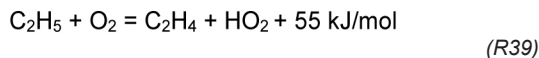
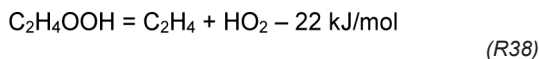
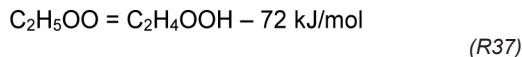
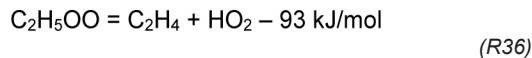
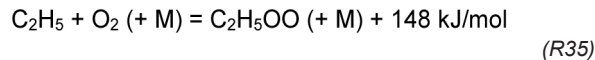
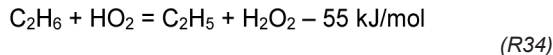
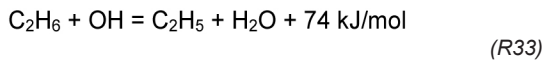
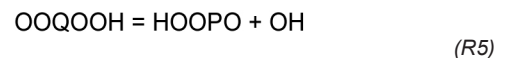


Figure 4. Profiles of Overall Heat Release Rate against Temperature Increase during Ignition Delay Times of Single-Component Fuels

For C_2H_6 (Figure 6, right), the contribution ratio of (R12) is quite high in the low-temperature range where the principal OH formation path is described as (R33), (R34), (R35), (R36), (R37), (R38), (R39), (R15), and (R12). Although the contribution ratio of (R40) and the sum of those of the reactions with O and H increase with initial temperature, the contribution ratio of (R12) remains higher than 50 % throughout the entire range of initial temperatures. The contribution ratio of (R41) to C_2H_5 removal also increases with initial temperature, which does not interfere with OH formation because (R41) is followed by (R16). Therefore, the overall activation energy of OH formation is determined by (R12) over a wide range of initial temperatures.



For C_3H_8 , $i-C_4H_{10}$, and $n-C_4H_{10}$ (Figure 7, left, center, and right, respectively), the ignition delay time of $n-C_4H_{10}$ is clearly influenced by low-temperature OH chain branching, while those of C_3H_8 and $i-C_4H_{10}$ are not, as shown in Figure 2 (upper). However, the relationships between initial temperature and OH formation rate are similar. The relationships between initial temperature and contribution ratios to OH formation also are similar. The sum of the contribution ratios of (R5) and (R6) is quite high in the low-temperature range where H_2O_2 is generated and accumulated primarily by (R8), (R42), (R43), (R44), (R45), (R46), and (R15). The sum of the contribution ratios of (R9) and (R10) increase initially and then decrease as initial temperature increases. The contribution ratio of (R12) is high, but lower than 50 %, in the high-temperature range where H_2O_2 is generated primarily by (R47), (R48), (R49), (R29), (R41), (R16), (R8), and (R15). Because of (R5), (R6), (R9), and (R10), which do not appear for CH_4 and C_2H_6 , the overall activation energy of OH formation is low in the low-temperature range.



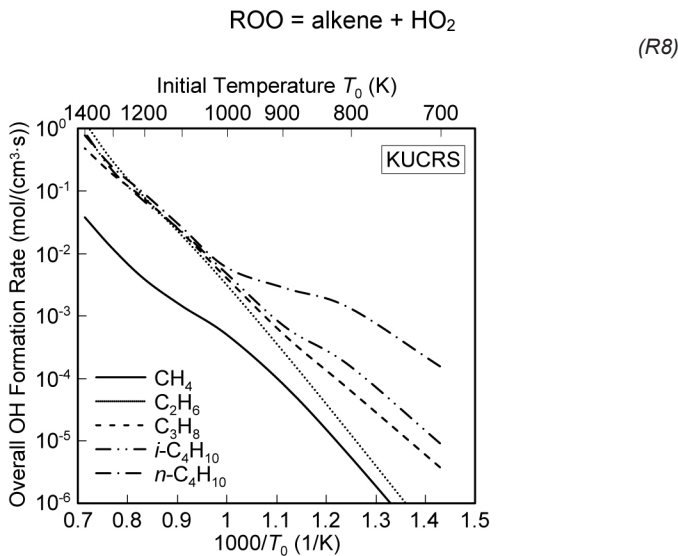


Figure 5. Relationships between Initial Temperature and Overall OH Formation Rate at 5 K Increase Point for Single-Component Fuels

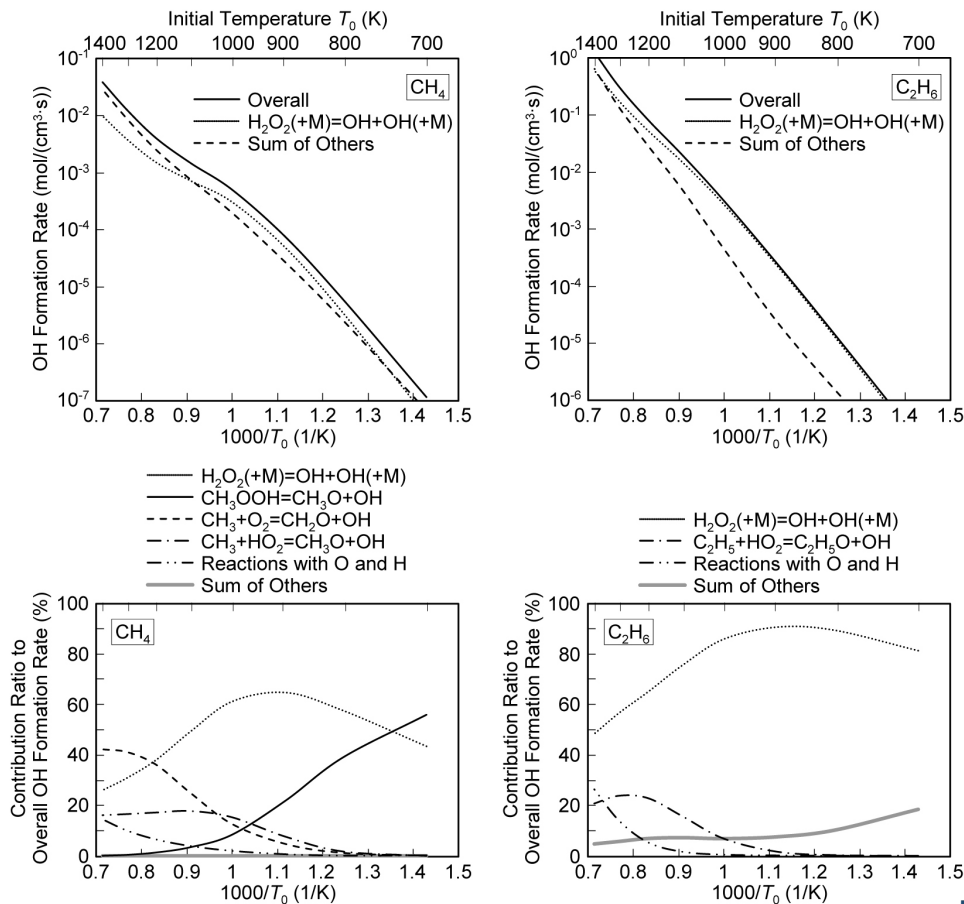
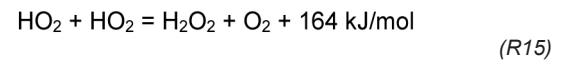
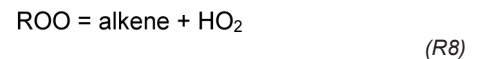
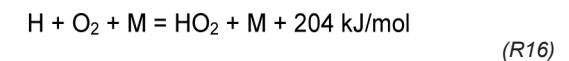
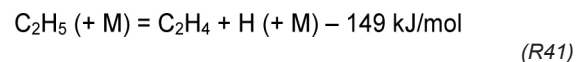
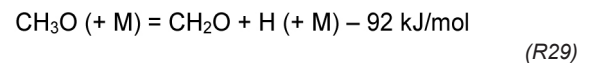
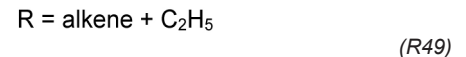
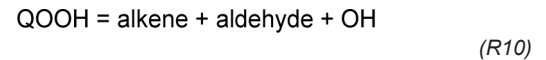
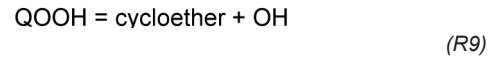
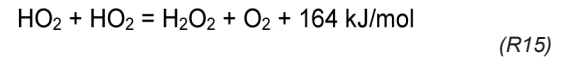
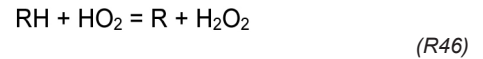
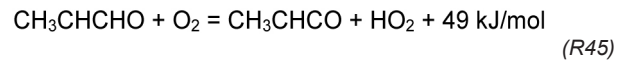
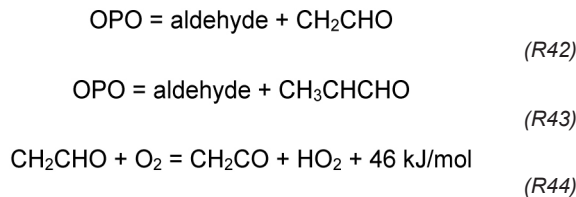


Figure 6. Relationships between Initial Temperature and OH Formation Rate of (R12) and Sum of Those of Other Reactions, and Relationships between Initial Temperature and Contribution Ratios of Significant Reactions to Overall OH Formation Rate at 5 K Increase Point for CH₄ and C₂H₆