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**Chemical Kinetics Study on Ignition Characteristics of Natural-Gas
Components: Fuel Design Concept for Robust Ignition in
Compression Ignition Engines**

Main author

Hiroki Tanaka
Osaka Gas Co., Ltd.
Japan

Co-author

Takahiro Sako
Osaka Gas Co., Ltd.
Japan

Hiromitsu Ando, Yasuyuki Sakai
University of Fukui
Japan

Kazunari Kuwanhara
Osaka Institute of Technology
Japan

1. Abstract

Ignition process chemistry of each single-component of natural gas, methane, ethane, propane, n-butane and isobutane, was analyzed using detailed chemical kinetic computations. Ethane exhibits low ignitability, close to that of methane, when the initial temperature is below 800 K, but higher ignitability, close to those of propane, n-butane and isobutane, when the initial temperature is above 1100 K. Furthermore, ethane shows a higher heat release rate during the late stage of the ignition process. This is because H_2O_2 is accumulated with a higher concentration within the lower temperature range and promotes the OH formation rate of $\text{H}_2\text{O}_2(+\text{M})=\text{OH}+\text{OH}(+\text{M})$ in the higher temperature range. These ignition characteristics are reflected in those of methane-based dual-component fuels with the sub component of ethane.

In a homogeneous charge compression ignition (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.

2. Introduction

The potential for HCCI engines using a variety of fuels has been examined with a view to achieving higher thermal efficiency and lower NO_x emissions. Sako et al., have considered the requirements for HCCI engines using natural gas, a fuel with extremely low ignitability, and established that the operating range under high-load conditions is limited by rapid combustion with heavy knocking and cycle-to-cycle variation [1]. This narrow operating range is the main obstacle for an HCCI engine. Many studies have examined ways to expand the operating range, such as supercharging, exhaust gas recirculation (EGR), and stratification [1, 2, 3].

Kuwahara et al., have analyzed the ignition process chemistry of n-heptane using a detailed chemical kinetic model and a contribution matrix method. They have also proposed an approach that divides the hydrocarbon ignition process into five phases and seven reaction groups listed below [4]. The thermal ignition preparation phase is the process in which the relatively slow heat release by the H_2O_2 loop reaction raise the temperature to the thermal ignition point at which the branching chain reactions of the hydrogen oxygen system become dominant.

- Phases: LTO preparation / LTO (low-temperature oxidation) / NTC (negative temperature coefficient) / Thermal ignition preparation / Thermal ignition
- Reaction groups: Fuel series chemistry / Fuel fragment chemistry / H_2O_2 loop chemistry / HO_2 chemistry / Hydrogen oxygen system chemistry / CO_2 chemistry / HACA (H abstraction C_2H_2 addition) chemistry

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

This paper presents an analysis based on chemical kinetics of the ignition process chemistry of each component of natural gas, methane (CH₄), ethane (C₂H₆), propane (C₃H₈), n-butane (n-C₄H₁₀) and isobutane (i-C₄H₁₀), and proposes a fuel design concept which optimizes the composition of methane-based blends with a view to reducing cycle-to-cycle variation and expanding operating range of HCCI engines. Ignition robustness against in-cylinder disturbances during the expansion stroke for a dual-component methane-based blend with a primary component of CH₄ and a secondary component of C₂H₆, C₃H₈, n-C₄H₁₀ or i-C₄H₁₀ was estimated using detailed chemical kinetic computations, and the validity of the concept was verified through engine tests.

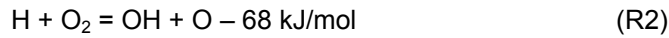
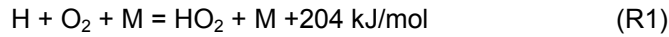
3. Ignition Characteristics of Each Component of Natural Gas

3.1 Computational Method and Conditions

A detailed chemical kinetic model for the oxidation of CH₄, C₂H₆, C₃H₈, n-C₄H₁₀, i-C₄H₁₀ and blends thereof was created using KUCRS. The model is composed of 145 chemical species and 658 elementary reactions. KUCRS (Knowledge-basing Utilities for Complex Reaction System) is the automatic detailed chemical kinetic model generation software, developed by Miyoshi [5, 6, 7, 8]. The model includes H₂/O₂ reactions in the Leeds CH₄ model [9], and C₁ and C₂ reactions in the LLNL isooctane model [10]. The unimolecular reactions of alkyl peroxy radicals (ROO), hydroperoxy alkyl radicals (QOOH), and hydroperoxy alkyl peroxy radicals (OOQOOH) were discussed [7], and the molecular-size dependent fall-off rate constants of O₂ addition to alkyl radicals and thermal decomposition of hydroperoxy carbonyl compounds (HOPO) were introduced [8]. Thermodynamic data were generated by THERM [6]. The computational ignition delay times of n-heptane and isooctane (2,2,4-trimethylpentane) in air using the model of primary reference fuels, the blends of n-heptane and isooctane, agree well with experimental data in a shock tube [4, 11].

Using the chemical kinetic computation software CHEMKIN-PRO, zero-dimensional calculations for the ignition of a mixture of a single-component fuel (CH₄, C₂H₆, C₃H₈, n-C₄H₁₀ or i-C₄H₁₀) and air (O₂: 21 vol. %, N₂: 79 vol. %) in an adiabatic closed constant-volume vessel were carried out. 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 O₂ molar concentration at 160.5 mol/m³, and the initial N₂ molar concentration at 603.7 mol/m³. These values correspond to the initial component molar concentrations in a CH₄/air mixture at an equivalence ratio of 0.5, initial temperature of 1000 K and initial pressure of 6.687 MPa. The calorific value of the fuel was defined as the heat of formation that assumes complete oxidation. For each mixture, initial temperature was varied, while the initial fuel, O₂, and N₂ concentrations were kept constant to determine the relationship between initial temperature and

ignition delay time. The point at which the rate of reaction (R2) exceeds that of reaction (R1) was defined as the thermal ignition point, and ignition delay time was determined [4].



3.2 Ignition Delay Time and Profile of Heat Release Rate

Figure 1 shows the relationship between initial temperature and ignition delay time for a single-component fuel/air mixture. The ignition delay time is the longest for CH₄, followed in order by C₂H₆, C₃H₈, i-C₄H₁₀ and n-C₄H₁₀, in line with the generally known trend. However, the ignition delay time of C₂H₆ is as long as that of CH₄ when the initial temperature is low, approximately 800 K, and approaches those of C₃H₈, n-C₄H₁₀ and i-C₄H₁₀ when the initial temperature is high, approximately 1200 K. The ignition delay time of C₂H₆ is the shortest with initial temperature above about 1250 K. The apparent activation energy of C₂H₆ is higher than those of the other single-component fuels over a wide range of initial temperatures, which has been reported from experimental studies using a flow reactor by Beerer et al. [12] and using a rapid compression machine by Furutani et al. [13].

Figure 2 shows ignition delay times and breakdowns for initial temperatures of 1000 K and 1200 K. Under these conditions, the ignition process for each fuel begins in the thermal ignition preparation phase, bypassing LTO. Ignition delay time is divided at the points where temperature increases by 1 K, 10 K and 100 K. When the initial temperature increases from 1000 K to 1200 K, the ignition delay time of C₂H₆ approaches those of C₃H₈, n-C₄H₁₀ and i-C₄H₁₀, in particular because the ratio of the time between the start of the reaction and the point at which temperature increases by 10 K is shortened (see the white and light gray areas). When the initial temperature is 1200 K, the time between the points where temperature increases by 100 K and the ignition point is shorter for C₂H₆ than for C₃H₈, n-C₄H₁₀ and i-C₄H₁₀ (see the black areas in the lower graph).

Figure 3 shows heat release rate plotted against increasing temperature during an ignition process. The heat release rate of C₂H₆ is lower than those of C₃H₈, n-C₄H₁₀ or i-C₄H₁₀ when the temperature increase is in the region of several tens of K for an initial temperature of 1000 K, and when the temperature increase is several K for an initial temperature of 1200 K (see the white arrows). However, it is higher in most of the temperature range thereafter (see the black arrows).

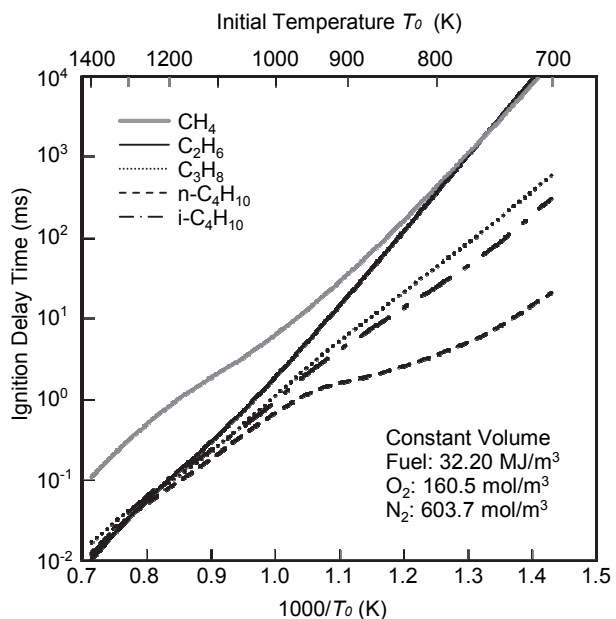


Figure 1. Relationship between initial temperature and ignition delay time for single-component fuels

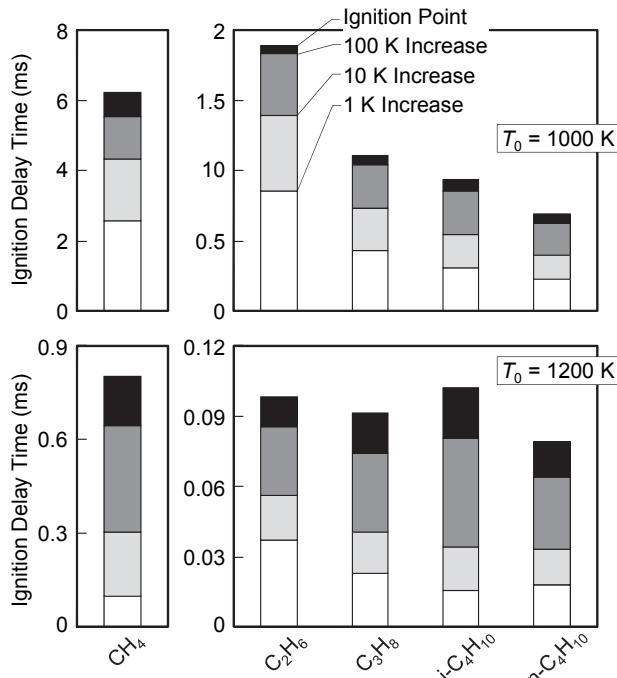


Figure 2. Ignition delay times and breakdowns of ignition delay time for single-component fuels

The above heat release profiles for C_2H_6 can be explained as follows. Figure 4 shows overall OH formation rate (sum of OH formation rates of all related forward reactions) and H_2O_2 concentration against increasing temperature during an ignition process, for an initial temperature of 1000 K. According to a reaction path analysis using the contribution matrix method proposed by Kuwahara et al. [4], the major reaction paths in the fuel series chemistry of C_2H_6 are reactions (R3)-(R7). In other words, the HO_2 formation path is dominant and the OH formation paths (R8) and (R9) are not significant. Furthermore, H_2O_2 accumulates from the HO_2 removal reaction, $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$. 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 [4] becomes active, heat release is accelerated by the high H_2O_2 concentration.

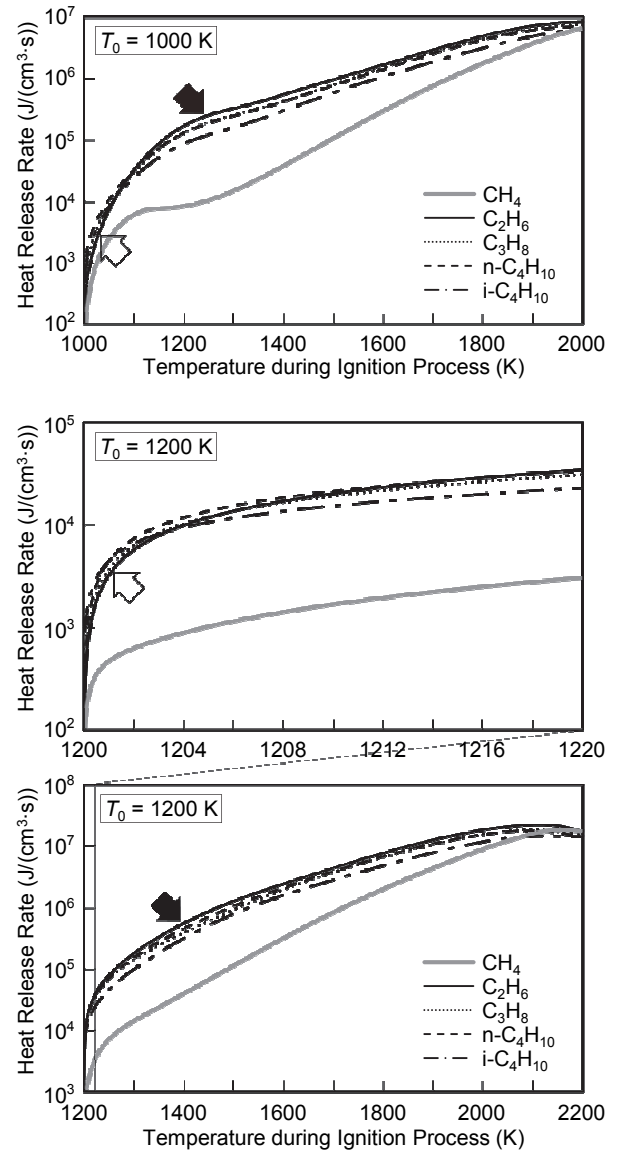
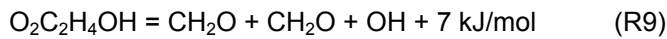
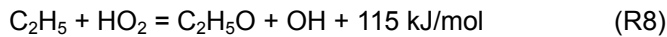
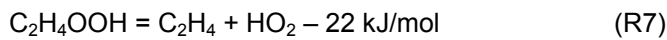
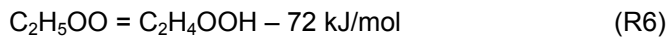
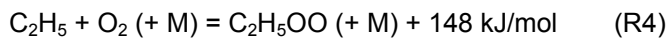
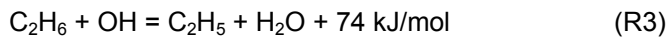


Figure 3. Profile of heat release rate for single-component fuels

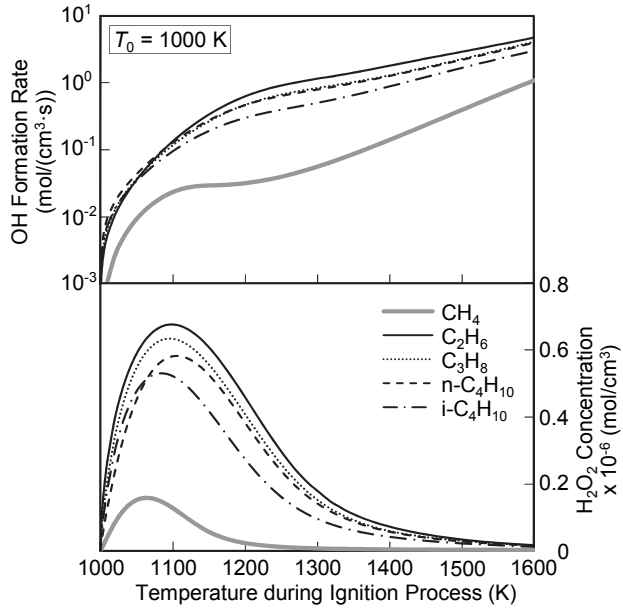


Figure 4. Profile of OH formation rate and H_2O_2 concentration for single-component fuels

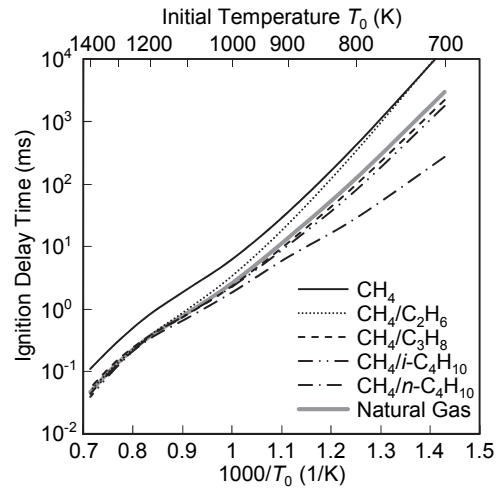


Figure 5. Relationship between initial temperature and ignition delay times of dual-component CH_4 -based blends

4. Ignition Characteristics of Dual-Component Methane-Based Blends

4.1 Computational Conditions

Zero-dimensional computations were conducted for the ignition delay times of dual-component fuels of CH_4 as the primary fuel and C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ as secondary fuels with air in an adiabatic closed constant-volume vessel. Computations also were conducted for the model natural gas with CH_4 , C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ molar fractions of 88 %, 6 %, 4 %, 1 %, and 1 %, respectively. Initial O_2 and N_2 concentrations were set at 160.5 mol/m^3 and 603.7 mol/m^3 . The overall quantity of heat was set at 32.20 MJ/m^3 . Initial CH_4 concentration was chosen to release 24.54 MJ/m^3 , which is the quantity of heat of CH_4 in 32.20 MJ/m^3 of the model natural gas. Initial C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, and $n\text{-C}_4\text{H}_{10}$ concentrations were chosen to release the remaining 7.66 MJ/m^3 . Initial temperature was varied from 700 K to 1400 K, while initial fuel, O_2 and N_2 concentrations were kept constant.

4.2 Ignition Delay Time and Profile of Heat Release Rate

Figure 5 shows the relationship between initial temperature and ignition delay times of dual-component fuels. This relationship is affected by the relationship between initial temperature and ignition delay times of single-component fuels shown in Figure 1. For example, ignition delay time is longer in the order of pure $\text{CH}_4 > \text{CH}_4/\text{C}_2\text{H}_6 > \text{natural gas} > \text{CH}_4/\text{C}_3\text{H}_8 > \text{CH}_4/i\text{-C}_4\text{H}_{10} > \text{CH}_4/n\text{-C}_4\text{H}_{10}$ over a wide range of initial temperatures. The ignition delay time of $\text{CH}_4/\text{C}_2\text{H}_6$ is as long as that of pure CH_4 in the low-temperature range. However, it becomes closer to those of the other dual-component fuels as initial temperature increases. The apparent activation energy of $\text{CH}_4/\text{C}_2\text{H}_6$ is higher than those of the other dual-component fuels over a wide range of initial temperatures. Although the C_2H_6 molar fraction is higher than that of C_3H_8 in natural gas, the ignition delay time of natural gas is close to that of $\text{CH}_4/\text{C}_3\text{H}_8$, not to that of $\text{CH}_4/\text{C}_2\text{H}_6$.

Figure 6 shows the breakdowns of ignition delay times with initial temperatures of 1000 K, 1200 K, and 1400 K. The ignition delay time of $\text{CH}_4/\text{C}_2\text{H}_6$ becomes similar to those of the other dual-component fuels 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 (see the gray areas), is relatively shortened. Figure 7 shows the breakdowns of the same ignition delay time with initial temperatures of 1118 K, 1100 K, 1103 K, 1084 K, and 1105 K for $\text{CH}_4/\text{C}_2\text{H}_6$, $\text{CH}_4/\text{C}_3\text{H}_8$, $\text{CH}_4/i\text{-C}_4\text{H}_{10}$, $\text{CH}_4/n\text{-C}_4\text{H}_{10}$, and natural gas, respectively. The period of time from the 10 K increase point to the ignition point (see the dark gray and

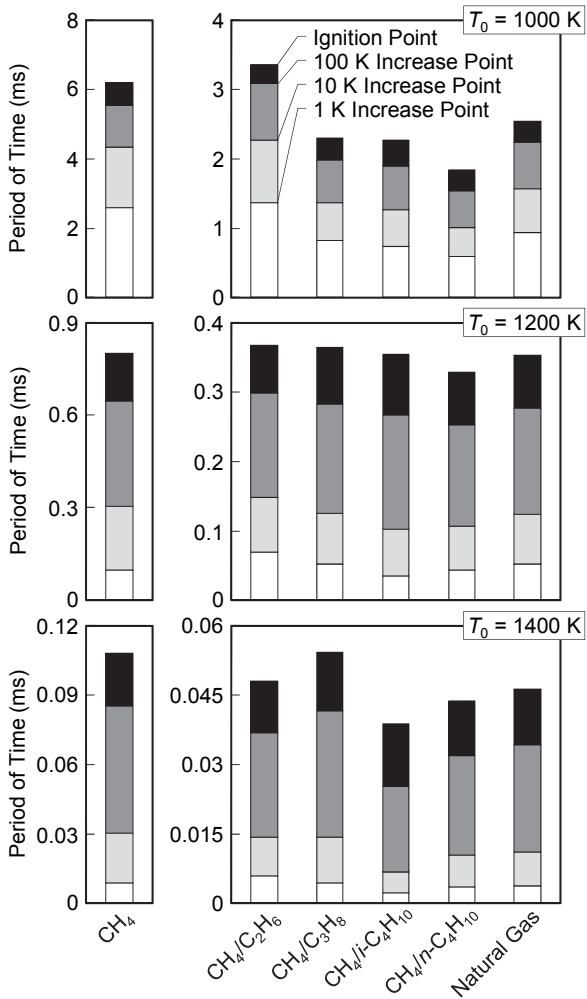


Figure 6. Breakdowns of ignition delay times of dual-component CH_4 -based blends

black areas) of $\text{CH}_4/\text{C}_2\text{H}_6$ is shorter than those of the other fuels.

Figure 8 shows the profiles of heat release rate during the ignition delay times shown in Figure 6. The overall heat release rate of $\text{CH}_4/\text{C}_2\text{H}_6$ becomes higher than those of the other dual-component fuels after a certain increase in temperature (see the black arrows), which is similar to the profiles of heat release rate of C_2H_6 and the other

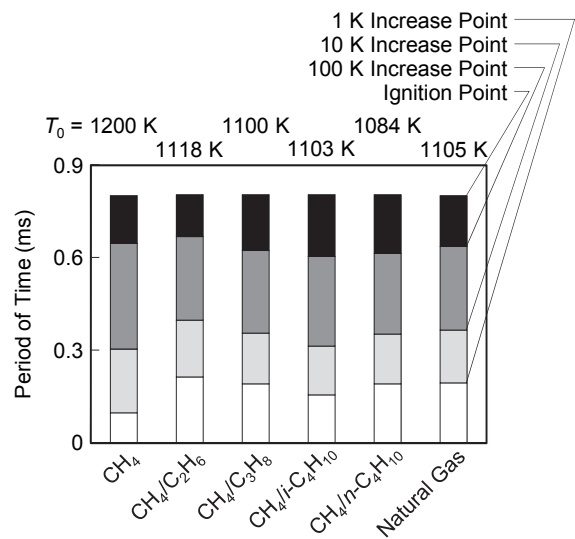


Figure 7. Breakdowns of same ignition delay time of dual-component CH_4 -based blends

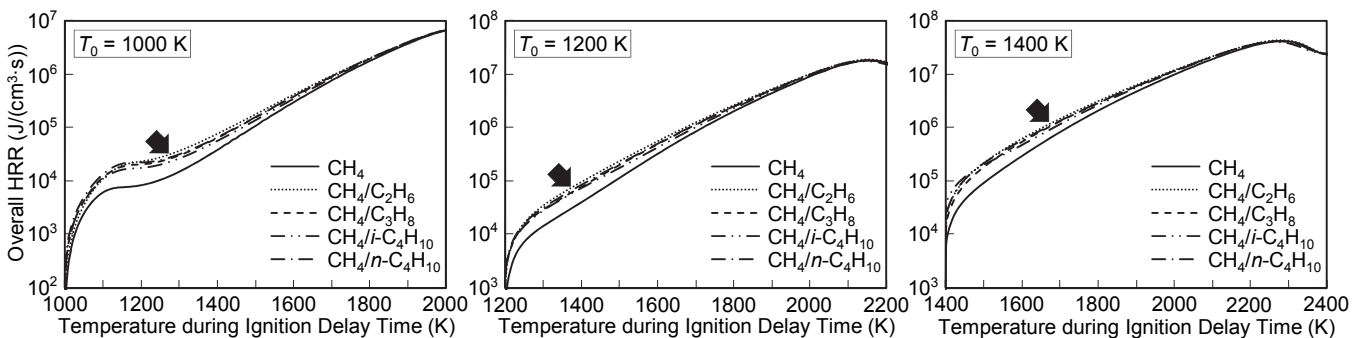


Figure 8. Profile of overall heat release rate during ignition delay times of dual-component CH_4 -based blends

single-component fuels shown in Figure 3. The profiles of heat release rate provide the breakdowns of ignition delay times shown in Figure 6.

5. Fuel Design Concept Based on Heat Release Profile

Calculation results revealed that the difference in fuel characteristics causes the difference not only in ignition delay times, but also heat release profiles. Even when the fuel ignitability index such as octane number is equivalent, heat release profiles may be different. If optimizing compression ratio and controlling intake temperature and cam phases can make an HCCI engine viable even when using a fuel with low ignitability [1, 2], then for robust ignition, it may be possible to design an optimum fuel on the basis of heat release profile rather than ignitability.

C_2H_6 shows a relatively short ignition delay time when initial temperature is high, and the heat release profile is gentle 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 robustness against in-cylinder disturbances during the expansion stroke is likely to be greater for CH_4/C_2H_6 than for the other dual-component fuels.

The concept was validated using an HCCI engine fueled with CH_4/C_2H_6 , CH_4/C_3H_8 , $CH_4/i-C_4H_{10}$, and $CH_4/n-C_4H_{10}$. An engine with a displacement of 547.4 cm^3 and a compression ratio of 28:1 was operated at a rotating speed of 900 min^{-1} . Intake air flow was controlled for $244\text{ cm}^3/\text{cycle}$ at 273.15 K and 0.1 MPa . The equivalence ratio of CH_4 in air was set at 0.404. Overall equivalence ratio was set at 0.5, 0.499, 0.497, and 0.497 for CH_4/C_2H_6 , CH_4/C_3H_8 , $CH_4/i-C_4H_{10}$, and $CH_4/n-C_4H_{10}$, respectively, to

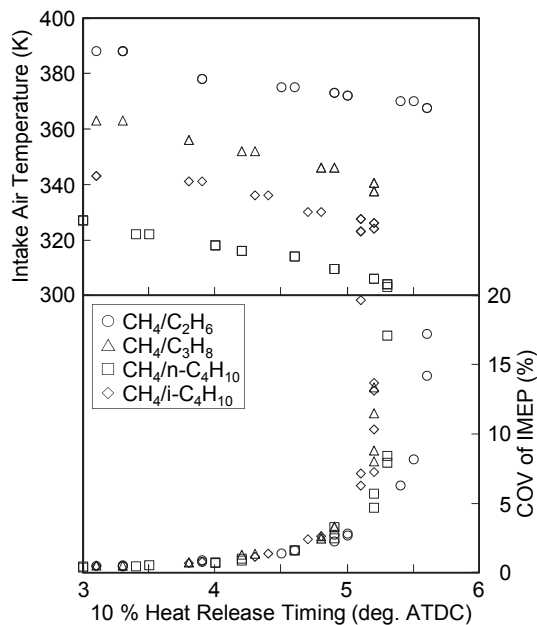


Figure 9. Relationship between intake air temperature and 10 % heat release timing, and between 10 % heat release timing and COV of IMEP

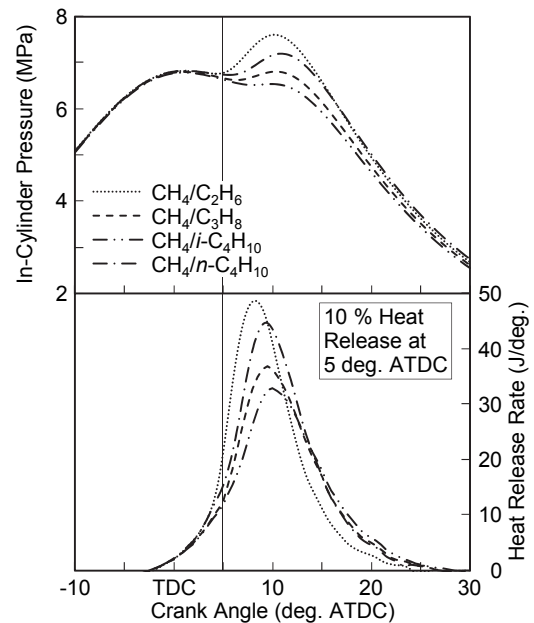


Figure 10. Cycle-averaged in-cylinder pressure and heat release rate with 10 % heat release timing of 5 deg. ATDC

release 464 J/cycle with complete oxidation of fuels into CO₂ and H₂O. Figure 9 shows the relationship between intake air temperature and 10 % heat release timing, and between 10 % heat release timing and coefficient of variance (COV) of indicated mean effective pressure (IMEP). 10 % heat release timing is retarded with a decrease in intake air temperature. Intake air temperature is higher in the order of CH₄/C₂H₆ > CH₄/C₃H₈ > CH₄/i-C₄H₁₀ > CH₄/n-C₄H₁₀ for the same 10 % heat release timing. When 10 % heat release timing is retarded after 5 degrees ATDC, COV of IMEP increases rapidly, and is higher in the order of CH₄/i-C₄H₁₀ > CH₄/C₃H₈ > CH₄/n-C₄H₁₀ > CH₄/C₂H₆ with the same 10 % heat release timing. Figure 10 shows the cycle-averaged in-cylinder pressure and heat release rate with a 10 % heat release timing of 5 degrees ATDC. Heat release rate at 5 degrees ATDC and thereafter is higher in the order of CH₄/C₂H₆ > CH₄/n-C₄H₁₀ > CH₄/C₃H₈ > CH₄/i-C₄H₁₀. This order provides the order of COV's of IMEP.

6. Summary/Conclusions

The ignition delay times and profiles of heat release rate of CH₄, C₂H₆, C₃H₈, i-C₄H₁₀, and n-C₄H₁₀ with air in an adiabatic closed constant-volume vessel were determined using the detailed chemical kinetic model generated by KUCRS. The apparent activation energy of C₂H₆ in the relationship between initial temperature and ignition delay time is higher than those of the other single-component-fuels. The heat release rate of C₂H₆ is higher than those of the other single-component-fuels in the late stage of ignition delay time because HO₂ is generated effectively by several reaction paths, and H₂O₂ is generated from HO₂ and accumulated with a higher concentration, which promotes the OH formation rate of H₂O₂(+M)=OH+OH(+M).

The ignition delay times and profiles of heat release rate of dual-component fuels of CH₄ as the primary fuel and C₂H₆, C₃H₈, i-C₄H₁₀, and n-C₄H₁₀ as secondary fuels in air also were determined. The ignition characteristics of C₂H₆ are reflected in those of CH₄/C₂H₆. For example, the apparent activation energy of CH₄/C₂H₆ in the relationship between initial temperature and ignition delay time is higher than those of the other dual-component fuels, and the heat release rate of CH₄/C₂H₆ is higher than those of the other dual-component fuels in the late stage of ignition delay time. 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 to reduce cycle-to-cycle variation during the expansion stroke. In this respect, ignition robustness against in-cylinder disturbances during the expansion stroke is likely to be greater for CH₄/C₂H₆ than for the other dual-component fuels.

The validity of the proposed concept was verified through engine tests. When the timing of 10 % heat release is set at the same crank angle in the expansion stroke, the maximum heat release rate is the highest for CH₄/C₂H₆, and, for this reason, a COV of IMEP is the smallest for CH₄/C₂H₆. These results suggest that CH₄/C₂H₆, with its superior ignition robustness in the expansion stroke, may be the optimal methane-based dual-component fuel for an HCCI engine.

7. References

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