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Effect of Fuel Composition and O2 Concentration on Autoignition Characteristics of n-heptane/methane Blended Fuels

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Abstract: This study numerically analyzed the effect of composition and temperature and oxygen concentration changes on the selfignition characteristics of n-heptane/methane blended fuels in order to cope with development of alternative fuels and international environmental regulations. CHEMKIN-PRO is used as the analysis program and the LLNL model is used as the reaction model. The numerical results revealed that on autoignition and ignition delay time were sensitive to changes in fuel composition and oxygen concentration. As the methane ratio increases, OH radicals causing ignition are delayed in generation and the concentration is lowered, thus longer the ignition timing. The oxygen concentration in the mixed fuels are changed to simulate the exhaust gas recirculation and a numerical analysis in then performed. As the oxygen concentration decreases, the ignition delay time longer because the nitrogen gas acts as a thermal load in the combustion chamber.

Keywords: Ignition delay time, N-heptane, Methane, Homogeneous Change Compression Ignition, Compression ratio, Exhaust gas recirculation

1. Introduction

In recent years, Globally, environmental pollution and the depletion of energy resources have become serious, the regulation law of hazardous emission gas has been strengthened. In the United States, Tire-4 has been applied since 2011 and European Union (EU) has adopted enhanced emission regulations such as EURO-6 from 2014. Therefore, the efficiecy improvement of the internal combustion engine and the method of reducing the pollutant emission is growing interest in, and a lot of researches related thereto have been carried out. High cetane fuels, such as diesel fuel, are mixtures of many hydrocarbon-based fuels. Among them, n-heptane, which has a high specific gravity of carbon, has a high cetane number similar to that of diesel, and two-step ignition (cold and hot flame) and ignition delay are well simulated in experiments and widely used as a surrogate fuels for CI. Such as high hydrocarbon components have a significant effect on fuel ignition due to high centane number. Therefore, in order to know the nitrogen oxides (NOx), soot, lead salts, iron, tar, carbonaceous material, and PAH reduction principle generated in the engine combustion chamber, understanding oxidation and combustion characterization mechanisms is essential [1].

Recently, a homogeneous charge compression ignition (HCCI) engine, which is an engine combining the advantages of a conventional gasoline engine (SI) and a diesel engine (CI), has been actively studied. The premixture of air and fuel in the combustion chamber during inspiration is formed by the SI engine method, Piston compression and ignition combustion is a CI engine method. It is a technology that combines the advantages of the CI and SI. HCCI technology can operate under lean conditions, can maintain low temperature combustion (LTC), can achieve a high compression ratio, can improve the thermal efficiency and reduce carbon dioxide (CO2), a greenhouse gas. in addion, The NOx and particulate matter (PM) emissions can be reduced at the same time by shutting off the local hot parts by forming a uniform mixture in the combustion chamber [1,2]. However, the operating range of the HCCI engine is limited at low and high loads. Under low load, incomplete combustion occurs due to low combustion temperature, resulting in excessive emission of CO and HC. In a high load, rapid combustion ignition increases the combustion pressure excessively, resulting in knocking and engine damage and noise. Therefore, in order to use the HCCI in a heavy-duty, constant-speed engine such as a power generation engine, many studies are being conducted on precision combustion control technology for controlling ignition delay through control of equivalence ratio, fuel mixture ratio and pressure [3,4]. On the other hand, much research is needed on alternative fuels as a way to solve the problem of resource depletion and environmental pollution of fossil. ExxonMobil, a US petrochemical company, predicts that by 2040, oil and natural gas will account for 60% of the world's energy supply and be a major energy source, according to a recent long-term energy outlook by 2040. Natural gas is expected to grow at its fastest rate, accounting for 40% of global energy demand growth. Compared to diesel fuel, natural gas, which consists mainly of methane, has the advantage of being able to effectively cope with CO2 regulations such as the Kyoto Protocol because of low PM and CO emissions. In addition, since methane has a high octane number, sufficient fuel and air premixing time can be secured during operation of the HCCI engine, allowing uniform pre-mixing. However, it has a low cetane number and has a disadvantage that the autoignition characteristic is very low. Methane fuels with these properties can meet SI and CI systems when mixed with high cetane of hydrocarbon fuels. Therefore, the verification and burning characteristics as heterogeneous mixed fuels have not been studied much today, and thus there is a need for research. In a previous study, Chunde et al. studied that three factors (oxygen partial pressure, heat capacity at constant volume, kinetic response) affecting ignition delay with the methane ratio of 40% and 80% in the simulation study of n-heptane and methaneblended fuel. In addition, kinetic response was performed by sensitivity analysis, mutual comparison performance of ignition delay were analyzed by constructing reduced mechanism using methane as Hung mechanism and n-heptane as Curran mechanism [5]. Aggarwal et al. (2002) investigated the ignition delay of n-heptane and methane in high-pressure conditions (30 atm, 55 atm) and equivalence ratios ($\varphi = 1, 2$). and Also, in the sensitivity analysis, heptyl (C_7H_{15}) and hydroxyl (OH) radicals were found to play an important role in determining ignition [6]. Mixer ignition system in HCCI combustion is chemical ignition, not physical ignition, such as spark plugs used in SI or injection nozzles used in CI. Chemical ignition due to chemical properties such as composition of matter, oxidation, combustion, and chemical reaction is controlled by temperature, pressure, and compression ratio, and combustion occurs. Therefore, ignition is promoted by shortening the ignition timing at a high compression ratio by using a fuel having good ignitability or an LTC combustion technique for low-temperature combustion by lowering the combustion temperature by EGR is needed. Thus, the optimum ignition timing for controlling the compression ratio, EGR, and combustion reaction is an important technique in HCCI combustion. In the previous research, the concentrations of OH radicals and intermediate chemical species, which promote oxidation reaction, the compression ratio changes, EGR are not considered, it was performed in this study. Therefore, the experiment was a basic study of combustion control technique, mixing n-heptane as a standard fuel and methane which was a recent interest as an alternative energy source. The purpose of this study is as follows. To analyze the effect of mixing ratio on ignition delay time of n-heptane/methane blended fuels at low temperature. EGR is simulated according to changes in oxygen concentration, and ignition delay time is analyzed as chemical species concentration. To do comparative research the ignition delay time and reaction rate of combustion according to the change of compression ratio (2.5, 3.0, 3.5, 4.0, 4.5). The fuel composition change and the sensitivity of oxygen concentration are compared and analyzed.

2. Experimental apparatus and method

RCM are used to simulate a single compression stroke of an internal combustion chamber without other reciprocating engine piston. It is an ideal device to simulate pre-mixed gas (fuel, oxygen, dilution gas) at the set temperature and pressure similar to the actual engine in the combustion chamber [7,8]. In addition, It is also possible to control the composition, compression ratio, equivalence ratio and compression temperature of the premixed fuel. besides, a constant compression pressure and the combustion phenomena at various compression temperatures can analyze.

2.1.Experimental apparatus

Figure 1 shows the schematic of RCM system that was used in this study [9]. The experimental apparatus consists of a combustion chamber in which autoignition combustion of fuel is performed, and a pneumatic cylinder (Impact Pneumatic Cylinder) which drives the piston with air pressure. The combustion chamber is a place where the crevice piston compresses and autoignition at a short time, and its shown in Fig 1. This is where the sensors and measuring equipment are installed to get the results of the experiment. The piston speed can be controlled by the pressure of the high pressure air tank and the compressed air is stored in the high pressure air tank by the air compressor. The compression ratio is a pneumatic device that can be adjusted from 6.5 to 2.5 by adjusting the length of the rod connected between the combustion chamber and the pneumatic cylinder. And the RCM device used in the experiment has very short compression drive time of less than 50ms. Also, the piston pushing phenomenon caused by the explosion, which can greatly affect the test result, is fixed so that the piston can not move after reaching the top dead point by using a brake arm so as not to be damaged by the explosion. In this study, creviced pistons were used to process the gap between the piston head and the cylinder and to minimize boundary vortices caused by the movement of the piston [7]. Table 1. shows the specifications of RCM used in this experiment.

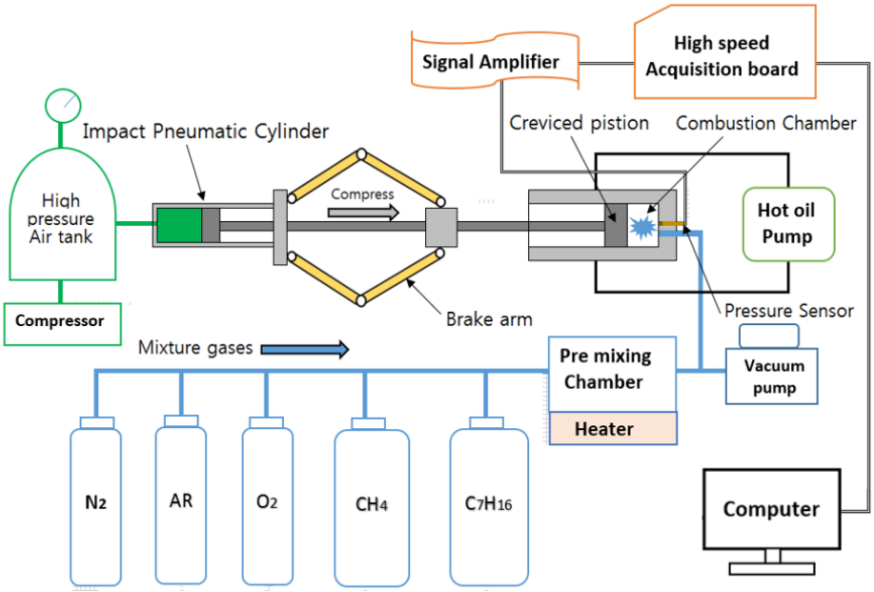

Figure 1. Schematic of RCM system.

Table 1. Specification of the RCM

Description	Specification

Cylinder bore	50 mm
Cylinder thickness	13 mm
Piston type	Creviced pistion
Piston stroke	218.2 mm
Compression ratio(C.R)	6.5～2.5
Compression time	～50 ms
Initial temperature	293 K
Initial pressure	1 atm

2.2. *Experimental method*

In this study, the contents of methane as 100, 75, 50, 25 mol.% were mixed with n-heptane as the main fuel. The mixed fuels should be vaporized in the pre-mix chamber to create a homogenous mixer. After the combustion chamber and the pre-mix chamber are creating a vacuum using a vacuum pump, fuel is injected into the pre-mix chamber using a syringe. The mixed gas was formed by controlling the ratio of N2, Ar, and O2 according to the temperature condition. The combustion chamber was subjected to one compression and explosion stroke, and after each combustion, the exhaust gas was removed by using a vacuum pump, the combustion chamber was evacuated, and the experiment was repeated. In addition, pressure changes in the combustion chamber were measured using a pressure sensor (Kistler 6125b) and a charge amplifier (Kistler 5015A), and data was collected by a computer using commercially available software (Labview 8.2). The K-type thermocouple was used to measure the temperature of the mixed gas supplied to the combustion chamber. Experiments were carried out at a temperature of 293 ± 0.5K. The compression temperature (Tc) was calculated using Equation (1) and adjusted to 600-1000K according to the change of compression pressure and dilution gas ratio [9,10]. Where T_0 and P_0 are initial temperature and pressure, T_c and P_c are compressed temperature and pressure of mixture at TDC and $\gamma(T)$ is specific heat ratio of mixture as function of temperature.

2.3. *Experimental condition*

Previous studies have confirmed that the ignition timing varies with the content of methane 40, 80 mol.% At high and low temperatures. In this experiment, the study was conducted under conditions simulating this. The fuel used for the numerical analysis is a n-heptane/methane blended fuels. Table 2 shows properties of fuels. Experiments were repeatedly carried out 5-10 times at same condition to check the reproducibility of results. Figure 2 is a pressure graph measured at a mixing ratio of n-heptane/methane of 5:5, a compression pressure of 15 atm, and a compression temperature of 800K. We can confirm excellent reproducibility. Figure 3 shows the definition of ignition delay time which is an important factor to understand combustion process in the engine. The ignition delay time was defined as the time until the piston reached max dP/dt in the TDC where compression was completed. In general, the ignition delay time is 10-20 ms.

Table 2. Specification of the RCM

Name	n-heptane	methane

Molecular Formula		C7H16	CH4
Molecular Weight		100.21	16.042
Density	g/m^3	0.688	0.664
Boiling Point	K	372	111.55
Autoignition Temperature	K	558	810
Low Calorifc Value	MJ/kg	44.240	49.94
RON		0	130
CN		56	0

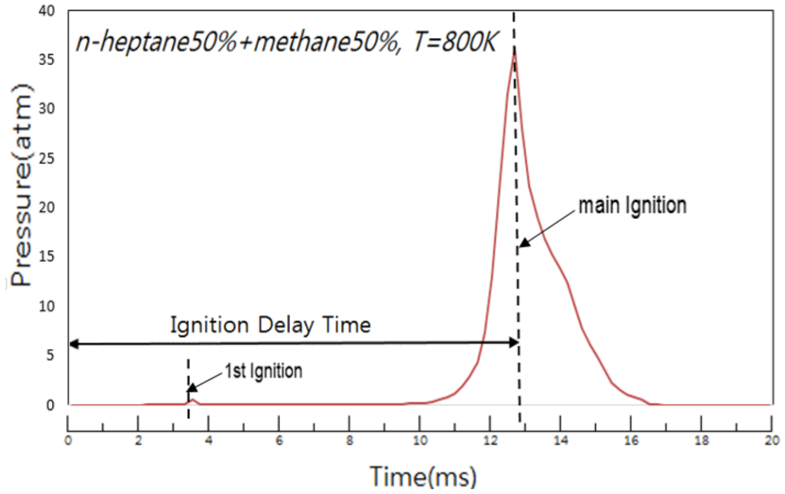

Figure 2. The reproducibility of experiments for E.R(φ)=1.0, P=15atm, C.R=3.5 and O2=21% condition with n-heptane 50% + methane 50%, at compression T0=800K.

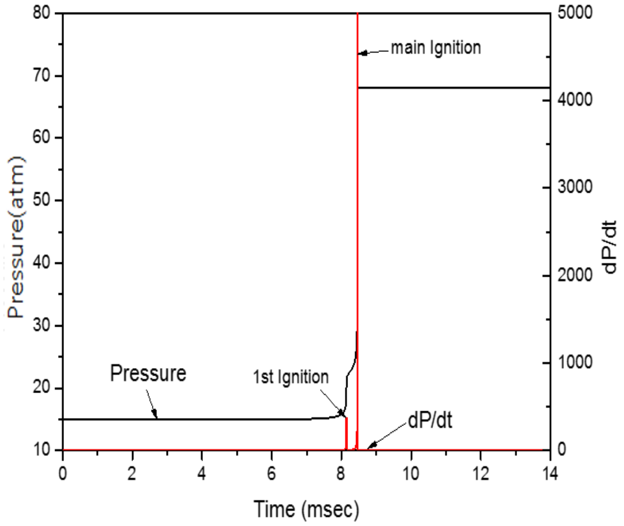

Figure 3. Definition of ignition delay time

3. Numerical analysis method

In this study, we used CHEMKIN-PRO [11] as an analysis program to verify the ignition delay test results using a rapid compressor. the closed homogeneous constant volume module was employed to simulate initial condition with temperature and pressure when piston reaches the TDC. The chemical reaction model for the n-heptane/methane blended fuels were used reaction model developed by S. Dooley et al. [12], and the reaction model consists of 1599 chemical species and 6633 chemical reactions. Also, In the calculation for n-heptane, the n-heptane detailed reaction model of Mehl et al. [13] was used.

4. Results

4.1.Chemical Reactions

Chemical reactions are directly influenced by temperature during the combustion process of hydrocarbon(CH) fuels. Hydroxyl radicals (OH) are unstable active electrons, so they are not stable and have high energy states and very high reactivity. Figure 4 shows the C7H15OH generated to decompose rapidly with OH radicals reaction of n-heptane. When such radicals are reaching the predetermined level is the first ignition occurs. In the low temperature oxidation process of methane, the OH radical is greatly influenced by the H2O2 radical generated after the first ignition, and the oxidation reaction proceeds. the OH radical reaction decreases the rate of concentration increase due to the delay of OH radical production as the methane ratio increases, and the ignition temperature decreases by 40-100K or more. Therefore, the first ignition was delayed and the main ignition timing was also delayed. This is consistent with the previous study [5] in which OH radicals delay ignition time due to an increase in methane.

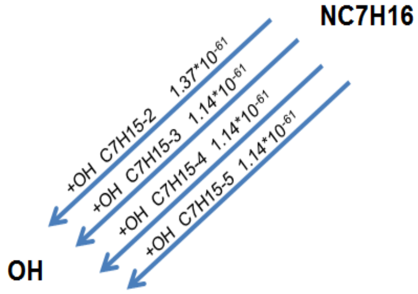

Figure 4. OH Radicals reaction of n-Heptane.

Figure 5 shows the reaction path of the pure n-heptane reaction path on the right and the n-heptane/methane blended fuels on the left. n-heptane separates H atoms from the initial fuel at low temperature combustion, and the resulting alkyl groups react with oxygen to form RO2 radicals. This is changed to QOOH radical, which is the main reaction mechanism, at low temperature combustion through isomeric reaction. As the temperature increases, the strong exothermic reaction, R + O2 ⟶ RO2 is converted to RO2 ⟶ R + O2. It decomposes into an oxidation reaction of QOOH radical as well as conjugate olefin and cyclic ether species. This chain reaction reduces the reactivity of the overall system. As a result, a NTC region is created [14]. The difference in the reaction path of pure n-heptane and mixed fuels at Figure 5 was marked in the red dotted box. Methane reacts with O2 due to the OH radicals of methane generated in the low temperature region, thereby promoting the oxidation reaction to produce formaldehyde (CH2O). Since formaldehyde is widely known as a stable molecule, the ignition delay time increases with increasing methane in the blended fuels. Also, in the case of a mixture of methane and n-heptane, methane reduces the production of H2O2 radicals at low temperature and suppresses the generation of active OH radicals leading to oxidation, thereby reducing the low temperature chain reaction. When mixed with fuels such as n-heptane having high reactivity at low temperatures, the oxidation reaction can be promoted by a plurality of radicals generated by the reaction of n-heptane. At high temperatures OH radicals are rapidly promoted and decomposed by H2O2 radacal formation. Due to this effect, OH radicals, which play an important role in the oxidation reaction, are being competitively consumed in n-heptane/methane blended fuels. Therefore, the main reaction is the second chain oxidation reaction after the first oxidation reaction of n-heptane. OH radicals of methane are mainly produced by two promotional reactions H_2O_2 (+ M) = 2OH (+ M), HO_2 + CH_3 = OH + CH_3O [5,16]. This results in a major oxidation reaction with the n-heptane species even in the n-heptane/ methane blended fuels, resulting in short ignition delay time due to explosive combustion at high temperature.

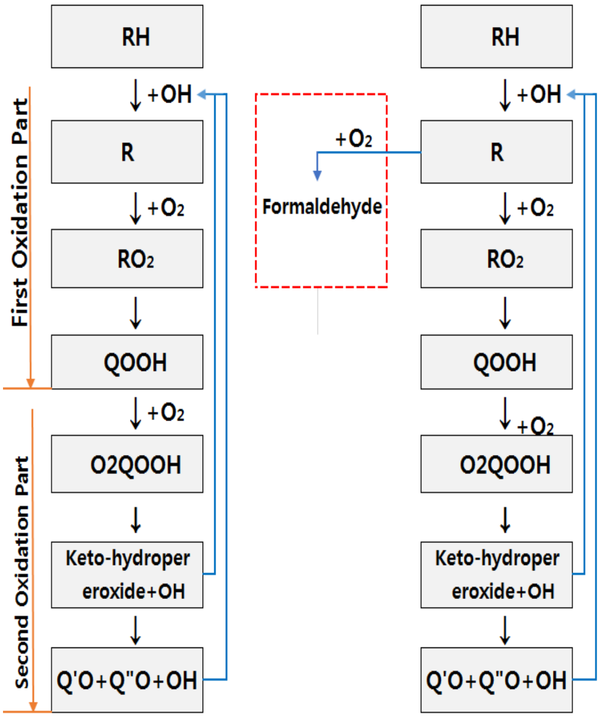

Figure 5. Reaction pathways of pure n-heptane(left) and n-heptane/methane blended fuels(right)

4.2.Chain reaction

The main chain reaction in the high temperature region is H + O2 = O + OH, and the overall chemical decomposition reaction proceeds through rapid combustion of the alkyl radical by β-scission. Methane converts the OH radicals to H_2O_2 by low temperature oxidation and acts as a suppression against n-heptane ignition. However, the combustion reaction at high temperature shows a large difference from the low temperature region. As the H_2O_2 is decomposed rapidly in excess of 1000 K, at the same time, the n-heptane initiates the reaction and H atom is released by the OH radical preferentially. (H atom-abstraction : C_7H_{15}), Then, first oxidation reduction ($C_7H_{15}O_2$), isomerization ($C_7H_{15}O_2 \leftrightarrow C_7H_{14}OOH$), second oxidation reducton, and chain reaction proceed sequentially.

4.3.Effects of blended fuels ration change

The notation of blended fuel is H/M, H is n-heptane, and M is methane. For example, 50 mole% of n-heptane + 50 mole% of methane was named H50M50.

4.3.1. The combustion chamber temperature and pressure changes

Figure 6 is a graph showing the ignition delay time according to the change in the fuel composition ratio of the n-heptane/methane blended fuels. Since the horizontal axis is the reciprocal of the temperature, the right side is the low temperature part and the left side is the high temperature part. The equivalence ratio was 1, the compression pressure was 15 atm, the oxygen concentration was 21%, and the composition ratio of methane was carried out varying at intervals of 25%. The ignition delay time was calculated while varying the compression temperature from 600 to 1000K in increments of 50K. It was confirmed that the ignition delay time decreases as the compression temperature increases. The ignition characteristics of n-heptane, the NTC region and the two-stage ignition, were observed up to 75% methane, except when methane was 100% in the blended fuels. The NTC region is an zone in which the ignition delay time is increased or maintained constant while the temperature is increased. In this study, the NTC region was observed at a specific temperature of around 850K. Regardless of the mixing ratio, ignition delay time increased as the compression temperature increased, as well as the combustion characteristics of n-heptane. Previous studies such as Chunde et al. [5] and Aggarwal et al. [6], did not show the NTC region at high temperatures when methane was used as a single fuel. This is in agreement with the results of this study as a whole.

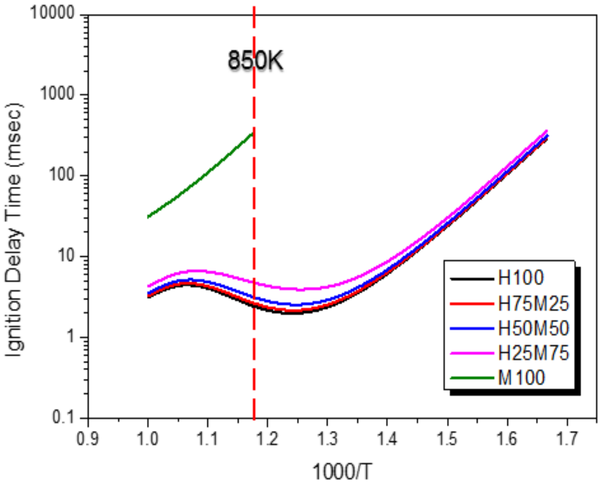

Figure 6. Ignition delay times of blended fuels at E.R(φ)=1.0, P=15atm, C.R=3.5 and O2=21% condition

Figure 7 is the change in compression temperature and ignition delay time when the methane content is increased to 25%, 75% at compression ratio 3.5. As a method of increasing the actual engine power, there is a method of increasing the intake air amount, increasing the engine rpm, and increasing the compression ratio. As the compression ratio is increased, the mixed gas is strongly compressed and the temperature is increased, and the ignition delay time is shortened. As the compression ratio increased to 2.5 ⟶ 3.0 ⟶ 3.5 ⟶ 4.0 ⟶ 4.5, the compression pressure increased by an average of 20%, and the ignition delay time decreased by an average of 25%. The change of compression pressure was higher as the compression temperature was lower. Also, the higher the compression temperature, the lower the maximum compression pressure change in the combustion chamber. In H75M25, the compression temperature was high and the ignition delay time was short because of high n-heptane ratio. In H25M75, the methane ratio was high, so the compression temperature was low and the ignition delay time was long. The NTC region occurred around 850K-950K regardless of compression ratio. Also, as the compression ratio was higher than 4.5 and the pressure was higher than 50 atm, the range became narrower as the pressure increased.

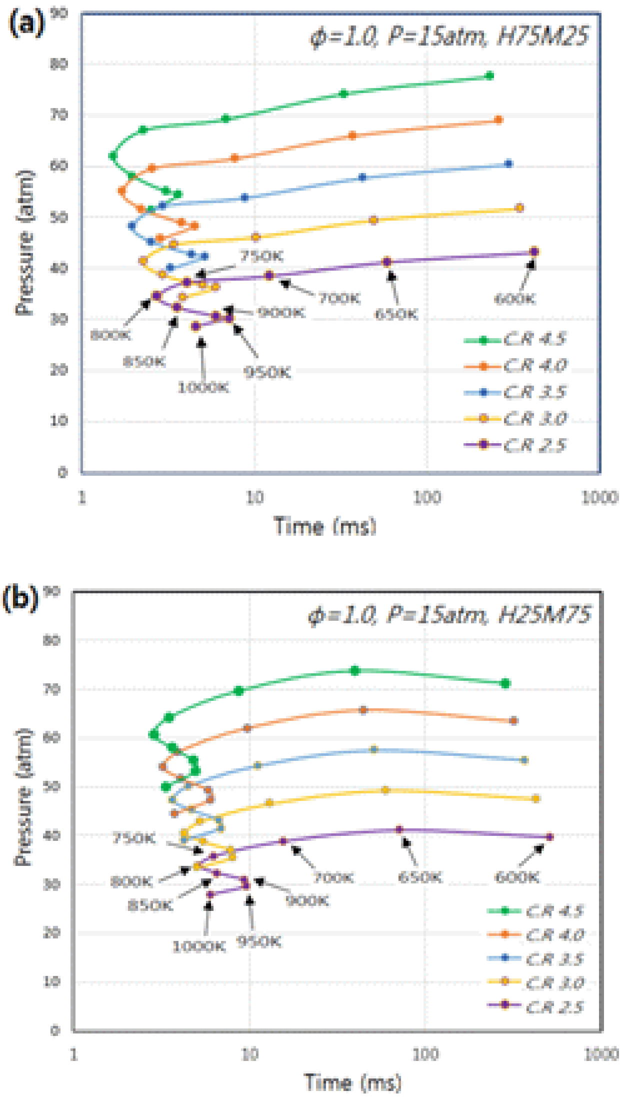

Figure 7. Pressure curve with ignition delay times of blended fuels at E.R(φ)=1.0, P=15atm, C.R=2.5-4.5 and O2=21% condition and methane ratio (a) H75M25, (b) H25M75.

Figure 8 analyzes the time required for first ignition and main ignition for each fuel mixture when the compression ratio is 3.5. The increase of methane at the compression temperature of 700K-850 K has increased the first ignition time and the main ignition time. In addition, the main ignition time increased by 46% when methane in mixed fuel was increased from 25% to 75%, and increased by 87% at 800K and 83% at 850K. Regardless of the blending ratio of the blended fuel, only the main ignition occurred at the compression temperature of 900K or more without the first ignition. It can be seen from this that the increase of methane inhibited the ignition of n-heptane. The ignition inhibition of methane by increases the ratio of methane, the methane reaction (CH4 + OH = CH3 + H2O) suppresses the ignition and lengthens the ignition delay [6,16]. The reason is that after the H atom is abstracted from the methane by the OH, the low temperature chain reaction does not generate more OH after the second oxidation of the alkyl group like n-heptane [5].

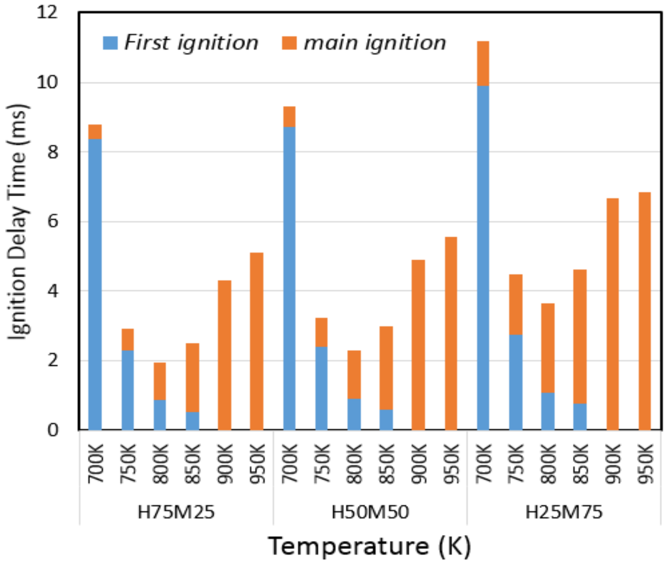

Figure 8. First/Main ignition delay times of blended fuels at E.R(φ)=1.0, P=15atm, C.R=3.5 and O2=21% condition.

Figure 9 shows the combustion chamber temperature distribution and the ignition delay time when the compression initial temperature from 600K to 900K changes at a compression ratio of 2.5 to 4.5. The combustion chamber temperature assumes that compression process is an adiabatic process, "so that heat loss due to heat transfer occurs only through the boundary layer around the cylinder wall surface, and heat transfer does not occur in the core". Calculated by equation (1). Ignition delay time is shorter at compression temperature 800K than compression temperature 900K (NTC region). Also, it can be seen that as the methane ratio increases, the ignition delay time increases as the initial compression temperature lower. As the compression ratio is increased, the compression temperature is high and the ignition delay time is reduced. Compression temperatures were highest at 900K-950K at H75M25 and H25M75, highest at 950K-1000K at H50M50. The ignition delay time was the shortest at 800K and the longest at 600K regardless of the mixing ratio. As the methane ratio increases, the temperature variation pattern is constant but ignition delay time is different. When the compression ratio increased by 2.5 to 4.5, (a) the combustion chamber temperature increased to 3823 K at H75M25, and the ignition delay time was shortened to 2.84 ms⟶ 1.5 ms. (b) the combustion chamber temperature increased to 3783 K at H50M50, and the ignition delay time was shortened to 3.5 ms⟶ 1.7 ms. (c) the combustion chamber temperature increased to 3774 K at H50M50, and the ignition delay time was shortened to 5.1 ms⟶ 2.8 ms. When the compression ratio is increased 1.8 times, the ignition delay time was reduced twice. This reaction is because when n-heptane is mixed with methane, the n-heptane promotes the combustion reaction of methane and the flame speed is accelerated. As the compression ratio increased, the ignition delay time became shorter and the compression temperature and compression pressure increased.

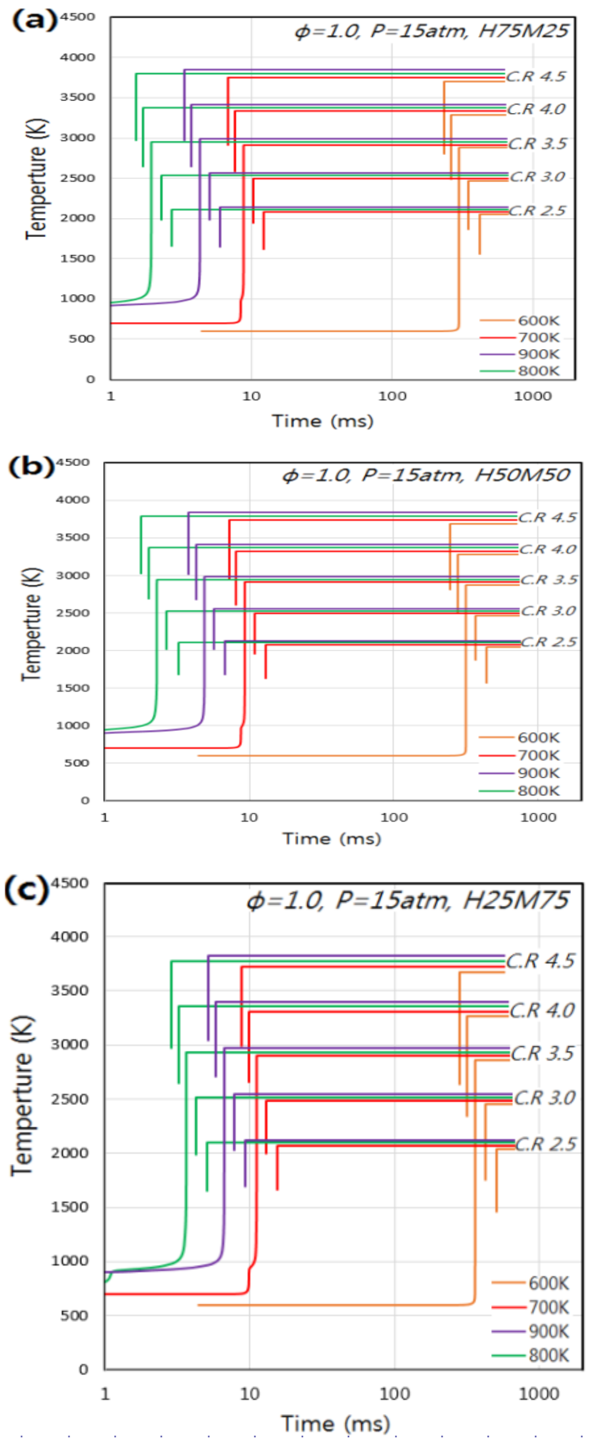

Figure 9. Temperature curve with ignition time of blended fuels at E.R(φ)=1.0, P=15atm, C.R=2.5-4.5, and O2=21% condition and methane ratio (a) H75M25, (b) H50M50, (c) H25M75

Figure 10 is an analysis of the compression pressure, ignition delay time, ignition temperature, fuel consumption (n-heptane, methane) according to the compression temperature. As the n-heptane ratio increased, the ignition temperature was higher, the ignition delay time was shorter and as the methane ratio increased, the ignition temperature was lower, the ignition delay time was longer. In addition, the oxidation reaction was delayed at low temperature and the amount of chemical species was also decreased. In particular, the oxidation of the cool flame generated during the combustion of n-heptane proceeds before the main ignition occurs. It can be isomerized by modifying the chemical bonds of the fuel molecules, affecting the overall reactivity [15]. And incomplete combustion occurs due to heat generated by the chemical decomposition of the fuel during combustion. The generation of cool flame in n-heptane/methane blended fuel affected the main ignition and shortened the ignition delay time. However, as the methane ratio increased, the ignition delay time increased. This indicates that the OH radical reaction is not active at the low temperature described above, and the ignition time is prolonged. The two - stage ignition and NTC phenomena which are the combustion characteristics of n-heptane in the low temperature region, also occurred in this experiment using n-heptane/methane blended fuels. This is because the high temperatures, the low-temperature chain reaction is omitted and the high-temperature reaction proceeds at a high rate, so that the cool flame disappears and rapid combustion occurs. The main oxidation function RO2 = QOOH plays an important role at high temperature, and the important reaction for controlling ignition is H2O2 = OH + OH, CH3 + HO2 = CH3O + OH, H + O2 = OH + O and NC7H16. As these oxidation reactions are changed into decomposition reactions, the rate of OH formation during the methane reaction increases [5].

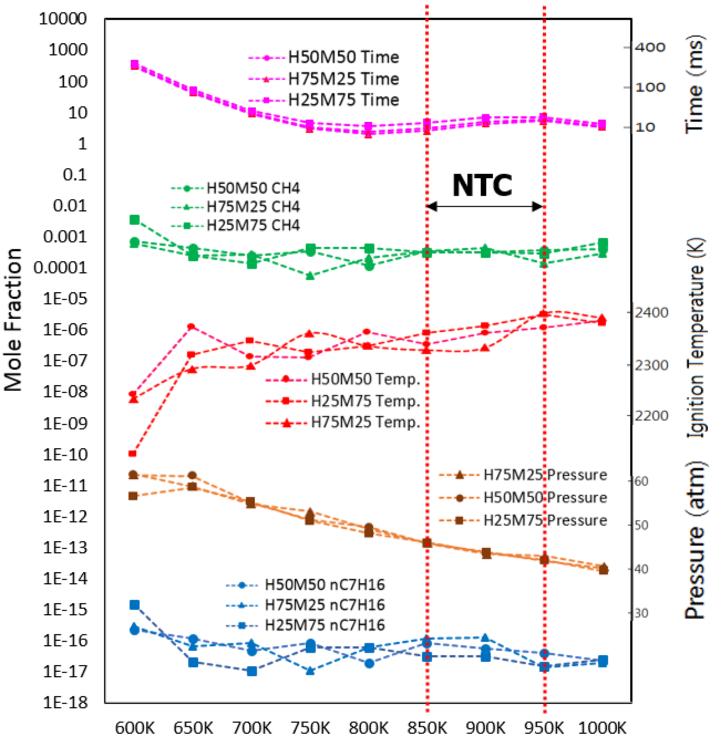

Figure 10. Computed combustion analysis of blended fuels at E.R=1.0, P=15atm, C.R=3.5 and O2=21% condition

4.3.2. Chemical species concentration analysis

It was confirmed that the total ignition delay time increases in the low temperature region as the proportion of methane in the mixed fuel increases. In order to analyze the result of the analysis in detail, concentration analysis of OH radical and H2O2 species according to the mixing ratio of methane was performed. Figure11 shows the results for the chemical species concentration by increasing the methane ratio by 25% in the n-heptane / methane blended fuels. These chemical species are important radicals that affect ignition. In the n-heptane/methane blended fuels, OH radicals are generated by low temperature chain reaction. When this OH radicals reaches a certain level, first ignition occurs and main ignition occurs. As the proportion of methane increases, the generation of OH radicals decreases and the time required to reach the point of first ignition increases. also it was confirmed that the temperature rise also decreased at the first ignition point. As for fuel consumption, it can be seen that methane is slower in decomposition combustion than n-heptane because of the high octane number and autoignition temperature of methane fuel. As a result, methane was burned according to the accelerated combustion pattern of n-heptane with a high cetane number.

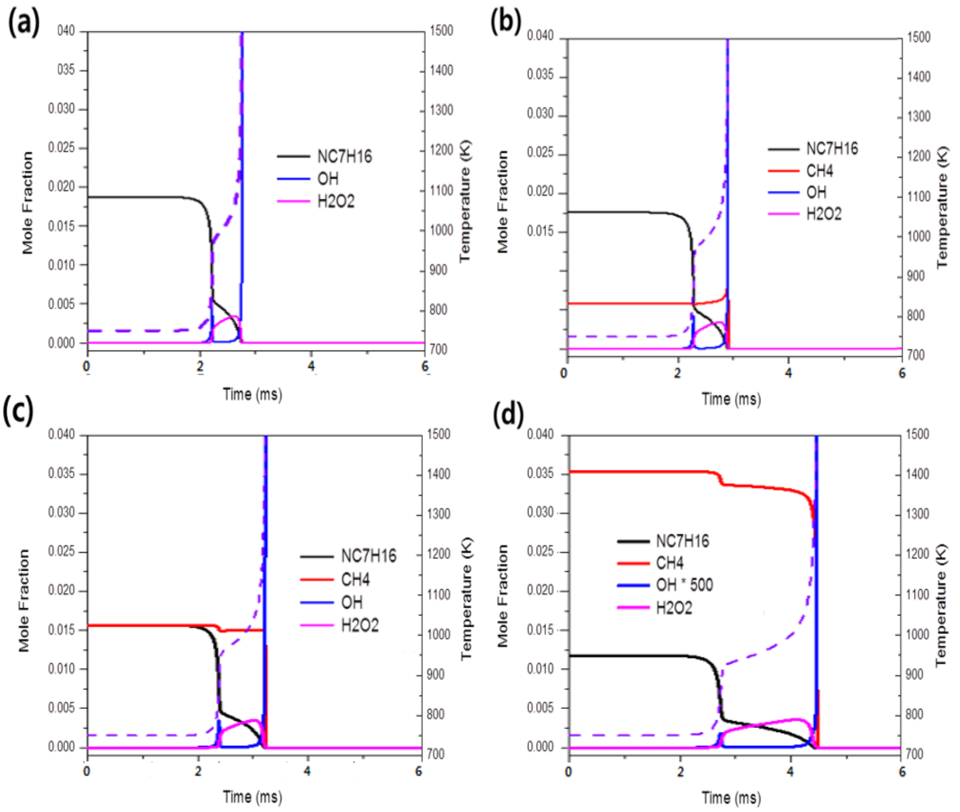

Figure 11. Computed combustion temperature and species concentrations of blended fuels at E.R=1.0, P=15atm, C.R=3.5, and O2=21% condition (a) H100, (b) H75M25, (c) H50M50 (d) H25M75.

Figure 12 shows the formation of H2O2 when the methane ratio is changed to 25%, 50%, and 75% at a compression temperature of 900K. The increase in H2O2 production is after the first ignition, but the annihilation point differs depending on the methane ratio. At high temperatures OH radicals are rapidly promoted and decomposed by H2O2 production. At low temperatures, however, the amount of H2O2 produced depends on the compression temperature, and as the methane ratio increases, the production amount decreases and the production time also becomes longer. This is due to the H atom-abstraction reaction of methane, which consumes a large amount of OH radicals and O2, leading to a lack of OH radicals and O2 necessary for the oxidation reaction of n-heptane, thus longer the first oxidation. As a result, the first ignition delay time becomes longer and the second oxidation action becomes slower. This is a major cause of delays in main ignition. In other words, the ignition phase control can control the ignition timing according to the mixing ratio of the mixed fuels.

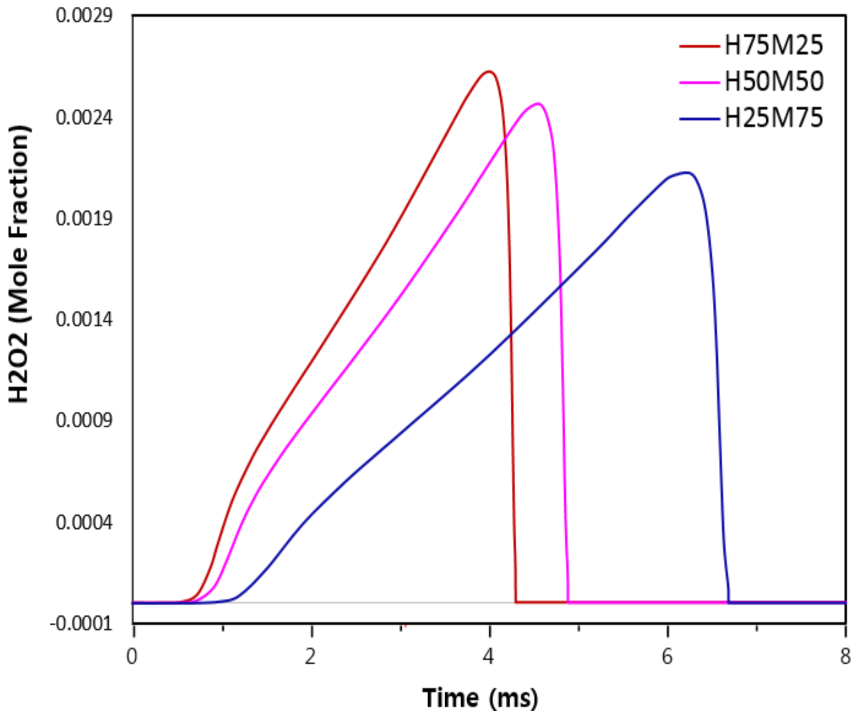

Figure 12. Mole Fraction H2O2 of blended fuels at Pressure temperature 900K, E.R(φ)=1.0, P=15atm, C.R=3.5 and O2=21% condition.

Figure 13 is the result of calculating the ignition delay time according to the oxygen concentration change of the n-heptane/ methane blended fuels. The equivalent ratio was 1.0, the compression pressure was 15 atm and the fuel composition ratio of n-heptane/ methane was adjusted to 5 : 5. By reducing the oxygen concentration in the air by 10%, 20% and 30%, the oxygen concentration was changed to 18.9%, 16.8%, and 14.7%, and the ignition delay time was calculated. The compression temperature was changed from 600K to 1000K at intervals of 50K, and the temperature was indicated in reverse order. As can be seen in Figure 13, the total ignition delay time increased with decreasing oxygen concentration of mixed fuel. It was compared of ignition delay time according to the oxygen concentration and mixing ratio. The mixing ratio was adjusted methane ration by 25%⟶ 50%⟶ 75% depending on the oxygen concentration. When the oxygen concentration was 18.9%, the ignition delay time increased from 26%⟶ 6%⟶ 2% depending on the methane ratio. When the oxygen concentration was 16.8%, the ignition delay time increased from 44%⟶ 29%⟶ 9% depending on the methane ratio. When the oxygen concentration was 14.7%, the ignition delay time increased from 55%⟶ 44%⟶ 27% depending on the methane ratio. As a result, when the oxygen concentration decreased by 10% ⟶ 20%⟶ 30%, the average ignition delay time was increased to 42% in H75M25, 26% in H50M50 and 13% in H25M75. This is because, as the oxygen ratio decreases in the combustion chamber, the reaction of the main oxidation reaction alkyl radical and the RO2 radical formed through O2 bond is greatly reduced at low temperature. In order to analyze the effect of oxygen concentration on total ignition delay time, the concentration of OH radicals generated by chain reaction at low temperature was calculated by oxygen concentration, respectively.

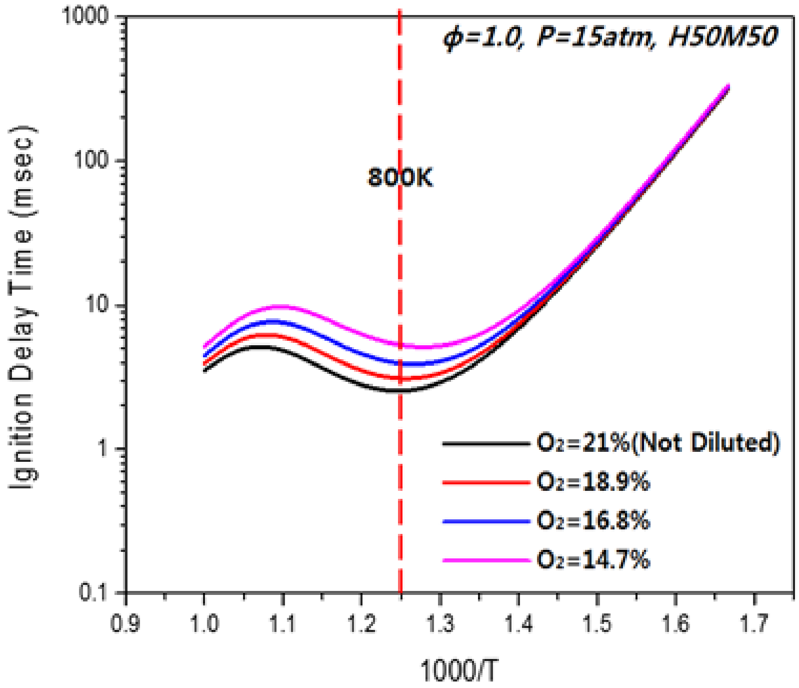

Figure 13. Main ignition delay times with changing oxygen concentration at E.R(φ)=1.0, P=15 atm, C.R=3.5

Figure 14 are a graph showing the concentration of OH radicals and the temperature in the combustion process according to changes in oxygen concentration. Figure 14 (a) shows the condition with the oxygen concentration of 21%, and (b) shows the condition with the oxygen concentration of 14.7%. As a result of the analysis, it can be confirmed that when the oxygen concentration is lowered, the increase in the concentration of the OH radical is lowered when the first ignition occurs. Also, it was found that the OH radicals was lowered when the oxygen concentration was 14.7% compared to the case where the oxygen concentration was 21% at the first ignition timing. As a result, the time required for the first ignition and the main ignition increased, and the overall ignition delay time increased. The reason for this result is that more than 70% of the exhaust gas is nitrogen when exhaust gas recirculation (EGR) is simulated. This is because the nitrogen contained in the mixed gas entering the combustion chamber acts as the heat load of the heterogeneous fuel in the combustion chamber. Thus, nitrogen lowers the temperature rise in the combustion chamber and reduces the production of intermediate species. In addition, the nitrogen gas itself has a high specific heat. These characteristics of nitrogen were also judged to be the cause of lower temperature rise.

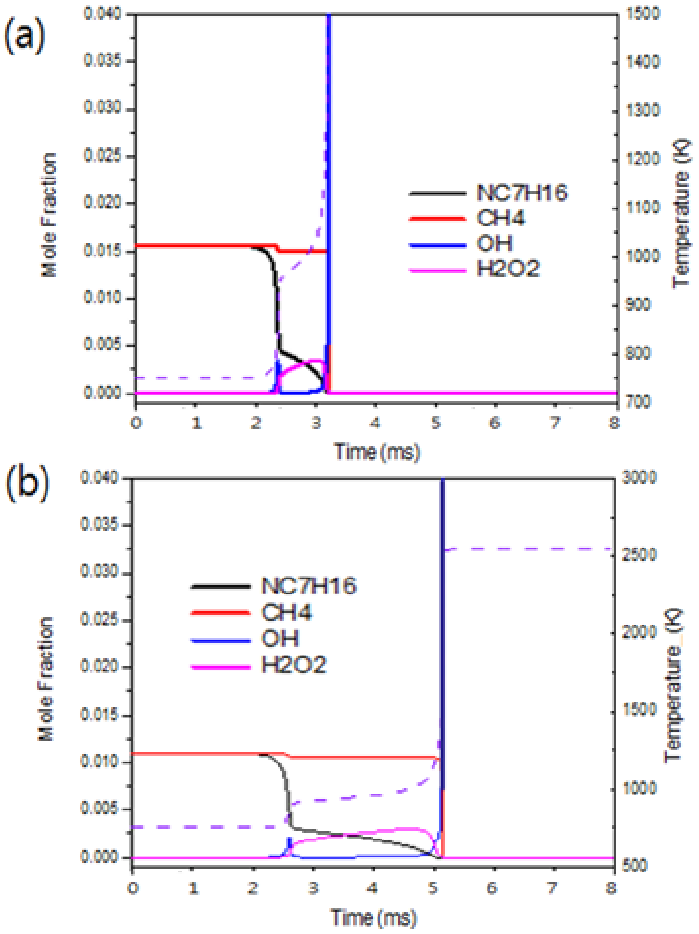

Figure 14. Computed mole fraction of OH radical and temperature for (a) O concentration=21% and (b) O concentration=14.7%, E.R(φ)=1.0, P=15 atm, C.R=3.5 and T0=750K

4.3.3. Sensitivity analysis

In previous studies, the n-heptane/methane blended fuels studies of Chunde et al. (2015) and Aggarwal et al.(2011), the combustion phenomena consistent with the results of this study have occurred. Figure 6, the blended fuels are able to observe the NTC region at 0~75% methane. In this region, as the compression temperature increases, the ignition delay time becomes longer. Sensitivity coefficients are positive and negative indicate ignition suppression reaction and ignition promotion reaction. The NTC region for mixed fuels is 850K~950K.

The 900 K is an NTC region, and the OH radical reaction accelerates the main oxidation reaction are promotion reactions. The HO2, H2O2, and CH4 + OH = CH3 + H2O reactions which inhibit the main ignition are suppression reactions. At 900 K, the OH radical inducing the oxidation reaction does not react with the n-heptane leading to the combustion reaction in the low temperature region and is consumed by methane, so that the mixed fuel has a strong oxidation suppression react against n-heptane. As a result, the reactivity is reduced and an NTC region is generated. Therefore, the ignition time becomes longer. At 900 K, the ignition inhibited HO2 and H2O2 species that are suppressed by methane are changed to ignition acceleration at 1100 K, and ignition delay time is shortened due to explosive combustion of n-heptane species.

5. Conclusions

Experiments were carried out using n-heptane/methane blended fuels using RCM simulating HCCI combustion technology under the combustion condition considering EGR. The following conclusions were obtained.

1) As a result of analyzing the reactivity of the n-heptane / methane blended fuels by adjusting the oxygen concentration to simulate a high EGR rate, changes in oxygen concentration were more sensitive than changes in composition of mixed fuels. As the oxygen concentration decreased by 10%, 20% and 30%, the ignition delay time increased by 11%, 27% and 42%, respectively, compared to the composition change of the mixed fuels. Totality ignition delay time increased by 27% on average.

2) As the methane increases, the ($CH4 + OH = CH3 + H2O$) oxidation reaction, which is a chain decomposition reaction of methane, limits the strong low-temperature oxidation of n-heptane with respect to the change in the mixed fuels ratio. Therefore, cool flame which is combustion characteristic by n-heptane is weakened, fuel consumption rate is decreased, and temperature rise is lowered. In addition, it was confirmed that the ignition delay time was increased by the change from the ignition promotion reaction to the suppression reaction.

3) In mixed fuels, methane suppresses autoignition due to high octane number, and n-heptane promotes autoignition with high cetane number. the NTC region and the two-stage ignition, which are the combustion characteristic of n-heptane, were observed at 0-75% of the methane content of the blended fuels during the compression ignition, and it was confirmed that the reaction of n-heptane was more dominant in the mixed fuels.

4) In the analysis of the chemical species inducing ignition, OH radicals promoted oxidation. OH radical generation was less as methane ratio increased in mixed fuels. The main ignition time was largely influenced by the first ignition, which is the occurrence of cool flame, so that the main ignition time was shortened due to the occurrence of cool flame.

5) The higher the compression ratio, the higher the compression temperature and pressure and the shorter the ignition delay time. It was confirmed that the combustion performance was improved by increasing the compression ratio.

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