

Article

Effects of n-Heptane/Methane Blended Fuel on Ignition Delay Time in Pre-Mixed Compressed Combustion

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Abstract: This study analyzed factors that influence the ignition delay characteristics of n-heptane/methane-blended fuel. The effects of chemical species, exhaust gas recirculation rate, compression ratio, cool/hot flames, and combustion chamber conditions (temperature, pressure, and O₂ concentration) were determined and analyzed using CHEMKIN Pro. The experiment conditions for verification were 550–1000 K at 15 bar with 50% H₂/50% CH₄ fuel. The main combustion reactions were confirmed through reactivity analysis and sensitivity analysis on the ignition delay time. The ignition delay time at 14.7% O₂ concentration was significantly higher than that at 21% O₂ concentration by more than 30%. In addition, a higher ratio of methane in the blended fuel increased the ignition delay time as a result of methane dehydrogenation, delaying the ignition of heptane.

Keywords: ignition delay time; n-heptane; methane; compression ratio; exhaust gas recirculation



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1. Introduction

Due to the depletion of fossil fuels and the environmental impacts, strong emission regulations such as EURO-6 and Tier-5 are implemented around the world. As a result, there is a growing interest in improving the efficiency of internal combustion engines and reducing their pollutant emissions [1]. An ongoing active area of study is homogeneous charge compression ignition (HCCI) engines, which combine the advantages of conventional gasoline engines (SI), diesel engines (CI), reactivity-controlled compression ignition (RCCI) engines, and partially pre-mixed combustion ignition (PPCI) engines [2,3]. In the HCCI system, a pre-mixture of air and fuel is formed in the combustion chamber during intake just like in the SI, while the piston compression and ignition combustion are performed similar to the CI. The combination of these technologies allows for engine operation in sparse conditions, achieving a high compression ratio (CR) by applying exhaust gas recirculation (EGR) to maintain low-temperature combustion (LTC), reducing carbon dioxide (CO₂) emission by improving the thermal efficiency, and simultaneously decreasing the emission of NO_x and particulate matters (PM) by forming a consistent mixture in the combustion chamber while preventing local hot spots during combustion [1,4]. However, the operation range is still limited at low loads and high loads. At low loads, a low temperature leads to incomplete combustion, causing an excessive discharge of carbon monoxide (CO) and hydrocarbons (HCs). At high loads, rapid ignition combustion increases the combustion pressure drastically, which results in engine knocking, damage, and noise.

Conventional diesel fuel is a mixture of various HCs with a high cetane number. Among the components, n-heptane with a high carbon number has a cetane number

comparable to that of diesel. Hence, n-heptane is widely used as an alternative to diesel in experimental settings to effectively simulate two-stage ignition, cool flames, hot flames, and ignition delays. Also, many studies have been conducted on precise combustion control techniques to control the ignition delay by adjusting the fuel mixing ratio, pressure, and equivalence ratio [5,6]. ExxonMobil, a U.S. petrochemical company, recently predicted in its long-term energy outlook that oil and natural gas would remain the main sources of energy, accounting for 60% of the world's energy supply by 2040. Particularly, the consumption of natural gas was expected to grow the fastest to meet 40% of the global energy demand. Mainly composed of methane, natural gas allows for an effective response to CO₂ regulations, such as the Kyoto Protocol, with its lower emissions of PM and CO₂ when compared to diesel fuel. Therefore, many researchers have been studying combustion characteristics such as ignition delay time, ignition temperature for operating pressure, burning velocity, etc., for alternative fuels [7–18].

Li et al. [7] studied the autoignition characteristics of gasoline/diesel/ethanol/PODE fuels. The effect of ethanol on chemical ignition delay is higher than that of physical ignition delay, and a higher EGR ratio also leads to a longer ignition delay time.

Kuszewski [8] conducted an experimental study of n-butanol-diesel blends to achieve low nitrogen oxides and smoke emissions from the diesel engines. The autoignition properties were tested by standard diesel fuel with oxygen compounds such as alcohols.

In the study of Wang et al. [9], ignition delay time gradually decreases with a high pressure and equivalence ratio which conditions show lower reactivity. The simulation results are in good agreement with experiment results. The gas-phase autoignition of methanol/diesel mixture was studied by Zhu et al. [10]. They observed the typical two-stage ignition of a mixture with an NTC response over the whole temperature regime. In terms of various fuels that have been studied, n-heptane/methane blends have also attracted focus. N-heptane has been used as a standard fuel in fundamental studies on fuel control methods, and methane recently gained attention as an alternative fuel. The high octane number of methane increases the ignition delay, providing sufficient time for the pre-mixing of fuel and air during engine operation and allowing for consistent pre-mixing [11]. However, the low cetane number of methane results in poor auto-ignition properties [12]. A reasonable way to meet the requirements of both SI and CI is mixing methane with hydrocarbon fuel having a high cetane number. There is an urgent need to verify the dual fuel system and analyze its combustion properties.

Yao et al. [5] simulated the ignition delay for n-heptane/methane blended fuel at different mixing ratios. They investigated the effects of three factors (oxygen partial pressure, specific heat, and chemical reaction) on ignition delay at 40 and 80% methane. They also carried out a comparative study through chemical reaction sensitivity analysis on the ignition delay, by designing reduced chemical mechanisms for methane (Hung mechanism) and for n-heptane (Curran mechanism). Aggarwal et al. [6] simulated the ignition delay time in n-heptane/methane-blended fuel under high-pressure conditions (30 and 55 atm) and equivalence ratios ($\Phi = 1$ and 2). The methane ratios were 0, 20, 80, 95, and 100%. Their sensitivity analysis revealed that the heptyl (C₇H₁₅) and hydroxyl (OH) radicals played a significant role in ignition.

Our research team has been studying autoignition characteristics for n-heptane-based fuels such as n-heptane/hydrogen and n-heptane/ethanol with various operating conditions [13,14]. The EGR ratio, operating temperature, diluting ratio etc., have been studied with various fuels, and this study analyzed various factors affecting the chemical ignition of n-heptane/methane-blended fuel, including the combustion chamber environment (temperature, pressure, and O₂ concentration), changes in OH radicals, and intermediate chemical species promoting oxidation reactions, cool/hot flames, and CR. No relevant information has been reported before. The goal here was to understand how the combustion reaction and ignition delay time of n-heptane/methane-blended fuel under low-temperature conditions are affected by the mixing ratio, heat production, concentration of intermediate

chemical species, CR (2.5, 3.0, 3.5, 4.0, and 4.5), ignition delays by a cool/hot flame, and O₂ concentration through EGR simulations.

2. Experimental Device and Method

2.1. Experimental Device

The rapid compression machine (RCM) is an ideal device for simulating pre-mixed gas (fuel, oxygen, and dilution gas) at a set temperature and pressure in a combustion chamber similar to the actual engine. The composition, CR, equivalence ratio, and compression temperature of the pre-mixed fuel can be adjusted. The combustion phenomenon at constant pressure may be measured and analyzed by varying the temperature [19,20]. Figure 1 illustrates in detail the RCM system consisting of two parts: a combustion chamber where the piston quickly compresses fuel for auto-ignition combustion, and an impact pneumatic cylinder (IPC) that operates the piston pneumatically. There is a pre-mixing chamber, a vacuum pump, and sensors and measurement equipment for acquiring experimental data. A piston compressed by air is installed inside a pneumatic cylinder where compression pressure is generated. The piston speed can be adjusted by the pressure inside a high-pressure air tank fed by an air compressor. The CR is adjusted using a pneumatic device that moves a rod connecting the combustion chamber and the pneumatic cylinder. The RCM used here is capable of very short compression times of less than 30 ms. To address the piston-slip phenomenon caused by the explosion, which may significantly affect the experimental results, a brake arm is used to fix the piston once it reaches the top dead center to prevent damage by the explosion. Table 1 provides detailed information on the RCM system.

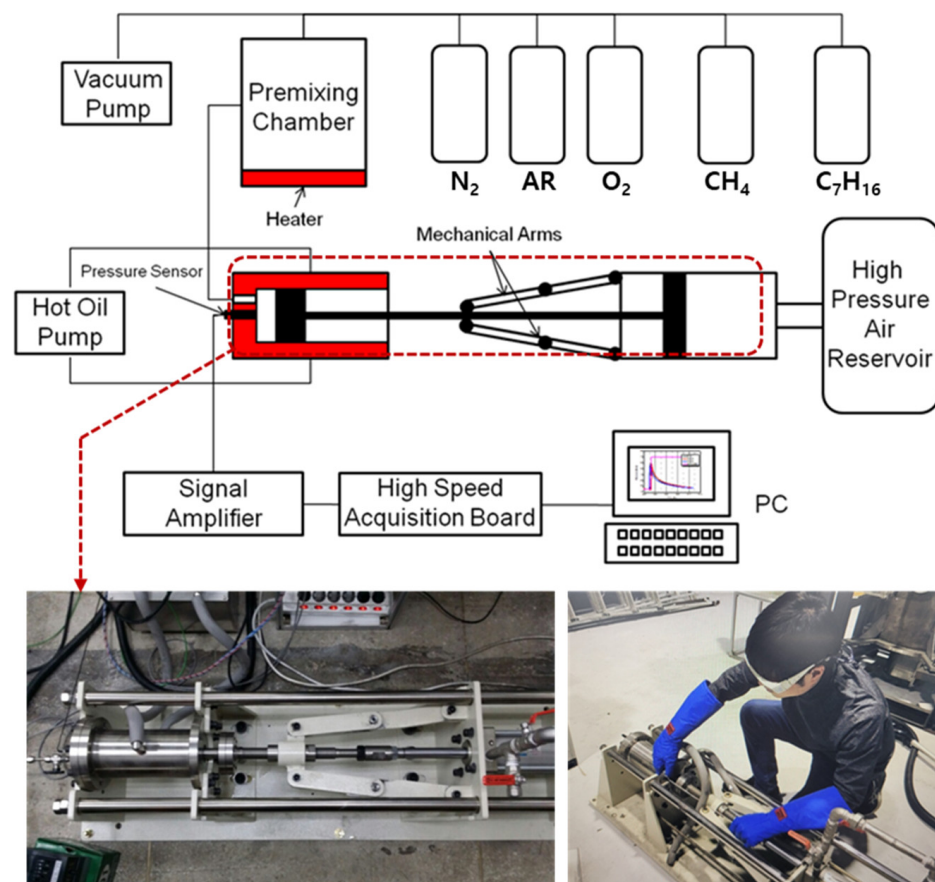


Figure 1. Schematic of the rapid compression machine (RCM) system.

Table 1. Specification of the RCM system.

Description	Specification
Cylinder bore	40 mm
Cylinder thickness	13 mm
Piston type	Crevice piston
Piston stroke	100–200 mm
Compression ratio (CR)	2.5–4.5
Compression time	20–30 ms
Initial temperature	293 K
Initial pressure	1 atm

2.2. Experimental Method and Conditions

This study used a blended fuel of n-heptane and methane with the mixing ratio of methane set at 100, 75, 50, and 25 mol.%. A uniform mixture was produced by vaporizing the blended fuel in the mixing chamber with magnetic stirrer, and the amount of injected gas and fuel was determined by calculating the absolute pressure and adjusted by measuring the partial pressure. A vacuum was created in the combustion chamber with a vacuum pump, and the fuel was injected into the pre-mixing chamber with a syringe. The experiment was conducted once the fuel tank, gas supply line, and combustion chamber reached a constant temperature of 293 ± 0.5 K. After a compression and explosion stroke were completed in the combustion chamber, the emissions were removed using the vacuum pump, and the experiment was repeated 6 to 10 times under the same conditions and an operating pressure of 8 bars to confirm reproducibility. The pressure changes inside the combustion chamber were measured by opening the solenoid valve, for the period from when the piston in IPC started operating to when the pressure value of the rear cylinder in IPC was opened following the explosion. The output signals of the pressure sensor (Kistler 6125b) and pressure transducer (Kistler 6041A) were amplified by the signal amplifier (Kistler 5018). The amplified analog output was acquired through a high-speed A/D board (Kistler 5018) at a sampling speed of 10,000 Hz and transformed with commercial software (LabVIEW 8.2). A K-type thermocouple was used to measure the temperature of the mixture supplied to the combustion chamber. The compression temperature (T_c) was calculated using Equation (1), assuming that compression inside the RCM was the adiabatic process of an ideal gas [21,22]:

$$\int_{T_0}^{T_c} \frac{\gamma(T)}{\gamma(T) - 1} \frac{dT}{T} = \ln\left(\frac{P_c}{P_0}\right) \quad (1)$$

where T_0 and P_0 are the initial temperature and pressure, T_c and P_c are the temperature and pressure of the mixture compressed at the top dead center, and $\gamma(T)$ is function of temperature corresponding to the ratio of specific heat of the mixture.

The ignition timing was analyzed by varying the ratio of methane from 100 to 25 mol.% in the blended fuel at low temperatures, as well as the O_2 concentration (14.7–21%) and $CR = 2.5$ –4.5 for EGR simulations. Table 2 provides the properties of the blended fuel used in the experiment.

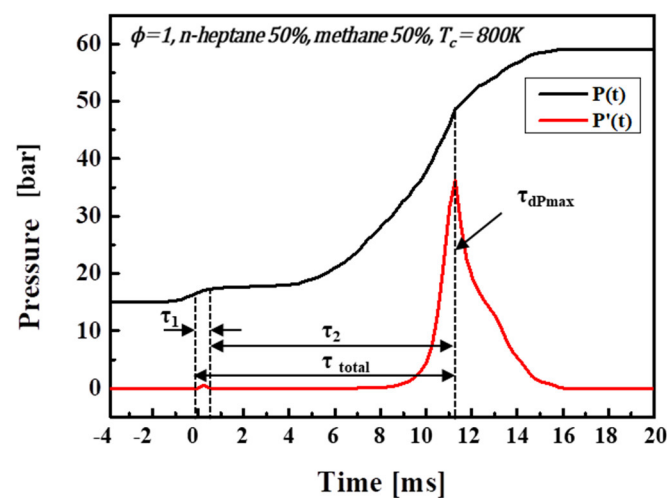
Table 2. Fuel properties.

Name		n-Heptane	Methane
Molecular formula		C ₇ H ₁₆	CH ₄
Molecular weight		100.21	16.042
Density	g/m ³	0.688	0.664
Boiling point	K	372	111.55
Auto-ignition temperature	K	558	810
Low calorific value	MJ/kg	44.24	49.94
RON		0	130
CN		56	0

3. Numerical Analysis

To verify the results of the ignition delay experiments conducted with the RCM, theoretical calculation was performed using the commercial analysis program CHEMKIN-PRO [23]. A closed homogeneous constant-volume combustion module was adopted to simulate the initial state at the temperature and pressure when the piston reached the TDC. A reaction model developed by Dooley et al. consisting of 1599 chemical species and 6633 chemical reactions was used for the n-heptane/methane-blended fuel [4]. The model was interpreted using a jet-stirred reactor, and it can be applied to a wide temperature range for low- and high-temperature reactions. In addition, the model is capable of calculating complex chemical reactions with a high carbon number. The detailed n-heptane reaction model proposed by Mehl et al. [24] was adopted for the calculations of n-heptane. The calculation was conducted at $\Phi = 1$, $P_c = 15$ bar, $T_c = 600$ – 1000 K. The auto ignition characteristics for 0, 25, 50, 75, 100% of methane ratios in fuel mixture, 2.5, 3, 3.5, 4, and 4.5 of CR, and 0, 10, 20, and 30% of N₂ dilution were considered.

The ignition delay time, an important factor in this study, is defined according to Figure 2. The Figure illustrates the time-dependent pressure and its change rate (dP/dt). The ignition delay (τ_1) was measured from the end of the compression to the occurrence of a cool flame, and τ_2 is the duration from the occurrence of the cool flame to the beginning of ignition. The total ignition delay time (τ_{tot}) is defined as $\tau_1 + \tau_2$, or the time interval from completing the compression stroke to the maximum value of dP/dt .

**Figure 2.** Schematic of ignition delay time.

4. Results and Discussion

4.1. Reaction Pathways of Blended Fuel

Figure 3 shows the reaction pathways of pure n-heptane (left) and n-heptane/methane-blended fuel (right) [25–28]. The difference between the two systems is indicated by the red dotted box. Methane reacts with O_2 to promote an oxidation reaction and produces formaldehyde (CH_2O), using OH radicals formed from methane in the first oxidation reaction in the low-temperature range. Since formaldehyde is widely known as a stable molecule, the ignition delay time increases as the methane ratio in the blended fuel increases [29,30]. Also, in the n-heptane/methane mixture, methane reduces the production of H_2O_2 radicals at low temperatures and inhibits the production of active OH radicals that induce oxidation, thereby suppressing the low-temperature oxidation reactions. As n-heptane is highly reactive at low temperatures, the oxidation of mixed fuels can be promoted by a number of radicals produced by the reaction of n-heptane.

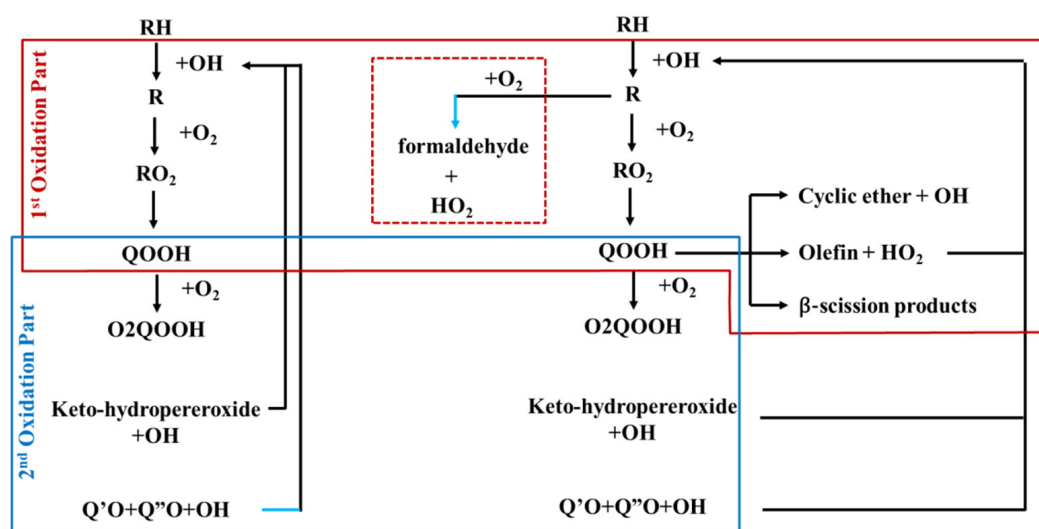
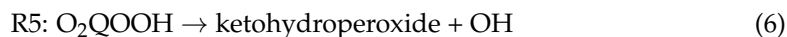


Figure 3. Reaction pathways of pure n-heptane (left) and n-heptane/methane-blended fuels (right).

4.2. Chain Reactions

The following chain reactions R1–R5 are the main oxidation reactions [31]:



Alkyl groups are formed from n-heptane after H atoms are separated in the early stage of low-temperature combustion, and they react with oxygen to form RO_2 radicals. These radicals are converted to QOOH radicals through isomerization, which is the key reaction mechanism in low-temperature combustion. As the temperature increases, the strongly exothermic reaction $R + O_2 \rightarrow RO_2$ is reversed to $RO_2 \rightarrow R + O_2$. RO_2 decomposes into cyclic ether + OH, conjugate olefin + HO_2 , in addition to the QOOH radicals. These chain reactions reduce the reactivity of the overall system, resulting in the development of a region with negative temperature coefficient (NTC) [32]. The NTC refers to the phenomenon that the ignition delay time of a fuel mixture increases with an increasing initial temperature within a certain temperature range [33–37]. The high-temperature combustion proceeds quite differently from the low-temperature one. In the high temperature range above 1000 K, the main chain reaction is $H + O_2 = O + OH$, and the overall chemical decomposition reaction

takes place in rapid combustion through β -scission of alkyl radicals [38]. As a result, OH radicals play an important role in the oxidation reaction and promote the reaction of n-heptane/methane-blended fuel.

4.3. Production of OH and H_2O_2 Radicals

For simplicity, in the following discussion we denote different blended fuels as $xH(100-x)M$, where x is the mol.% of n-heptane and $(100-x)$ that of methane. For example, an equimolar mixture of n-heptane/methane is referred to as H50M50.

Figure 4 shows the timing for the formation of OH and H_2O_2 radicals. Due to their unpaired electron, OH radicals are high in energy and very reactive. The first step of n-heptane oxidation is dehydrogenation to form C_7H_{15-1} to C_7H_{15-4} . The reaction of oxidized HO_2 ($HO_2 + HO_2 = H_2O_2 + O_2$) produces H_2O_2 radicals, which significantly affect the formation of OH radicals in the second oxidation reaction. In panel (a) for H75M25 and panel (b) for H25M75, OH and H_2O_2 radicals are formed in proportion to each other during the low-temperature oxidation process. As the methane ratio increases, the amount of H_2O_2 produced by the oxidation of n-heptane decreases, and the delay time increases. This is the main difference between the first oxidation time and the second oxidation time. The amounts of the formed products also vary significantly, which affects the temperature rise at the time of the first oxidation. The formation of H_2O_2 increases after the first ignition, but the extinction point depends on the methane ratio. When these radicals reach a certain level, the main ignition occurs [39,40].

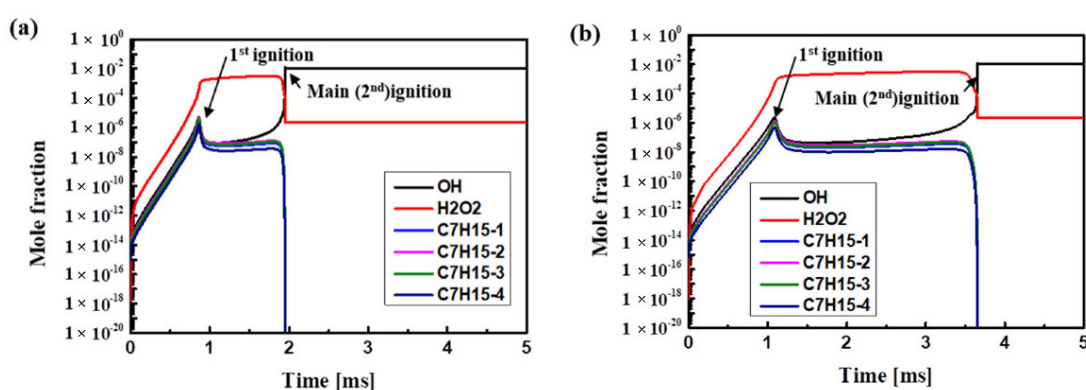


Figure 4. Computed concentrations of various radical species (OH, H_2O_2 , and C_7H_{15}) at the conditions of $\Phi = 1.0$, $P_c = 15$ bar, $CR = 3.5$, $O_2 = 21\%$ for (a) H75M25 and (b) H25M75.

Figure 5 shows the amount of H_2O_2 produced at various methane concentrations. The amount of H_2O_2 was similar when the methane concentration remained at 50% or less. As mentioned above, H_2O_2 production at low temperatures depends on the compression temperature T_c . As the methane ratio increases, the production time of H_2O_2 is delayed, which reduces the amount of generated H_2O_2 . The main ignition is also delayed when the rate of H_2O_2 accumulation is slower, and the ignition temperature is reduced by 40–100 K, which delays the first ignition. It was confirmed that the total ignition delay time in the low-temperature region increased when the methane ratio in the blended fuel increased. This is consistent with previous studies [5,6,39], which showed that OH radicals produced at a higher methane ratio delay the ignition time. This is attributed to the H-abstraction reaction of methane, which consumes large amounts of OH radicals and oxygen, and the consequent lack of OH radicals and oxygen required for the oxidation of n-heptane is the major cause of the ignition delay. However, at high temperatures, OH radicals are rapidly promoted and decomposed by the production of H_2O_2 . That is, ignition timing can be controlled with the mixing ratio of the blended fuel [5,6,39,40].

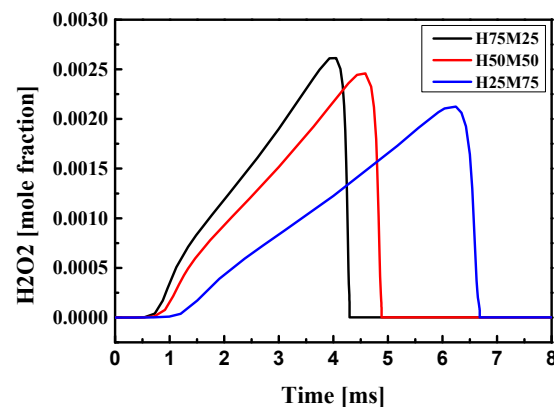


Figure 5. Mole fraction of H_2O_2 for blended fuels at $T_c = 900$ K, $\Phi = 1.0$, $P_c = 15$ bar, $\text{CR} = 3.5$, and $\text{O}_2 = 21\%$.

4.4. Analysis of Blended Fuel Reaction

4.4.1. Effect of Fuel Composition

Figure 6 shows the ignition delay time for n-heptane/methane-blended fuels at different compositions. Since the horizontal axis is the reciprocal temperature, the right-hand side represents the low-temperature region and vice versa. The methane ratio in the fuel was 0, 25, 50, 75%, and 100% while fixing the equivalence ratio at one, the compression pressure at 15 bar, and the O_2 concentration at 21%. The ignition delay time was calculated while varying T_c from 600 to 1000 K in steps of 50 K. As T_c increased, the ignition delay time decreased. Even at a high methane ratio of 75%, an NTC region and the second ignition were observed, although this did not occur for 100% methane. Regardless of the mixing ratio, the ignition delay time decreased as T_c increased, which is the typical combustion characteristic of n-heptane. However, the ignition delay time started to increase or remained constant as the temperature increased near to the specific temperature of 800 K in the NTC region [39,40].

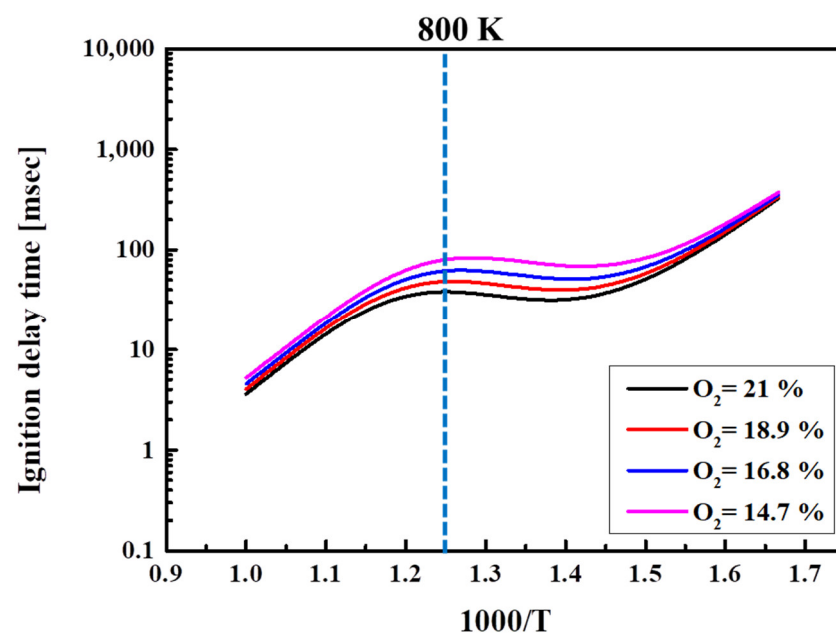


Figure 6. Ignition delay times of blended fuels at $\Phi = 1.0$, $P_c = 15$ bar, $\text{CR} = 3.5$, and $\text{O}_2 = 21\%$.

4.4.2. Temperature and Pressure Changes in the Combustion Chamber

Figure 7 shows the temperature distribution in the combustion chamber and the ignition delay time, as T_c is varied from 600 to 900 K and the CR from 2.5 to 4.5. For the

combustion temperature, the combustion process was assumed to be adiabatic, whereby heat loss due to heat transfer only occurs through the boundary near the cylinder wall but not in the core.

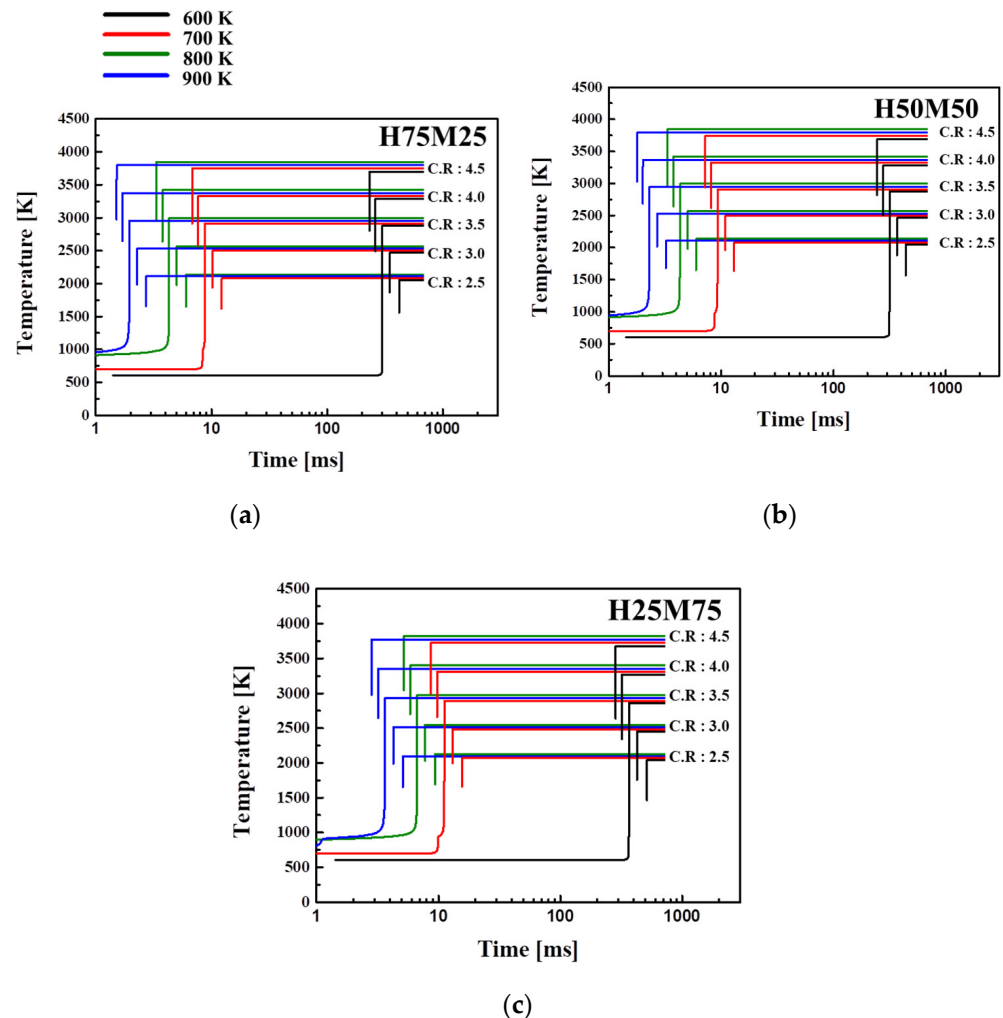


Figure 7. Temperature dependence of ignition delay times for blended fuels at $\Phi = 1.0$, $P_c = 15$ bar, and $O_2 = 21\%$ in (a) H75M25, (b) H50M50, and (c) H25M75-blended fuels.

T_c was calculated using Equation (1), and the ignition delay time at $T_c = 800$ K was shorter than that at 900 K, which fell in the NTC region. Also, as the methane ratio increased and the initial T_c decreased, the ignition delay time increased [39–41]. T_c was the highest at 900–950 K for H75M25 and H25M75 and at 950–1000 K for H50M50. Regardless of the mixing ratio, the ignition delay time was the shortest at 800 K and the longest at 600 K. When the methane ratio increased, the pattern in temperature change was similar, but the ignition delay time changed. For H75M25 in (a), as the CR increased from 2.5 to 4.5, the combustion chamber temperature rose to a maximum of 3823 K, and the ignition delay time decreased from 2.84 to 1.5 ms or less. For H50M50 in (b), the combustion chamber temperature increased to a maximum of 3783 K, and the ignition delay time decreased from 3.5 to 1.7 ms or less. For H25M75 in (c), these values were 3774 K, 5.1 ms, and 2.8 ms, respectively. The ignition delay time decreased as a result of an increase in CR, and T_c and the compression pressure also increased. This reaction was attributed to the faster flame speed, because n-heptane promotes the combustion reaction of methane when the two components are blended. [40–42].

4.4.3. Concentration of Produced Chemical Species and Heat Production Analysis

Figure 8 compares heat production at the time of ignition depending on the concentration of the chemical species, when the methane ratio in the blended fuel is increased stepwise by 25%. For H75M25 in Figure 8a, n-heptane promotes the oxidation reaction of blended fuel and disappears quickly after the first ignition, but methane is oxidized and decomposed under the influence of n-heptane. This is because n-heptane promotes the oxidative decomposition of methane. The heat production was also found to increase rapidly. For H50M50 in Figure 8b, methane is consumed after n-heptane is consumed. For H25M75 in Figure 8c, n-heptane and methane are oxidized and consumed at the same time points during the first ignition and the main ignition. This was attributed to the delay of methane oxidative decomposition due to the lack of oxidizing agents for n-heptane. OH radicals are produced by low-temperature chain reactions of the blended fuel, as described above, and H_2O_2 radicals formed after the first ignition promote the production of OH radicals and disappear at the time of the main ignition. As the proportion of methane increases, the production of H_2O_2 decreases and its production period increases, resulting in a decrease in OH radicals and a longer time required for the main ignition to occur. Heat production was also confirmed to decrease as the methane ratio increased, and the cool flame took place at the first ignition. The amount of produced heat increased as T_c increased, but there was less heat production in the NTC region at 850 K. This is because the weak oxidation at low temperatures decreased the reactivity. Regarding fuel consumption, the decomposition and combustion of methane were slower than those of n-heptane due to the high octane number and auto-ignition temperature of methane. As a result, methane was combusted according to the promoted combustion pattern of n-heptane with a high cetane number.

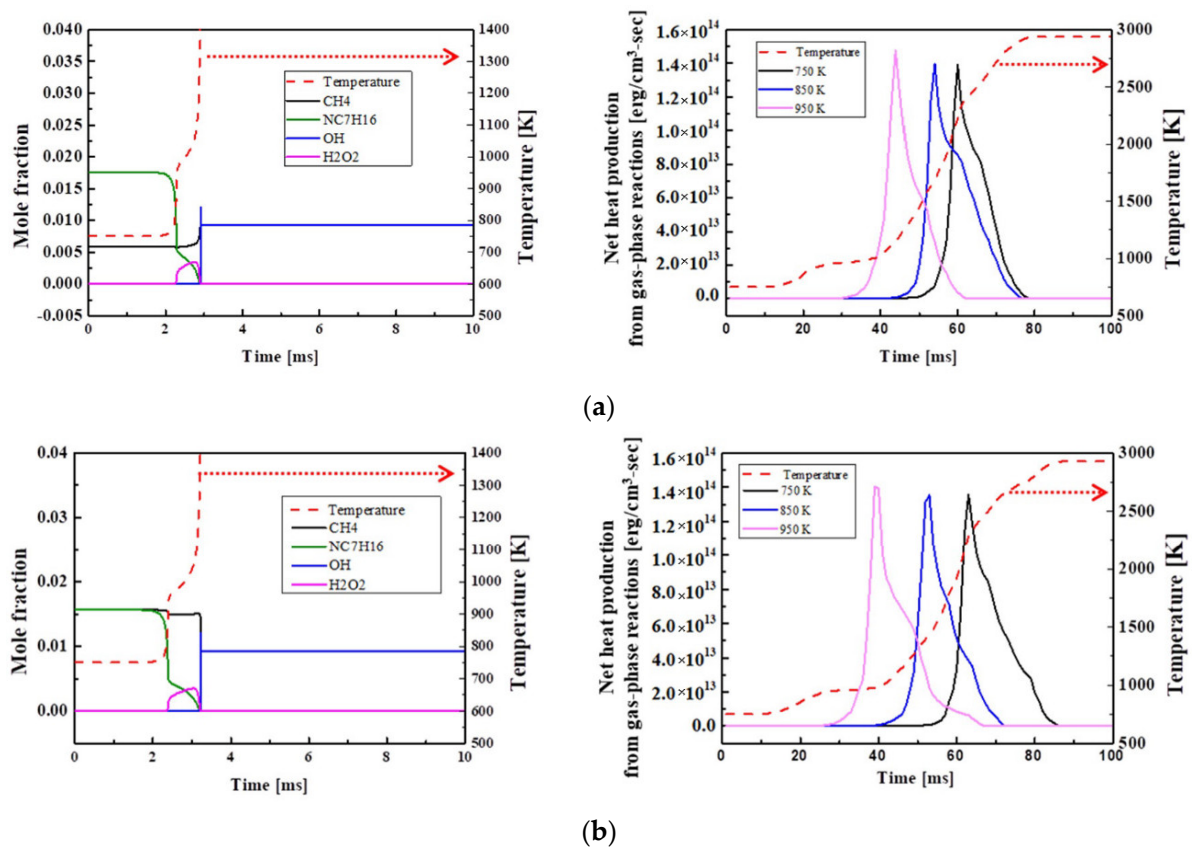


Figure 8. Cont.

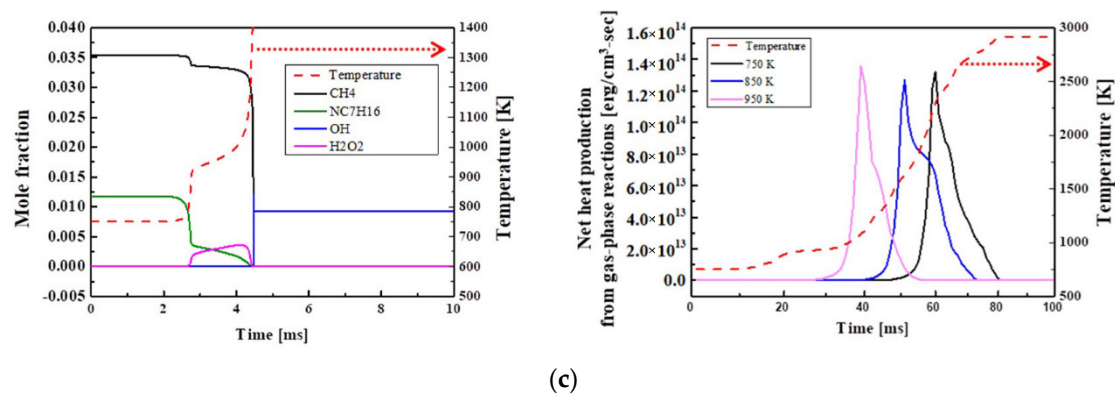


Figure 8. Computed combustion temperature, net heat production, and the concentrations of fuel and other important species at $\Phi = 1.0$, $P_c = 15$ bar, $T_c = 750$ K, $CR = 3.5$, and $O_2 = 21\%$ for (a) H75M25, (b) H50M50, and (c) H25M75-blended fuels.

4.4.4. Analysis of Ignition Delays by Cold and Hot Flames

Figure 9 compares the delay times for the first ignition and the main ignition for each blended fuel composition at $CR = 3.5$. The first ignition time is exponentially decreased, and the second ignition delay time is exponentially increased by increasing temperature. At a higher methane ratio and $T_c = 700$ – 850 K, the first ignition and the main ignition were delayed [41,42]. The main ignition delay time increased by 46% when methane ratio in the blended fuel increased from 25 to 75%, and the delay time increased by 87 and 83% at $T_c = 800$ and 850 K, respectively. Regardless of the fuel composition, only the main ignition occurred without the first ignition when $T_c \geq 900$ K. This indicates that a higher methane ratio suppresses heptane ignition. The chain reaction for methane decomposition ($CH_4 + OH = CH_3 + H_2O$) increases with the methane ratio, which in turn increases the consumption of OH radicals.

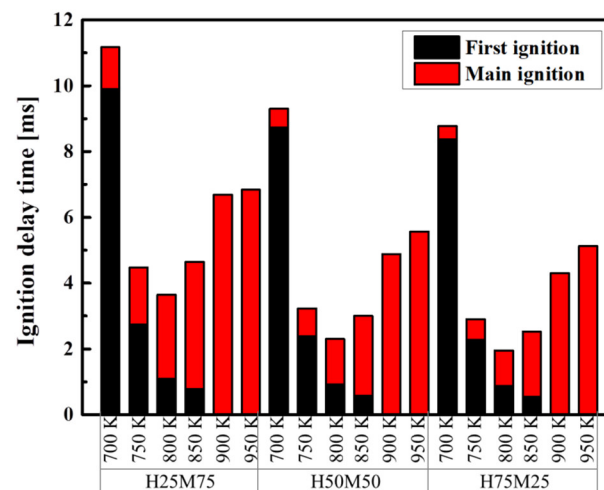


Figure 9. Delay times for the 1st and main ignition of blended fuels at $\Phi = 1.0$, $P_c = 15$ bar, $CR = 3.5$, and $O_2 = 21\%$.

This inhibits the ignition of n-heptane while delaying the ignition further. During the combustion process, a cool flame occurs at the first ignition, and a hot flame occurs at the main ignition. High-carbon fuels such as n-heptane allow a cool flame to occur prior to the ignition, which may affect the overall combustion reaction by isomerizing and decomposing fuel molecules [43]. The first and main ignition delay time can be controlled by the modulation of not only operating conditions but also the methane/n-heptane ratio. The sensitivity to first and main ignition delay time was greater for T_c when compared to the mixture ratio.

4.4.5. Effects of N₂ Dilution Ratio

Prior to the LTC method, it is necessary to form a uniform pre-mixture in the cylinder to achieve simultaneous compression ignition at multiple points. LTC is the most common method to reduce NO_x and PM by decreasing the oxygen concentration with a high EGR rate and lowering the combustion temperature [44,45]. Previous studies had used the following EGR rates and oxygen concentration ranges for LTC. NO_x was reported to be reduced at 50–55% EGR (12–14% O₂ conditions) but the amount of soot was significantly increased, while a smaller amount of NO_x was emitted at 55–60% EGR (9–10% O₂) and the amount of soot decreased drastically [46,47]. Low-temperature combustion was also found to be possible at an EGR of 60% or higher (<12% O₂) in a naturally aspirated engine [48].

In the current study, the effect of O₂ concentration was first analyzed before simulating the EGR rate. Figure 10 shows the ignition delay time at different O₂ concentrations by N₂ dilution for the n-heptane/methane-blended fuel. T_c was varied from 600 to 1000 K in steps of 50 K, and the temperature was shown in reverse order. The fuel composition was kept at H50M50. By reducing the O₂ concentration in the atmosphere by 10, 20, and 30%, the oxygen concentration was controlled, respectively, at 18.9, 16.8, and 14.7%. According to the calculation results, the ignition delay time increased as the O₂ concentration in the blended fuel decreased. In addition, the increase in ignition delay time was large at 800–900 K. This corresponds to the NTC region, where the production of OH radicals is insufficient at a lower O₂ concentration and low temperatures, resulting in reduced oxidation reactions and an inhibited ignition.

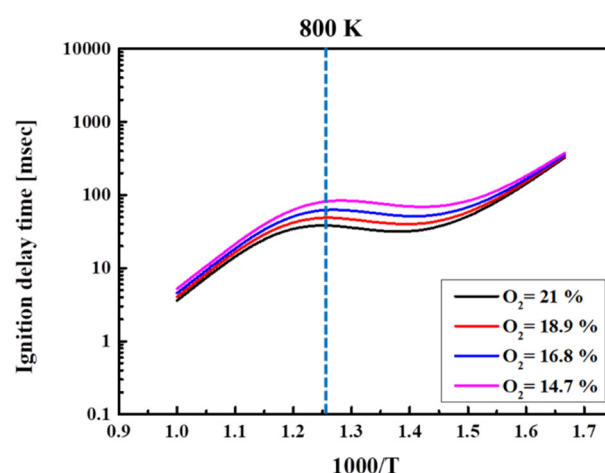


Figure 10. Ignition time for different O₂ mol.% in H50M50 at $\Phi = 1.0$, $P_c = 15$ bar, and $CR = 3.5$.

Figure 11 illustrates the ignition delay times and the mole fractions of OH radicals, H₂O₂ radicals, and the fuel at different O₂ concentration by applying EGR. Panel (a) shows the results at 16.8–21% O₂, and panel (b) shows the results at 14.7% O₂. When the O₂ content was lowered from 21 to 18.9, 16.8, and 14.7%, the ignition delay time increased by 9.6, 29.5, and 59.9%, respectively. It was confirmed that the OH production rate decreased as the O₂ content decreased. The analysis indicated that the temperature of the first ignition was 791 K at 21% O₂ and lowered to 687 K at 14.7% O₂. As a result, the delay times for the first ignition and the main ignition increased, in agreement with the analysis of chemical species that demonstrated lower concentrations of intermediate species and OH radicals at lower O₂ concentrations. Therefore, the time required for the main ignition, as well as the total ignition delay time, increased. This increase is explained by the fact that the inert gas N₂ comprises 70–80% of the exhaust gas in the EGR simulation. N₂ in the blended fuel introduced into the combustion chamber acts as a thermal load for the fuel inside. Therefore, it inhibits temperature increases in the combustion chamber and suppresses the production of intermediate chemical species. In addition, N₂ gas itself has a high specific

heat. These properties of N_2 are responsible for the low temperature. The N_2 ratio is an effective parameter to control ignition delay time and temperature.

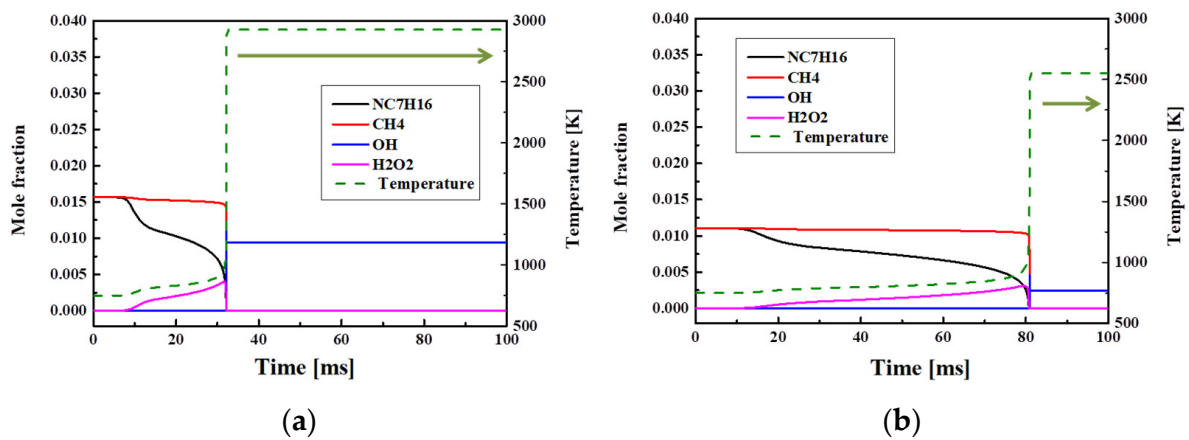


Figure 11. Computed mole fractions of OH and H_2O_2 radicals and the temperature at (a) 21% O_2 and (b) 14.7% O_2 conditions. The other conditions were fixed at $\Phi = 1.0$, $P_c = 15$ bar, $T_c = 750$ K, and $CR = 3.5$.

4.4.6. Changes in Compression Ratio

The engine output may be increased by increasing the air intake amount, the number of engine revolutions, or the CR. As CR increases, the blended gas is significantly compressed and the temperature of the mixture increases, thereby reducing the ignition delay time. Figure 12 shows the ignition delay time in H50M50 at different CR values. CR = 3.5 (solid line) corresponds to the experimental data, and data for the other CR values were from theoretical calculations (indicated by points). There is average error of 3% in all temperature ranges. As CR increased sequentially from 2.5 to 3.0, 3.5, 4.0, and 4.5, the compression pressure increased by 20% and the ignition delay time decreased by 25%, on average. The lower the T_c , the larger the change in the maximum compression pressure in the combustion chamber, and vice versa. In H75M25, the T_c value was lower, and the ignition delay time was longer due to the high methane content. The NTC region was observed near 800–950 K regardless of the CR. Also, at $CR \geq 4.5$ and a pressure of 50 atm or higher, the NTC region became narrower as the CR and the pressure increased. The CR is an effective parameter to control ignition delay time in an especially low-temperature region.

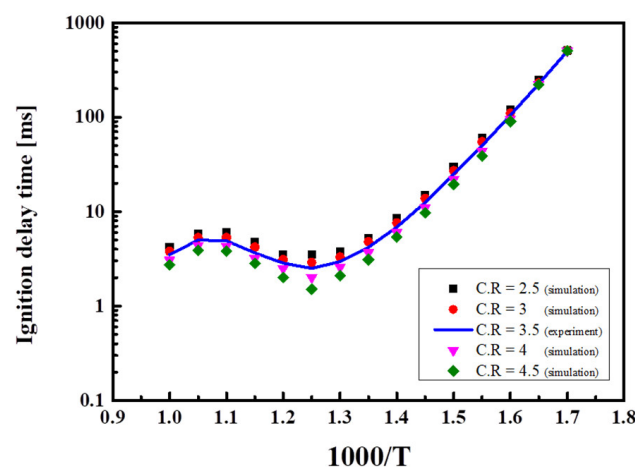


Figure 12. Ignition delay times at various compression ratios ($CR = 2.5$ – 4.5) for blended fuels at $\Phi = 1.0$, and $O_2 = 21\%$.

4.4.7. Reactivity Analysis of Ignition Delay Time

The fuel composition, O₂ concentration, CR, and combustion chamber environment (temperature and pressure) all influence the ignition reaction of the blended fuel. In this experiment, H100 represents the ignition performance of 100% diesel, and M100 represents that of 100% gasoline. The ignition reaction in blended fuels containing 50% or less methane approximated the diesel ignition performance, and therefore the ignition reactivity of other blended fuels was expressed relative to H50M50. In Figure 13, we analyzed the ignition reactivity by setting the ignition delay time of H50M50 to one, and values below and above one are expressed as “+” and “−”, respectively. Figure 13a shows that the fuel composition significantly affects the ignition performance. In the oxidative decomposition of methane ($\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$, RO_2 , QOOH), since OH radicals cannot react with n-heptane (which dictates the combustion reaction at low temperatures) and are consumed by methane instead, the methane/n-heptane blended fuel is ultimately subjected to a strong inhibition in its oxidation reaction for the ignition of n-heptane. As the methane ratio increases, the ignition greatly decreases, and the ignition performance decreases. This indicates that the methane fuel is not compressed and is decomposed due to its high octane number and low cetane number. Figure 13b shows the ignition characteristics at different O₂ concentrations from 21 (outside air) to 18.9, 16.8, and 14.7%. As the O₂ concentration was reduced, the ignitability was reduced by 8 to 35% due to inhibited ignition. A previous study by Cho et al. [48] found that low-temperature combustion was possible under an EGR rate of 60% or higher (12% or less O₂ condition). In the present experiment, the ignition performance at 14.7% O₂ was 37.5% lower than that at 21% O₂, meaning that a lower O₂ concentration is correlated to poorer ignition performance. Figure 13c shows that the ignition performance is dependent on the CR, which was increased from 2.5 to 4.5 at intervals of 0.5. When CR increased from 3.5 to 4.5, the ignition performance improved by more than 35%, and inversely, when CR was decreased the ignition performance was reduced by 10% on average. Additionally, a higher CR improved the performance by 20–25% on average. This result is attributed to the faster flame speed, as n-heptane promotes the combustion reaction of methane when the two components are blended. At a higher CR, the ignition performance improved, and T_c and the compression pressure increased. A higher CR was found to increase the combustion temperature, and the ignition of the methane fuel was promoted in proportion to the combustion temperature.

Figure 13d shows the effect of T_c on the ignition performance. T_c has a large effect on chemical ignition. The graph compares the changes in ignitability within T_c = 700–1000 K, normalized against the value at T_c = 750 K. A higher T_c leads to a higher ignitability, and the NTC region was clearly observed at 850–950 K. Regarding the compression pressure, a lower T_c is correlated to a higher maximum compression pressure change in the combustion chamber, and vice versa. As the compression pressure increased, T_c increased more rapidly, and the ignitability improved.

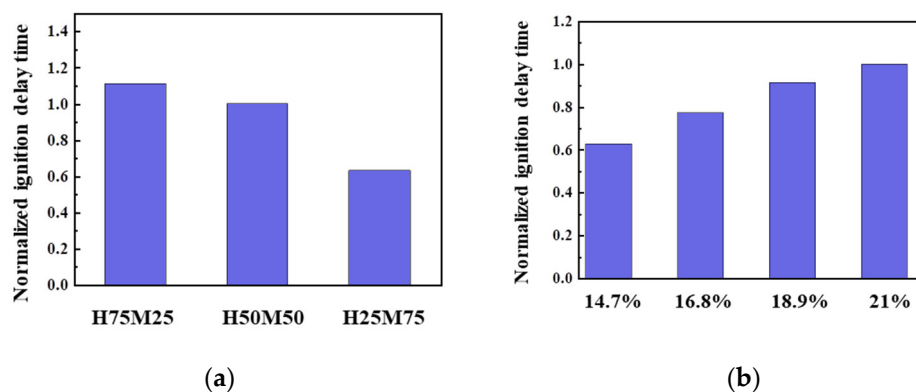


Figure 13. Cont.

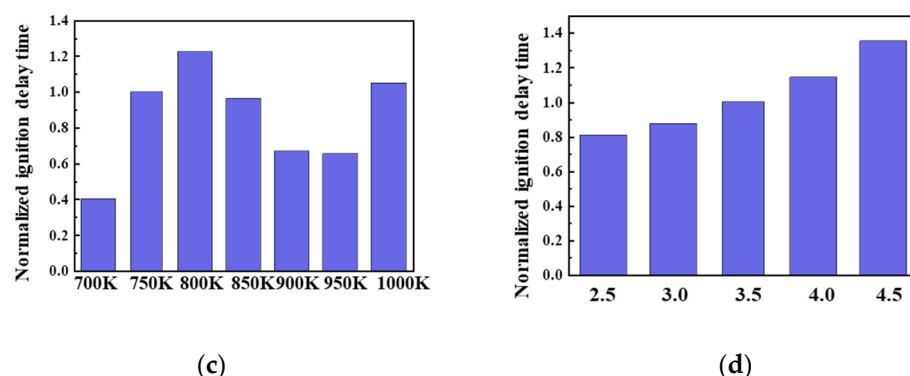


Figure 13. Normalized ignition delay time in H50M50 at various (a) fuel compositions, (b) O_2 concentrations, (c) CR values, and (d) T_c values at $\Phi = 1.0$, $P_c = 15$ bar, $T_c = 750$ K, and $CR = 3.5$.

4.4.8. Sensitivity Analysis

Figure 14 shows the results of sensitivity analysis to determine the main combustion reactions with high reactivity, in the case of H75M25 fuel under the conditions of a low temperature (850 K), 15 atm, and EGR (14.7% or 21% O_2). Positive and negative sensitivity coefficients indicate reactions that inhibit and promote the ignition reactions, respectively. Particularly, $CH_4 + OH \rightleftharpoons CH_3 + H_2O$ is a typical chain propagation reaction that inhibits methane ignition at 21% O_2 . At 14.7% O_2 , most of the reactions inhibit ignition due to the lack of oxygen. The chain initiation step ($CH_3 + HO_2 \rightleftharpoons CH_4 + O_2$, the first oxidation reaction induced by methane dehydrogenation at low temperatures) and the decomposition reaction ($CH_2O + CH_3 \rightleftharpoons HCO + CH_4$) were found to have significant effects on methane decomposition. For the n-heptane/methane-blended fuel, an NTC region was observed at 0–75% methane and the temperature range of 800–950 K. In this region, as T_c increases, the ignition delay time increases. OH radicals, which induce oxidation at 850 K, do not react with n-heptane. Instead, large amounts of OH and oxygen are consumed by methane dehydrogenation in a low temperature range, resulting in a shortage of them for the first oxidation reaction of heptane and strong inhibition of oxidation in the blended fuel. As a result, the reactivity is reduced, an NTC region is created, and thus the ignition delay time becomes longer. The HO_2 and H_2O_2 species, which inhibit ignition through methane at 850 K, promote ignition at 1100 K, and the ignition delay time is shorter due to the explosive combustion of n-heptane species.

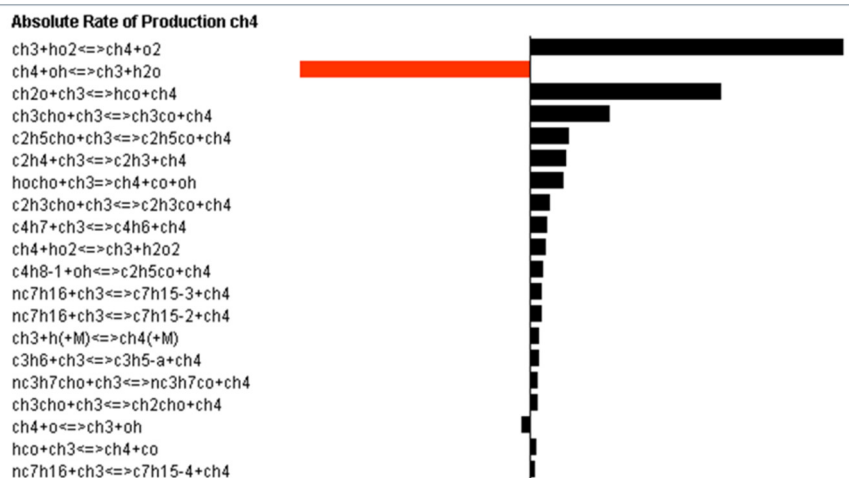


Figure 14. Sensitivity analysis to identify factors that significantly affect the combustion of H75M25 at 14.7% or 21% O_2 .

5. Conclusions

An RCM system was employed to simulate the pre-mixed combustion technology. The autoignition characteristics of n-heptane/methane-blended fuel for various temperatures, CRs, and N₂ dilution ratios were analyzed using simulations in this study.

- (1) Ignition reactivity is sensitive to the compression ratio and fuel composition. Even an increase of 0.5 in the compression ratio reduced the ignition delay time by more than 20%. An increased n-heptane ratio in the fuel significantly promoted ignition, whereas an increased methane ratio greatly inhibited it.
- (2) The ignition delay time was significantly longer (by more than 30%) at 14.7% O₂ when compared to that at 21% O₂ because a shortage of O₂ inhibited the oxidation reaction.
- (3) The cool flame occurred in the range of T_c = 750–850 K therefore, the main ignition time was shorter when compared to that at T_c = 900–950 K, where only hot flames would occur. Therefore, oxidizing agents are important for achieving the low-temperature oxidation of fuel that is sensitive to temperature.
- (4) As the ratio of n-heptane in the blended fuel increased, the combustion reaction during the multi-point compression proceeded from a cool flame to NTC to a hot flame. The phenomena of second ignition and NTC were clearly observed as the characteristics of high-carbon fuel. This confirmed that the reaction of n-heptane was more dominant in the blended fuel.
- (5) The combustion performance similar to that of 100% n-heptane could be achieved when the ratio of methane was kept at less than 50%, because methane inhibits oxidation at low temperatures.

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