5 New Concept of Ignition Control Using Products of Pre-Cool-Flame Reaction

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A computation with a detailed chemical-kinetics mechanism was carried out to estimate, when a set of the products from the low-temperature oxidation of premixed fuel is mixed with fresh fuel, how the products affect the low-temperature oxidation and ignition of the fresh fuel. A set of the products from a "pre-cool-flame reaction" just before the cool-flame reaction promotes the ignition most effectively. Another set of the products after the cool-flame reaction promotes the ignition, but not effectively, because it prolongs a period so called τ_2. In this case, the cool-flame reaction of the fresh fuel is terminated at a lower temperature than those in cases that τ_2 is shorter. Then, a reaction loop starting with the production of OH from H_2O_2, via the production of HCO and HO_2, to the reproduction of H_2O_2, has to drive itself at the lower temperature toward the ignition. This is caused mainly by a temperature rise with the cool-flame reaction of the premixed fuel, not by the products from the cool-flame reaction.

***Keywords*: Engine, Engine Combustion, Diesel Engine, Fumigation, Ignition, Chemical Kinetics**

1. INTRODUCTION

Multiple injection and fumigation can be effective technologies for a diesel engine to promote the ignition of the fuel of main injection. The latter is a technology that a small portion of fuel is prepared into the intake air to make a premixed lean mixture, and then, a main portion of fuel is injected into the mixture in the cylinder. In case of fumigation, dual-fuel operation is a possible option, in other words, the premixed fuel can be something different from the main-injection fuel, to optimize the ignition promotion. When the compression ratio is decreased for the lower mechanical loss and better fuel economy, those technologies can be applied usefully to improve the cold-start operation, and to realize mild combustion and reduce the combustion noise at high loads.

With those technologies, the low-temperature oxidation of the premixed fuel goes forward ahead of the main fuel injection. Then, the products from the low-temperature oxidation are mixed with the main fuel, and affect the low-temperature oxidation and ignition of the main fuel. According to studies on ignition control with fuel additives, some out of the products, such as HO_2, H_2O_2 and OH, can be effective promoters for the ignition[1, 2]. To the contrary, others such as some aldehydes can be inhibitors against the ignition[1, 3-6]. However, there is not enough information on how a whole set of the products affects the ignition.

In the present study, by means of simulation with a detailed chemical-kinetics mechanism, sets of the products from the low-temperature oxidation of premixed fuel are extracted in different stages of the low-temperature oxidation. Then, each set of the products is mixed with fresh fuel. It is estimated how the different sets of the products affect the low-temperature oxidation and ignition of the fresh fuel.

2. INSIGHT FROM FORMALDEHYDE FUMIGATION

Figure 1 compares histories of the in-cylinder pressure and the effective rate of heat release, with and without CH_2O fumigation, as experimental results[5]. A direct-injection diesel engine was operated at an air excess

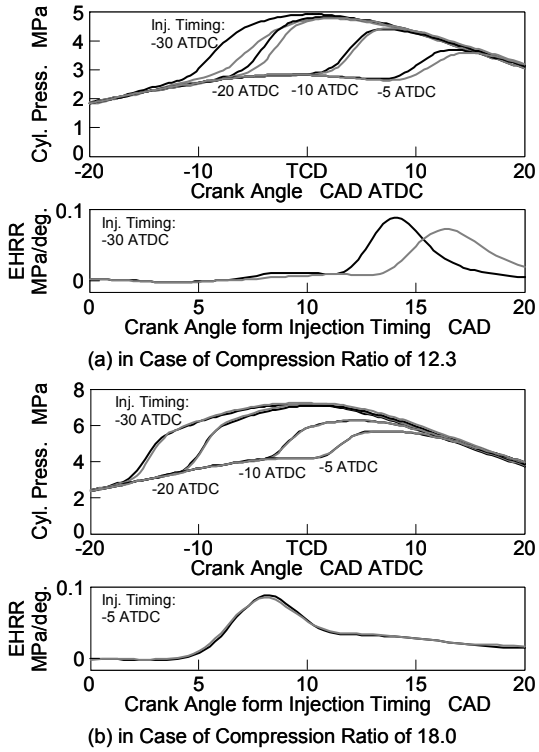


Fig. 1 Histories of In-Cylinder Pressure and EHRR with and without CH_2O Fumigation (Engine Speed: 1200 min^{-1}, Air Excess Ratio: 3.4, Injection Pressure: 50 MPa, Initial CH_2O: 1900 ppm)

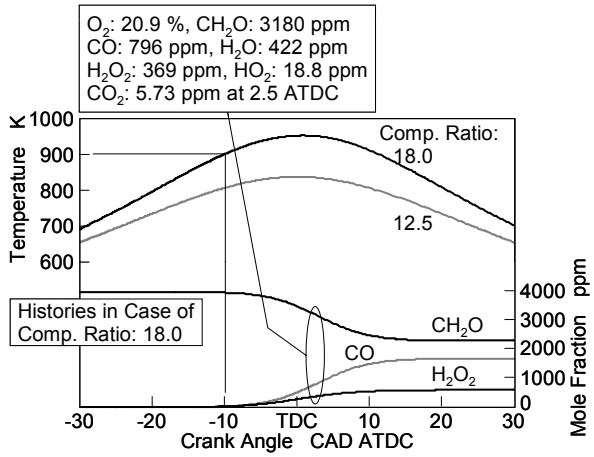


Fig. 2 Histories of Temperature and CH_2O and H_2O_2 Concentrations during Compression of CH_2O with Air (Compression Speed: 833 min^{-1}, Initial CH_2O: 4000 ppm)

ratio of 3.4, compression ratios of 12.3 and 18.0, and at an engine speed of 1200 min^{-1}. Vapor of CH_2O was added to the intake air at a concentration of about 1900 ppm. At the low compression ratio, the CH_2O addition definitely retards the ignition with any fuel injection timings. At the high compression ratio, to the contrary, there is a case that the CH_2O slightly advances the ignition with a late injection timing of -5 crank angle degrees ATDC.

The opposite effects of the CH_2O addition on the ignition were explained in the following way[5]. As shown in **Fig. 2**, when CH_2O with air is computationally piston-compressed at an initial concentration of 4000 ppm, an initial temperature of 320 K, and an initial pressure of 0.1 MPa, a compression ratio of 12.5, and a compression speed of 833 min^{-1}, it is hardly oxidized during the compression. At a compression ratio of 18.0, on the other hand, a part of CH_2O is oxidized into CO, HO_2 and H_2O_2 at temperatures above 900 K. The CH_2O itself can be an OH radical scavenger as $CH_2O+OH \rightarrow HCO+H_2O$, and against $RH+OH \rightarrow R+H_2O$ in the initial stage of the low-temperature oxidation of fuel. The HO_2 and H_2O_2 can be OH generators as $H_2O+H_2O \rightarrow H_2O_2+O_2$ and $H_2O_2+M \rightarrow 2OH+M$ in the late stage of the low-temperature oxidation. The opposite effects of CH_2O fumigation are based on the seesaw between the ignition-inhibiting effect of the CH_2O, and the promoting effect of the HO_2 and H_2O_2.

The above findings suggest that, with multiple injection or fumigation, if the ratios between the concentrations of aldehydes, HO_2 and H_2O_2 generated from the premixed fuel, are changed, the ignition of the fuel of main injection could be controlled.

Figure 3 shows histories of the concentrations of typical species, when premixed n-heptane is computationally piston-compressed, as mentioned later. The low-temperature oxidation goes forward, but not to the ignition. There are two kinds of histories during the low-temperature oxidation. The concentrations of some species such as CO, CO_2, aldehydes and H_2O_2 increase monotonously, until they are settled in a steady state where they are kept almost constant. On the other hand, the concentrations of the others including alkyl and alkyl peroxy radicals, HO_2 and OH increase and then, decrease, before being settled in the steady state. In other words, they behave just like overshooting. The peak of the

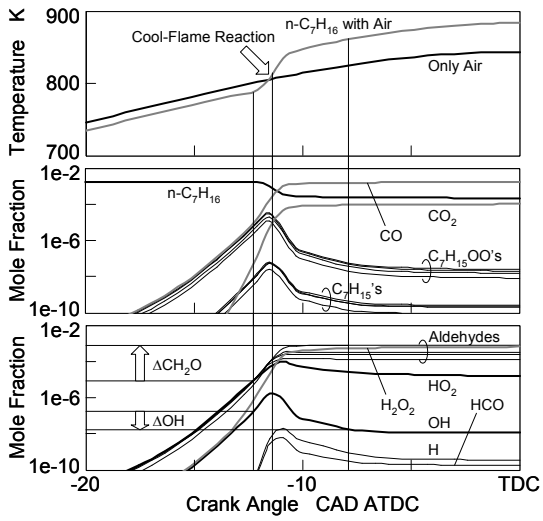


Fig. 3 Histories of Concentrations of Typical Species during Compression of $n\text{-}CH_7H_{16}$ with Air (Compression Ratio: 12.0, Compression Speed: 1000 min^{-1}, Equivalence Ratio: 0.1)

overshoot is coincident with a middle timing in the period of the cool flame reaction assumed with a temperature rise. Because of the two kinds of histories, at a timing a little before the peak of the overshoot, the concentrations of aldehydes are tens of times lower than those at a timing after the peak, while at the timing before the peak, the concentrations of some radicals are higher than those at the timing after the peak. That is, the ratios between the concentrations of aldehydes and some radicals out of the products from a "pre-cool-flame reaction" are considerably different from those out of the products from or after the cool flame reaction.

3. COMPUTATIONAL PROCEDURE

3.1 Simulation of Fumigation

A two-step simulation with a detailed chemical-kinetics mechanism of n-heptane[7] was carried out, making use of the reactor networking tool of the CHEMKIN 4.0[8].

In the first step of the simulation, n-heptane with air was piston-compressed at an initial temperature of 330 K, an initial pressure of 0.10 MPa, an equivalence ratio of 0.1, a compression ratio of 12.0, and at compression speeds of 1000, 2000, 3000, 4000 and 5000 min^{-1} (compression periods of 30, 15, 10, 7.5 and 6 ms from BDC to TDC). The low-temperature oxidation went forward during the compression, but did not turn to the ignition. Then, all the components at TDC were transferred into the second step. The compression speed was changed so that how forward the low-temperature oxidation went during the compression, could be controlled, and the concentrations of the components at TDC could be changed.

In the second step, fresh n-heptane was mixed with the components from the first step, to prepare a stoichiometric mixture. Then, the mixture was ignited on the constant-volume condition starting with the temperature and pressure at TDC in the first step. The initial conditions of the second step are summarized in **Table 1**. There was no consideration of the vaporization and mixing of the fresh fuel. N-heptane only with the compressed air was also ignited on the constant-volume condition, as in case without any fumigation.

Table 1 Initial Conditions of Constant-Volume Ignition Step
(Equivalence Ratio in Compression Step: 0.1 or 0.0, Equivalence Ratio in Constant-Volume Ignition Step: 1.0)

Comp. Speed and Comp. Period in 1st Step		w/o Fumigation	1000 min^{-1}, 30 ms	2000 min^{-1}, 15 ms	3000 min^{-1}, 10 ms	4000 min^{-1}, 7.5 ms	5000 min^{-1}, 6.0 ms
Initial Temp. and Press. in 2nd Step		844.3 K, 3.11 MPa	884.7 K, 3.27 MPa	872.3 K, 3.22 MPa	865.5 K, 3.20 MPa	836.7 K, 3.08 MPa	830.5 K, 3.06 MPa
Initial Mole Fractions of Typical Species in 2nd Step	n-c7h16	1.87e-02	1.70e-02	1.71e-02	1.72e-02	1.82e-02	1.87e-02
	o2	2.06e-01	2.01e-01	2.02e-01	2.02e-01	2.05e-01	2.06e-01
	co	None	1.88e-03	1.32e-03	1.03e-03	7.29e-05	1.64e-06
	c7h15-1	None	2.32e-10	4.44e-10	2.73e-09	7.41e-08	3.41e-09
	c7h15-2	None	2.91e-10	5.54e-10	3.29e-09	8.94e-08	4.13e-09
	c7h15-3	None	2.25e-10	4.28e-10	2.53e-09	7.11e-08	3.29e-09
	c7h15-4	None	9.93e-11	1.89e-10	1.12e-09	3.24e-08	1.51e-09
	c7h15o2-1	None	1.59e-08	3.98e-08	2.84e-07	1.46e-05	7.70e-07
	c7h15o2-2	None	2.57e-08	6.44e-08	4.46e-07	2.35e-05	1.26e-06
	c7h15o2-3	None	2.13e-08	5.37e-08	3.72e-07	2.05e-05	1.10e-06
	c7h15o2-4	None	8.63e-09	2.15e-08	1.48e-07	8.29e-06	4.47e-07
	ch2o	None	8.45e-04	7.35e-04	6.13e-04	4.59e-05	9.77e-07
	ch3cho	None	3.41e-04	3.09e-04	2.88e-04	5.57e-05	1.82e-06
	c2h5cho	None	2.54e-04	2.41e-04	2.31e-04	5.62e-05	1.97e-06
	n-c3h7cho	None	1.24e-04	1.34e-04	1.39e-04	5.00e-05	2.00e-06
	h	None	3.68e-10	6.24e-10	4.48e-09	2.32e-09	3.54e-12
	h2o2	None	6.80e-04	4.95e-04	3.42e-04	1.31e-05	9.09e-08
	hco	None	1.97e-10	2.42e-10	9.45e-10	1.10e-09	3.80e-12
	ho2	None	1.59e-05	2.36e-05	4.95e-05	4.30e-05	2.91e-06
	o	None	5.31e-10	6.56e-10	2.21e-09	2.27e-09	2.96e-12
	oh	None	1.18e-08	1.66e-08	8.76e-08	1.30e-06	5.04e-08
	c2h5	None	3.75e-09	5.93e-09	2.50e-8	1.88e-07	6.51e-09

3.2 Contributions of Elementary Reactions

Results from the second step of the simulation were analyzed on worksheets of the Microsoft Excel, employing the macro tool.

All elementary reactions together with the factors of the reaction rate constant equation in the kinetics mechanism, were arranged on a worksheet, and the thermodynamics data[7] on another worksheet. Histories of the temperature and the concentrations of all species, as output from the CHEMKIN, were arranged on a matrix of temperatures in the first column, and species in the first raw, on another worksheet. The enthalpy, entropy and specific heat at constant pressure of each species were derived from the thermodynamics data and the temperature, and were arranged on temperature-species matrices on other worksheets. The forward and backward reaction rate constants of each elementary reaction were derived from the factors of the reaction rate constant equation, the temperature, and the enthalpies and entropies of the related species, and were arranged on a matrix of temperatures in the first column, and elementary reactions in the first row, on another worksheet. The rate of heat release by each elementary reaction was derived from the concentrations and enthalpies of the related species, and the reaction rate constants, and was arranged on a temperature-reaction matrix on another worksheet.

With one species pointed out, the elementary reactions related to the species, were extracted. The forward and backward reactions were handled separately, in consideration of some species in the steady state, or some reactions in the state of partial equilibrium. The rate of production of the species by each of the forward and backward reactions was derived from the concentrations of the related species, and the reaction rate constant. The contribution of each of the forward and backward reactions to the production of the species was defined as

$$cnt_{j,k}=rop_{j,k}/(sm\_rop_{+,k}+|sm\_rop_{-,k}|),\ j=2i-1 \text{ or } 2i,$$

where $cnt_{j,k}(j=2i-1)$ is the contribution of the i^{th} forward reaction to the production of the k^{th} species, $cnt_{j,k}(j=2i)$ is the contribution of the i^{th} backward reaction, $rop_{j,k}(j=2i-1)$ is the rate of production of the k^{th} species by the i^{th} forward reaction, $rop_{j,k}(j=2i)$ is the rate of production by the i^{th} backward reaction, $sm\_rop_{+,k}$ is the sum of those with plus values out of the $rop_{j,k}$'s($i=1$ to N_k), and $sm\_rop_{-,k}$ is the sum of those with minus values. Finally, those out of the forward and backward reactions related to the species, of which the contributions were more than a threshold at least at a temperature in the histories of the temperature, were extracted as important reactions for the production of the species. The rates of production by the important reactions were arranged on a temperature-reaction matrix on another worksheet, and the contributions of the important reactions on a temperature-reaction matrix on another worksheet. The threshold was set at 0.03.

When thermally-important reactions were extracted, an expedient contribution factor was defined as

$$cnt\_therm_i=rohr_i/(sm\_rohr_+ +|sm\_rohr_-|),$$

where $rohr_i$ is the sum of the rates of heat release by the i^{th} forward and backward reactions, sm_rohr_+ is the sum of those with plus values out of the $rohr_i$'s($i=1$ to N), and sm_rohr_- is the sum of those with minus values. Those out of all the elementary reactions, of which the contribution factors were more than a threshold at least at a temperature in the histories of the temperature, were extracted, and arranged on a temperature-reaction matrix on another worksheet. The threshold was set at 0.03.

4. COMPUTATIONAL RESULTS AND DISCUSSION

4.1 Effects of Fumigation on Ignition

Figure 4 compares histories of the temperature in the compression and constant-volume ignition steps with and without the fumigation. In the compression step, as the compression speed is set higher, a temperature rise with the cool-flame reaction appears later in crank angle degrees. At compression speeds of 1000 to lower than 4000 min^{-1}, the cool-flame reaction appears before TDC. At 4000 min^{-1}, the cool-flame reaction is just about to start at TDC. At and above 4000 min^{-1}, therefore, the products

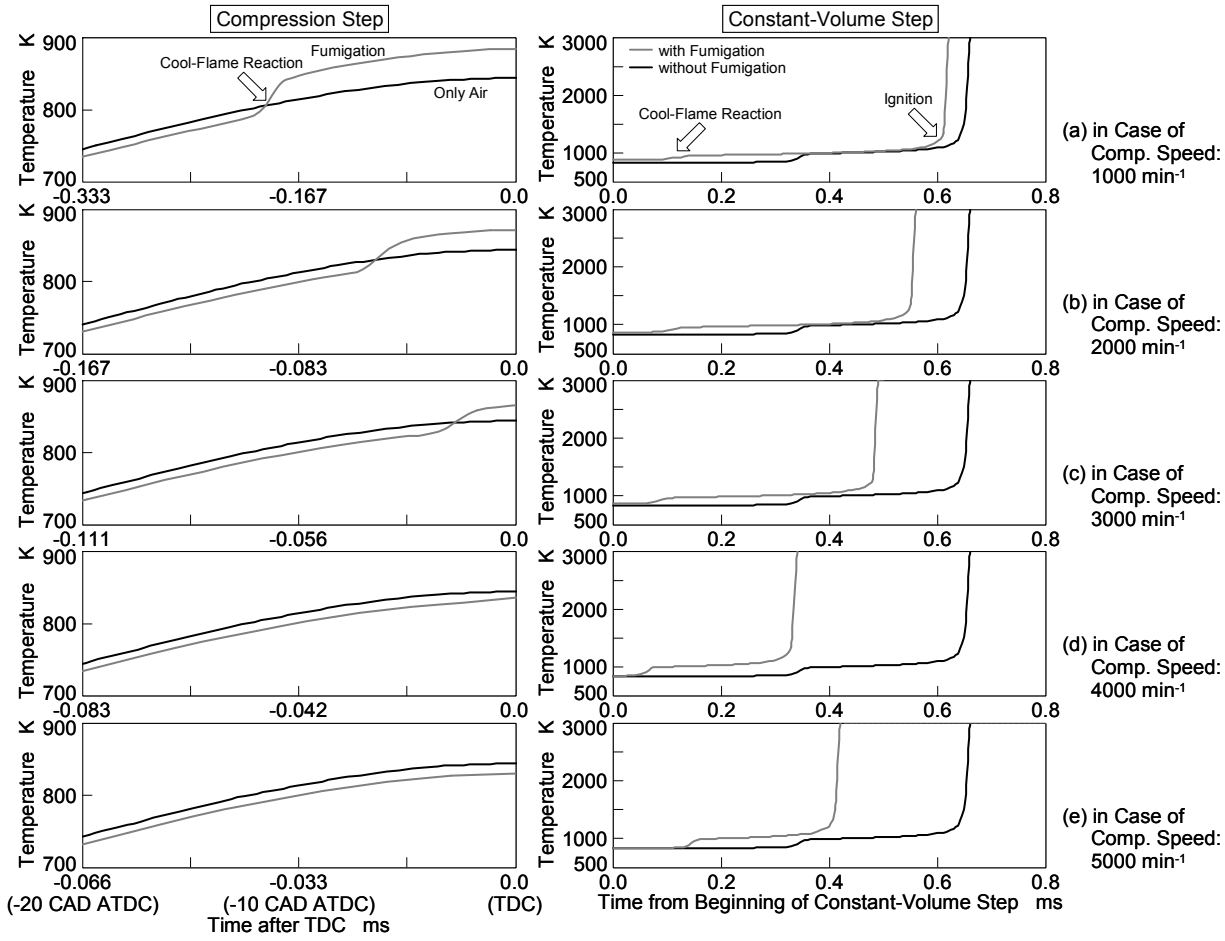


Fig. 4 Histories of Temperature in Compression and Constant-Volume Ignition Steps

from a "pre-cool-flame" reaction are prepared at TDC. Below 4000 min^{-1}, on the other hand, the products from or after the cool-flame reaction are prepared at TDC.

In the constant-volume step with the fumigation, a temperature rise with the cool-flame reaction appears, although it once appeared in the compression step. As the compression speed is set higher to 4000 min^{-1}, the ignition is more advanced from that without any fumigation. After the compression at 4000 min^{-1}, the ignition is most advanced, as a result that a period from the beginning of the step to the beginning of the cool-flame reaction, so called τ_1, is much shortened from that without any fumigation. Also, a period from the beginning of the cool-flame reaction to the ignition, so called τ_2, is most shortened, compared to those with the fumigation at the other compression speeds. Below 4000 min^{-1}, τ_2 is prolonged from that without any fumigation. At 5000 min^{-1}, the ignition is retarded from that at 4000 min^{-1}, as a result that τ_1 is prolonged. After all, a set of the products from a "pre-cool-flame reaction" just before the cool-flame reaction in the compression step can promote the ignition in the constant-volume step, most effectively.

4.2 Reaction Loop Dominating Ignition

Figure 5 shows temperature-domain histories of the concentrations of typical species, the sum of the forward and backward rates of heat release by important elementary reactions, and the contributions of important reactions to the production of typical species, in the constant-volume step without any fumigation.

In Fig. 4, the time-domain history of the temperature in the constant-volume step shows that a sudden temperature rise with the ignition appears, just after the temperature reaches about 1100 K. According to the temperature-domain history of the rate of production of OH, however, the rate of production by $H_2O_2+M \rightarrow 2OH+M$ which is assumed to play an important role in branching OH in the final stage of low-temperature oxidation, increases continuously, and does not change suddenly at about 1100 K.

In the late stage of the low-temperature oxidation, the most important reaction for the production of OH is $H_2O_2+M \rightarrow 2OH+M$. This is the main endothermic reaction. The most important one for the production of H_2O_2 is $2HO_2 \rightarrow H_2O_2+O_2$. The most important one for the production of HO_2 is $HCO+O_2 \rightarrow CO+HO_2$. And the most important one for the production of HCO is $CH_2O+OH \rightarrow HCO+H_2O$. These are important exothermic reactions, as well. Those reactions network a reaction loop, as shown in **Fig. 6**. This loop starting with $H_2O_2+M \rightarrow 2OH+M$, cannot reproduce H_2O_2 by itself, enough to drive itself again, because, especially, the branching ratio of the consumption of OH by $CH_2O+OH \rightarrow HCO+H_2O$ to the total consumption of OH is not so high. With the aid of OH, HCO and HO_2 produced by other reactions, however, the loop produces heat for the endothermic reaction to go forward continuously.

Figure 7 shows Arrhenius plots of the absolute values of the sums of the forward and backward rates of reaction of thermally-important reactions, in the constant-volume

step without any fumigation. As the cool-flame reaction is terminated, the rates of reaction except for that of $H_2O_2+M \rightarrow 2OH+M$ once decrease. On the other hand, the rate of reaction of $H_2O_2+M \rightarrow 2OH+M$ increases monotonously from low to high temperatures. It is considered that this reaction plays an important role in increasing the rates of reaction of the other reactions again after the cool-flame reaction. In the late stage of the low-temperature oxidation, the rates of reaction of the reactions in the loop increase almost linearly with almost the same gradients. This is evidence that the loop rate-determined by the endothermic reaction, dominates the late stage of the low-temperature oxidation. And also, the ignition is nothing peculiar at about 1100 K, but a stage of the reactions continuously going forward.

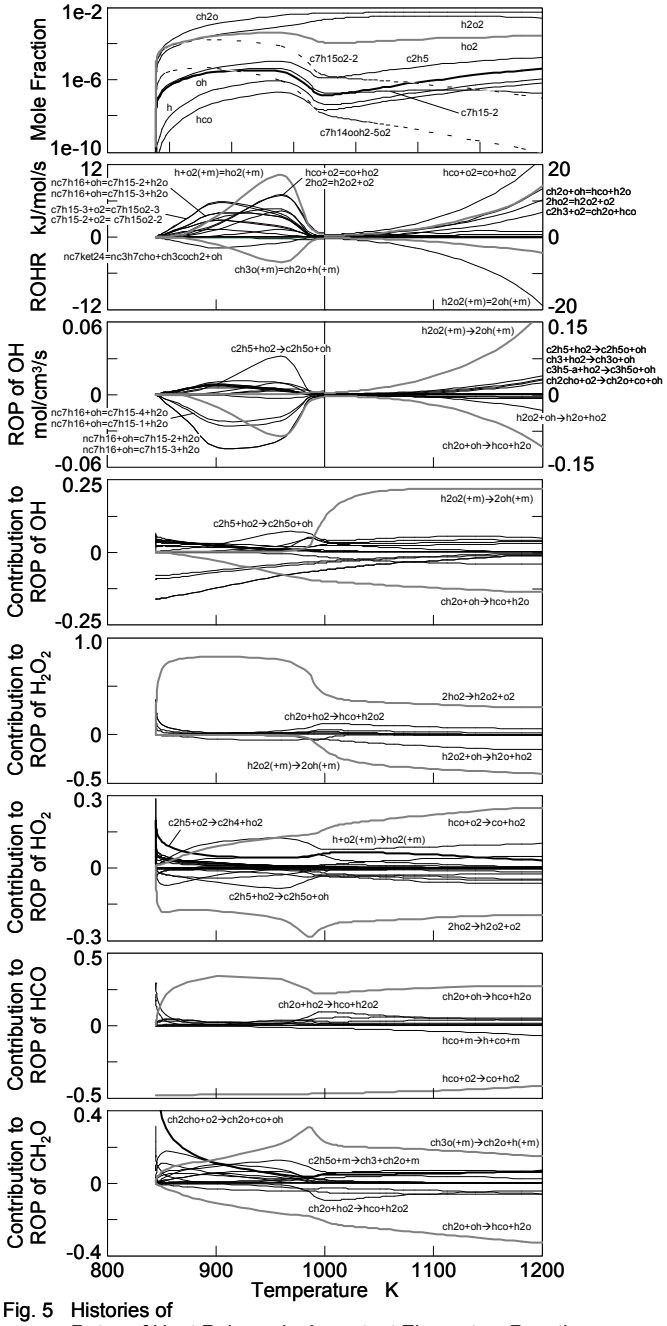


Fig. 5 Histories of
Rates of Heat Release by Important Elementary Reactions
and Contributions of Important Reactions to
Production of Typical Species
in Constant-Volume Ignition Step without Fumigation

4.3 Mechanisms of Effects of Fumigation

It is easily understood that τ_1 is shortened with the fumigation, because the species related to the cool-flame reaction, are prepared at the beginning of the constant-volume ignition step, and a period for the accumulation of them is shortcut.

Figure 8 shows temperature-domain histories of the concentrations of typical species, the sum of the forward and backward rates of heat release by important reactions, and the contribution of important reactions to the production of OH, with the fumigation after the compression at 1000 and 4000 min^{-1}. Regarding the consumption of OH at the beginning of the cool-flame reaction, $CH_2O+OH \rightarrow HCO+H_2O$ is not so interferential with $RH+OH \rightarrow R+H_2O$'s. That is, CH_2O with the other products from the fumigation is not an effective OH scavenger against the cool-flame reaction. The histories in the late stage of the low-temperature oxidation are not so different from those without any fumigation in Fig. 5. It is considered that the products from the fumigation can affect the cool-flame reaction, but cannot directly touch the late stage of the low-temperature oxidation.

At 1000 min^{-1}, or in case that τ_2 is most prolonged, the heat release with the cool-flame reaction is weakened. In detail, the heat release by $RH+OH \rightarrow R+H_2O$ and $R+O_2 \rightarrow ROO$, which accounts for the main part in the early stage of the cool-flame reaction, is weakened. And,

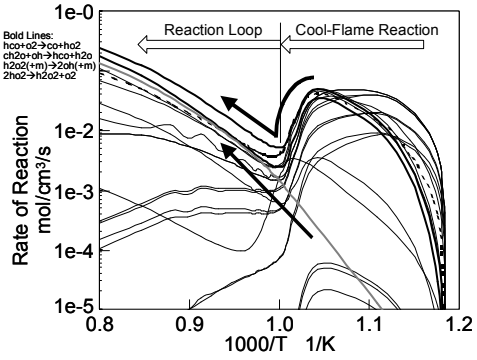
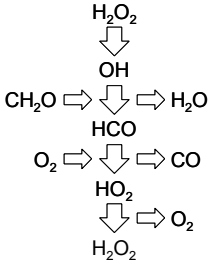
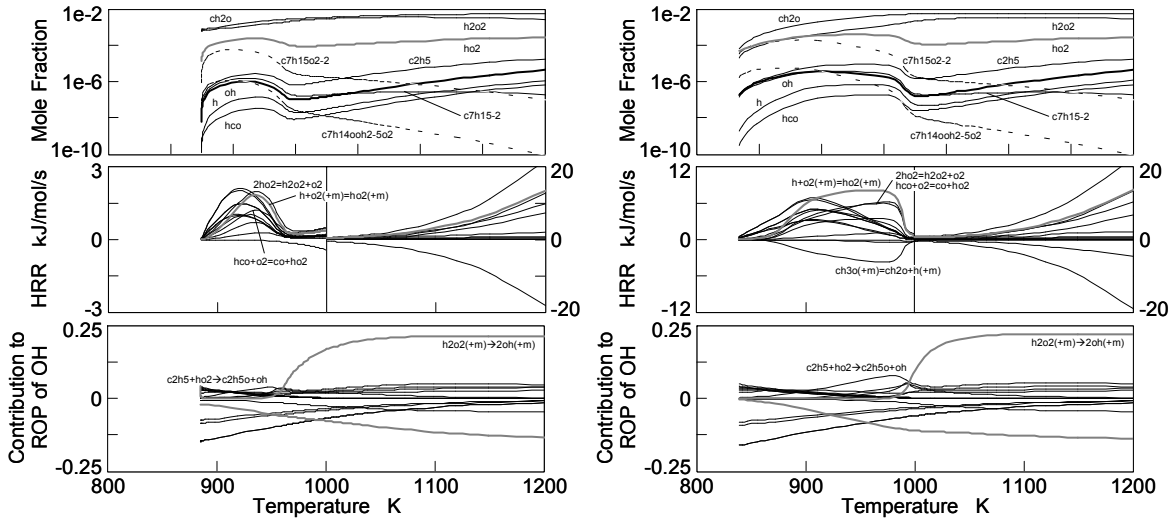


Fig. 7 Arrhenius Plots of Rates of Reaction of
Thermally-Important Elementary Reactions
in Constant-Volume Ignition Step without Fumigation



Species	Sum of Rates of Consumption (ROC's) of Species by Related Reactions at 1000 K mol/cm³/s	Elementary Reaction	ROC of Species at 1000 K mol/cm³/s	Ratio of ROC of Species by Reaction to Sum of ROC's %	Sum of Forward/Backward Rates of Heat Release kJ/cm³/s		
					1000 K	1050 K	1100 K
H_2O_2	2.36e-03	$H_2O_2+M+218\ kJ \rightarrow 2OH+M$	1.39e-03	58.9	-0.303	-1.42	-3.77
OH	1.20e-02	$CH_2O+OH \rightarrow HCO+H_2O+123\ kJ$	2.41e-03	20.1	0.295	0.854	2.38
HCO	5.45e-03	$HCO+O_2 \rightarrow CO+HO_2+139\ kJ$	5.09e-03	93.4	0.707	1.80	4.63
HO_2	1.61e-02	$2HO_2 \rightarrow H_2O_2+O_2+165\ kJ$	7.79e-03	48.4	0.644	1.16	2.56

Fig. 6 Reaction Loop Driving $H_2O_2+M \rightarrow 2OH+M$ at 1000 K



(a) after Compression at 1000 min^{-1} (b) after Compression at 4000 min^{-1}

Fig. 8 Histories of Rates of Heat Release by Important Elementary Reactions and Contributions of Important Reactions to Production of OH in Constant-Volume Ignition Step with Fumigation

the heat release by $H+O_2+M \rightarrow HO_2+M$ and $HCO+O_2 \rightarrow CO+HO_2$, which would account for a considerable part in the late stage, is remarkably weakened. It is considered that the latter is caused by the less accumulated CH_2O than those in the other cases, because, in the late stage of the cool-flame reaction, the most important reaction for the production of HCO is $CH_2O+OH \rightarrow HCO+H_2O$, and the most important one for the production of both H and CH_2O is $CH_3O+M \rightarrow CH_2O+H+M$. As a result that the products from the cool flame reaction are less accumulated, the cool-flame reaction is terminated at a lower temperature. **Figure 9** shows Arrhenius plots of the absolute values of the sums of the forward and backward rates of reaction of thermally-important reactions, after the compression at 1000 min^{-1}. The reaction loop has to drive itself at the lower temperature. Although it was not expected, after all, the longer τ_2 is caused mainly by the higher initial temperature in the constant-volume step in a range of the temperature, so called "the range of negative temperature dependence", not by the products from the fumigation.

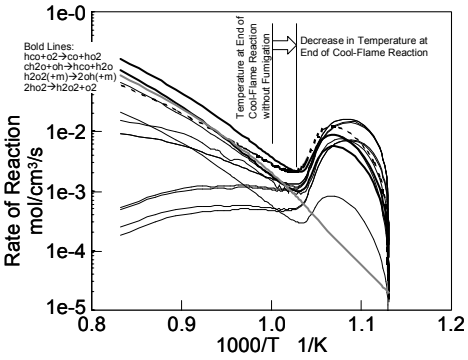


Fig. 9 Arrhenius Plots of Rates of Reaction of Thermally-Important Elementary Reactions after Compression at 1000 min^{-1} with Fumigation

5. CONCLUSION

A computation with a detailed chemical-kinetics mechanism of n-heptane was carried out to estimate, when sets of the products from the low-temperature oxidation of premixed fuel are extracted in different stages of the low-temperature oxidation, and then, each set of the products is mixed with fresh fuel, how the different sets of products affect the low-temperature oxidation and ignition of the fresh fuel. A set of the products from a "pre-cool-flame reaction" just before the cool-flame reaction promotes the ignition most effectively. Another set of the products after the cool-flame reaction promote the ignition, but not effectively, because it prolongs a period from the beginning of the cool-flame reaction to the ignition, so called τ_2, although it shortens another period to the beginning of the cool-flame reaction, so called τ_1.

Analysis of the contributions of all forward and backward elementary reactions to the production of typical species found out that CH_2O with the other products from the cool-flame reaction of the premixed fuel cannot be an effective OH scavenger against the cool-flame reaction of the fresh fuel, as expected. A reaction loop starting with the production of OH from H_2O_2, via the production of HCO and HO_2, to the reproduction of H_2O_2, dominates the late stage of the low-temperature oxidation to the ignition. In case that τ_2 is longer, the cool-flame reaction of the fresh fuel is terminated at a lower temperature than those in cases that τ_2 is shorter. Then, the reaction loop has to drive itself at the lower temperature. This is caused by a temperature rise with the cool-flame reaction of the premixed fuel, not by the products from the cool-flame reaction, as expected.

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