Impact of Formaldehyde Addition on Auto-Ignition in Internal-Combustion Engines*

Kazunari KUWAHARA**, Hiromitsu ANDO***, Masahiro FURUTANI**** and Yasuhiro OHTA****

By employing a direct-injection diesel engine equipped with a common-rail type of injection system, by adding formaldehyde (CH$_2$O) to the intake air, and by changing the fuel-injection timing, the compression ratio and the intake-air temperature, a mechanism for CH$_2$O as a fuel additive to affect auto-ignition was discussed. Unlike an HCCI type of engine, the diesel engine can expose an air-fuel mixture only to a limited range of the in-cylinder temperature before the ignition, and can separate low- and high-temperature parts of the mechanism. When low-temperature oxidation starts at a temperature above 900 K, there are cases that the CH$_2$O advances the ignition timing. Below 900 K, it always retards the timing. It is because, above 900 K, a part of the CH$_2$O changes into CO together with H$_2$O$_2$ as an ignition promoter. Below 900 K, on the other hand, the CH$_2$O itself acts as an OH radical scavenger against cool-flame reaction, from the beginning of low-temperature oxidation. Then, the engine was modified for its extraordinary function as a gasoline-knocking generator, in order that an effect of CH$_2$O on knocking could be discussed. The CH$_2$O retards the onset of auto-ignition of an end gas. Judging from a large degree of the retardation, the ignition is probably triggered below 900 K.

Key Words: Internal Combustion Engine, Ignition, Combustion, Auto-Ignition, Spray Combustion, Knocking, Ignition Control, Additive, Formaldehyde, Flame Light Emissions

1. Introduction

There are auto-ignition dominated subjects of combustion in internal combustion engines, that is, those of combustion control for homogeneous-charge compression-ignition (HCCI) types of engines, knocking control for gasoline engines, and new combustion modes for diesel engines to reduce both NO$_x$ and smoke emissions. Especially of HCCI engines, a lot of researchers have been making efforts to resolve one of its difficult problems, how to control the ignition timing and stabilize the sensitive timing, as they recognized its potential advantages of a high thermal efficiency and very-low NO$_x$ and zero smoke emission levels. Effects of directly-controllable factors such as fuel properties and engine-operating conditions of the intake-air temperature, the compression ratio, the air-fuel ratio and the EGR ratio on the ignition have been investigated. As another approach to HCCI timing control, ideas of making use of a fuel additive, for example, hydrogen peroxide$^{(1)}$ or ozone$^{(2)}$ as an ignition promoter, and formaldehyde$^{(3)-(5)}$ or methanol$^{(2)}$ as an ignition retardant, have been proposed. By Aceves et al. with the aid of calculation involving one-dimensional hydrodynamics transport and detailed chemical kinetics, hundreds of potential additives were ranked according to their capabilities for advancing the ignition timing$^{(6)}$.

Furutani and Ohta et al. proposed that formaldehyde (CH$_2$O), one of the typical intermediates out of low-temperature oxidation of a hydrocarbon fuel up to the following ignition, can be also an effective fuel additive in

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* Received 25th April, 2005 (No. 05-4028)
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controlling the ignition timing. Then, they presented effects of CH2O addition on HCCI\textsuperscript{(3),(4)}. In an experiment, a small amount of CH2O was added to an air normal-butane mixture. The in-cylinder temperature at TDC, assuming that any ignition did not occur, was changed by heating of the charge. As summarized in Fig. 1\textsuperscript{(4)}, the CH2O retarded the ignition timing, compared to that without the addition, in 800s K. When the temperature at TDC was increased up to 900 K, to the contrary, the CH2O slightly advanced the timing. There was also a range of the temperature, where the more addition less retarded the timing. It is well-known that auto-ignition of a general hydrocarbon fuel exhibits different profiles of low-temperature oxidation, according as a temperature at which the air-fuel mixture has been left immediately before the oxidation. In other words, the behavior turns from the cool-flame reaction dominant, through the negative temperature dependent, to the blue-flame reaction dominant, as the initial temperature is set higher. Taking this into account, the opposite effects of CH2O may be caused by possible interactions of CH2O with cool-flame reaction and blue-flame reaction in different ways. In the experiment using an HCCI engine, however, there is difficulty in understanding the phenomena, because of the complexity that, even in case of the blue-flame reaction dominant ignition with a high temperature at TDC, a mixture experiences also lower temperatures at which cool-flame reaction can be dominant, during the compression before TDC.

In the present study, a direct-injection diesel engine equipped with a common-rail type of injection system, is employed to prepare a fuel, gas oil, in a short period during the compression, and to expose the air-fuel mixture only to a limited range of the in-cylinder temperature. CH2O is added to the intake air in advance of the fuel preparation. Effect of the CH2O addition on the ignition delay is investigated, when the fuel-injection timing, the compression ratio, the intake-air temperature and amount, and the O2 level in the charge are changed. Next to the conventional use, the engine is modified for its extraordinary use as a spark-ignition engine, in order that effect of the CH2O on the knocking of an air-gasoline mixture can be investigated.

2. Experimental Procedure

2.1 Test engine and its operating conditions

A four-valve single-cylinder naturally-aspirated direct-center-injection diesel engine equipped with a common-rail type of injection system, was supplied for this study. A pressure transducer (AVL GU12S-10) was mounted on the cylinder head, in place of the glow plug. The intake-air temperature was measured 70 mm upstream of an intake valve. A part of the exhaust gas was by-passed into an exhaust-gas analyzer (Horiba MEXA-8220D). Table 1 lists specifications of the engine together with its operating conditions. In a conventional use of the engine fueled with gas oil (cetane index (JISK2280): 52), the compression ratio was set at 18.0 or 12.3. The fuel-injection timing was changed between −30 and −5 crank-angle degrees (CAD) ATDC. The injection timing of −30 CAD ATDC is close to the limit of the advancement, for fuel sprays out of the multi-hole nozzle to be captured within the piston cavity. But also, conveniently, it is almost coincident with a timing before which any cool flame could not appear at the low compression ratio, even in case of HCCI. There was also a case at the low compression ratio, that the intake-air temperature was increased by 50 K using a heater installed upstream of the intake manifold, in order that the in-cylinder temperature at TDC only with the air could be almost the same as that at the high compression ratio without any heating. In these ways, a temperature to which an air-fuel mixture was exposed before the auto-ignition, was changed between 660 and 930 K at a rough estimate with the intake-air temperature without any consideration of a residual gas and a heat loss. In another case at the low compression ratio, O2 was added to the intake air, and its level in the charge was increased up to 26.0%, so that the difference could be discussed, when the ignition delay was shortened by the high temperature or by the high O2 level.

Vapor of formaldehyde (CH2O) was continuously added to the intake air at a location between the intake-air heater and the intake manifold. The CH2O in the charge was kept at a roughly-constant level of 1 900 plus or minus 100 ppm, over the engine operation by the throttle wide-opened, in most cases. The fuel-injection duty as well as the injection pressure was fixed over all cases, although the overall air excess ratio was more or less different. It is because the focus of this study is on the ignition delay, not on the whole combustion, and at any rate, the strength of a local mixture where the ignition first occurs, is uncontrollable and assumed to be near the stoichiometric. In the local mix-
Table 1 Engine specifications and operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CI Diesel Combustion</th>
<th>SI Gasoline Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore / Stroke / Displacement</td>
<td>91.1 mm / 95.0 mm / 619 cm³</td>
<td></td>
</tr>
<tr>
<td>Engine Speed</td>
<td>1200 min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Comp. Ratio (Geometrically)</td>
<td>12.3 (11.4)</td>
<td>18.0 (16.7)</td>
</tr>
<tr>
<td></td>
<td>11.0 (9.5)</td>
<td></td>
</tr>
<tr>
<td>Combustion Chamber</td>
<td>Reentrant Type of Cavity (Min. Dia. / Max. Dia. / Depth: 46.0 / 54.9 / 23.2 mm)</td>
<td>Reentrant Type of Cavity (Min. Dia. / Max. Dia. / Depth: 44.2 / 49.3 / 18.2 mm)</td>
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<tr>
<td></td>
<td>Pancake Type</td>
<td></td>
</tr>
<tr>
<td>In-Cylinder Flow</td>
<td>Swirl-Control Valve Closed (Estimated Swirl Ratio of 3.7 at Differential Press. of 0.004 MPa through Steady-Flow Rig)</td>
<td></td>
</tr>
<tr>
<td>Fuel</td>
<td>Gas Oil (Cetane Index (JISK2280): 52)</td>
<td>Regular Gasoline (RON: 90.3)</td>
</tr>
<tr>
<td>Fuel Preparation</td>
<td>0.165-Hole Nozzle, Common-Rail Press.: 50 MPa</td>
<td>Intake-Port Injector</td>
</tr>
<tr>
<td>Location of</td>
<td>Nozzle: on Cylinder Axis</td>
<td>Plug: 18 mm off Cylinder Axis</td>
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<tr>
<td>Timing of</td>
<td>Injection: -30, -20, -10 and -5 CAD ATDC</td>
<td>Ignition: -10 CAD ATDC</td>
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<td>Air Charge</td>
<td>NA, WOT, No EGR</td>
<td>NA, WOT, 35% Charge, No EGR</td>
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<tr>
<td>Charge Temperature in Intake Port</td>
<td>305 K, 355 K (Heating)</td>
<td>305 K, 312 K (35% Charge)</td>
</tr>
<tr>
<td>Coolant Temperature</td>
<td>358 K</td>
<td></td>
</tr>
<tr>
<td>O₂ Level in Charge</td>
<td>Atmospheric, Rich (26 %)</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>CH₂O Level in Charge</td>
<td>1900 +/- 100 ppm</td>
<td>1900 +/- 100 ppm, 5000 ppm (35% Charge)</td>
</tr>
<tr>
<td></td>
<td>3000 ppm</td>
<td></td>
</tr>
<tr>
<td>Air or O₂ Excess Ratio Excluding CH₂O</td>
<td>3.4, 3.3 (Heating), 4.2 (28% O₂)</td>
<td>3.4, 1.2 (35% Charge)</td>
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<td>Stoichiometric</td>
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<tr>
<td>Temperature at Injection Timing</td>
<td>610, 700, 770 and 800 K, 720, 810, 900 and 930 K (Heating)</td>
<td>660, 770, 880 and 930 K</td>
</tr>
</tbody>
</table>

In the stoichiometric mixture, equivalent to 1/22 of the amount of gasoline in weight.

2.2 Formaldehyde feed

CH₂O-feeding conditions were set equally to those in the previous studies. In the studies, a part of in-cylinder gas had been directly sampled, and the level of CH₂O in it had been measured using a gas chromatograph equipped with a flame ionization detector (GL Science GC-390TTDF)(3),(4). The previous data could be used for calibration on the level of CH₂O in this study.

The amount of CH₂O was monitored also by means of its value derived from the difference in the total amount of C atoms in exhaust emissions with or without the CH₂O addition. Its validity is dependent on a previous result that, even in an extremely-lean HCCI engine, almost all of added CH₂O is oxidized into CO and CO₂ during the combustion, which are detectable using the exhaust-gas analyzer, as shown in Fig. 2(4). Actually, however, in many cases at the low compression ratio in the conventional use of the engine, the indicated total level of HC emissions with the CH₂O was higher than that without any addition. The difference was less than 200 ppm, although the value is unreliable. When the O₂ level in the charge was increased up to 26.0%, fortunately, the HC emission level was almost the same with or without the CH₂O at a late injection timing of −10 or −5 CAD ATDC. At the low compression ratio, therefore, the CH₂O amount was derived in...
In some engine-operating conditions, the indicated total level of HC emissions with the CH2O addition was higher than that without any addition, although the value of the difference is unreliable. The CO level with the CH2O was always higher than that without any addition. A part of the CH2O, distributed in local areas off from combustion, seems to be emitted as being something except for CO2 and H2O.

3. Results and Discussion

3.1 Effect on formaldehyde addition on auto-ignition in diesel engine

Figures 3 to 5 show histories of the in-cylinder pressure and the effective heat release rate (EHRR) with or without the CH2O addition, at the different compression ratios and charge temperatures, acquired every 0.125 CAD over continuous 30 cycles and cycle-averaged. Figure 6 shows ignition delays from the fuel-injection timings. Here, the ignition timing was defined as the timing when the gradient of an EHRR history first reaches 0.02 MPa/CAD2 (12.4 J/CAD2) in an empirical way. Cool-flame reaction or faint heat release before the ignition appears at the same timing with or without the CH2O, as drawn with a single dotted line. At the low compression ratio, the CH2O weakens the pre-ignition heat release, and retards the ignition timing with any injection timings, compared to that without any addition. This is remarkable with the earliest injection timing when a two-stage type of heat release characterized by cool-flame reaction, appears.

At the high compression ratio, to the contrary, there is a case that, with the injection timing of -5 CAD ATDC, the CH2O addition slightly advance the ignition timing.

Also, when the intake air is heated at the low compression ratio, there is another case of the advancement with the injection timing of -10 CAD ATDC. In the both cases, the estimated in-cylinder temperature at the start of the pre-ignition heat release is above 900 K.
3.2 When ignition delay is deceived

For an extended understanding of the opposite effects of the CH$_2$O addition, contrastive cases to the above ones were discussed. One that the ignition delay was shortened by the O$_2$ addition to the intake air, even at the low compression ratio without any assistant rise in the charge temperature, to the extent of the delay shortened by the charge heating. The other that the delay was extended by the intake-air throttling, even at the high compression ratio, to the extent of that at the low compression ratio.

Figure 7 shows ignition delays as well as histories of the in-cylinder pressure and the EHRR, at the high O$_2$ level in the charge. The CH$_2$O addition retards the ignition timing with any injection timings. With the injection timing of −10 CAD ATDC, even though the ignition delay

![Figure 5](image1.png)  
**Fig. 5** Histories of in-cylinder pressure and effective heat-release rate in case of low compression ratio and heating

![Figure 6](image2.png)  
**Fig. 6** Effect of CH$_2$O on ignition delay

![Figure 7](image3.png)  
**Fig. 7** Effect of CH$_2$O on ignition delay in case of low compression ratio and high O$_2$ level
is shorter rather than that by the charge heating, the CH$_2$O does not advance the ignition timing as it does in case of the heating.

What is interesting in the figure, is that, although the added O$_2$ always shortens the ignition delay as a whole, compared to that at the atmospheric O$_2$ level, unexpectedly, it can be a retardant against the start of cool-flame reaction with the earliest injection timing. Looking back at Fig. 6, the high compression ratio also retards the start of pre-ignition reaction with the earliest injection timing.

Figure 8 shows histories of the in-cylinder pressure and the EHRR, when the intake air was throttled at the high compression ratio. Even though the ignition delay is longer than that at the low compression ratio, the CH$_2$O addition still advances the ignition timing. Although a two-stage type of heat release appears, the CH$_2$O does not weaken the pre-ignition heat release as it does at the low compression ratio. The advancement is remarkable with the injection timing of $-5$ CAD ATDC when the ignition delay is much extended.

Taking these into account, the boundary between the opposite effects of the CH$_2$O addition must be dominated by the in-cylinder temperature and of course, also by the CH$_2$O level in the charge, but by neither the ignition delay nor a profile of the pre-ignition heat release.

3.3 Flame light emissions

Figure 9 shows light emission spectra every 2.0 CAD with the earliest injection timing at the low compression ratio. Unfortunately, any local cool flame could not be detected with the optics prepared. Light emissions are first detected as those of a blue-color flame at the ignition, and then change their spectrum distribution at the start of soot generation. Because of a momentary engine operation for preventing deposits on the window, the ignition delay is much longer than that in the fully warmed-up operation in Fig. 3. According to a result using an HCCI engine charged with an air normal-butane$^{(4)}$, in case of ignition triggered at a temperature in low 800s K, the emissions from cool-flame reaction appear and then shrink, before those from blue-flame reaction appear. Then, when CH$_2$O is added, emissions monotonously and slowly grow up to the ignition without any shrink, resulting in retarding the ignition timing. Looking at the emissions at the ignition in Fig. 9, those without the CH$_2$O addition include the apparent OH radical emission. With the addition, to the contrary, no OH radical emission appears.

Figure 10 shows spectra every 0.25 CAD at the latest injection timing at the high compression ratio. Light emissions are detected as those with soot generation from the beginning. According to another result using the HCCI engine$^{(4)}$, in case of ignition triggered at a high temperature of 900 K, regardless of whether CH$_2$O is added, emissions rapidly grow up to the ignition without any shrink. In Fig. 10, there is no perceptible difference in the emissions with or without the CH$_2$O addition, that is, the both including the OH radical emission. The OH radical emission does not disappear with the addition, differently from that in Fig. 9.

3.4 Mechanism of opposite effects

It is the simplest way to model the opposite effects of CH$_2$O on the ignition delay, employing a detailed chemical-kinetics mechanism of dimethyl ether (CH$_3$OCH$_3$)$^{(8),(9)}$. The modeling with CH$_3$OCH$_3$ is convenient for essentially understanding paths of low-temperature oxidation toward ignition, because CH$_3$OCH$_3$
is the simplest fuel exhibiting a characteristic profile of low-temperature oxidation, namely, the negative temperature dependent, and it has the most limited paths of low-temperature oxidation.

In the first step of the modeling, CH$_2$O was added to the air, and was compressed in an engine-operating condition, for example, with an initial level of CH$_2$O of 4000 ppm, an initial temperature of 320 K, and an initial pressure of 0.101 MPa, at a compression ratio of 12.5 or 18.0, and an engine speed of 833 min$^{-1}$. As a result, the CH$_2$O is hardly oxidized at the low compression ratio. At the high compression ratio, to the contrary, a part of the CH$_2$O is oxidized via HCO into CO together with H$_2$O$_2$ at in-cylinder temperatures above 900 K, as shown in Fig. 11. At 2.5 CAD ATDC, the H$_2$O$_2$ is accumulated at a level of 370 ppm.

In the second step, the fuel, CH$_3$OCH$_3$, was mixed with the first-step result of a set of chemical species at 2.5 CAD ATDC to prepare a stoichiometric mixture. The initial amount of CH$_2$O in the first step is 1/17.5 of that of the CH$_3$OCH$_3$ in mole fraction, or 1/26.8 in weight. Then, the mixture was auto-ignited in a constant-volume condition starting from the temperature and pressure at 2.5 CAD ATDC, that is, with an initial temperature of 830 or 950 K, and an initial pressure of 3.2 or 5.2 MPa, respectively corresponding to the values at the low or high compression ratio. A mixture without any CH$_2$O addition was also auto-ignited in the same condition. Finally, results of the ignition timing are consistent with the experimental ones, as shown in Fig. 12. With the low initial temperature, the CH$_2$O addition retards the ignition timing. With the high initial temperature, to the contrary, the CH$_2$O slightly advances the ignition timing.

Figure 13 shows histories of the rates of OH radical generation and consumption by key elementary reactions of the simplest low-temperature oxidation, to explain the main reason of the retardation. When CH$_2$O is added in advance of the low-temperature oxidation, it can be an OH radical scavenger as CH$_2$O + OH $\rightarrow$ HCO + H$_2$O, and against CH$_3$OCH$_3$ + OH $\rightarrow$ CH$_3$OCH$_2$ + H$_2$O from the beginning of the low-temperature oxidation. It can be explained with the curve of the former reaction being parallel to that of the latter reaction in the initial period with the CH$_2$O addition. If more CH$_2$O is added, the both curves are closer to each other, and the ignition timing is more retarded. It obstructs the initial stage of the low-temperature oxidation beginning with the CH$_3$OCH$_3$ generation. On this account, the CH$_2$O weakens the first one of a two-stage temperature rise, resulting in retarding the ignition timing.
As the initial temperature is set higher than 830 K, the first temperature rise is lower, and the CH₂O addition less retards the ignition timing.

With an initial temperature above 900 K, the H₂O₂ generated from a part of the CH₂O, can be an OH radical generator as H₂O₂ (+M) → OH (+M) in the final stage of low-temperature oxidation. In case that the H₂O₂ is accumulated up to a level high enough for its effect to overcome the opposite effect of the CH₂O itself, it results in advancing the ignition timing as a whole. When H₂O₂ is removed from the initial mixture in the second step, the advancement is lost, as shown in Fig. 14.

This is the simplest mechanism of the opposite effects of CH₂O addition. Even in case of a more complicated fuel, there must be a similar kind of mechanism, although it must be more complicated. The same mechanism was presented also by Konno et al., to explain effect of CH₂O on HCCI of an air-CH₃OCH₃ mixture, although any case of the advancement was untouched(5).

3.5 Effect of formaldehyde addition on auto-ignition of end gas in gasoline engine

It has been experimentally confirmed that CH₂O can be an ignition retardant, when it acts below 900 K, while, above 900 K, there is a case that it can be an ignition promoter. In other words, a fuel with CH₂O as a fuel additive can behave like another less-combustible fuel at a low temperature, and to the contrary, like another more-combustible fuel at a high temperature. This behavior seems to be convenient for controlling combustion in gasoline engines, in terms of a possibility of both the acceleration of flame propagation and the deterrence of auto-ignition of an end gas, or the deterrence of knocking.

Figure 15 shows histories of the in-cylinder pressure over continuous 30 cycles and the cycle-averaged EHR, when the engine was operated as a knocking generator. The CH₂O effectively retards the onset of auto-ignition, and causes a rise of the EHR after the auto-ignition to be gentler. Judging from a large degree of the retardation, the ignition is probably triggered below 900 K.

4. Conclusions

For close discussion about a mechanism for CH₂O as a fuel additive to interact with auto-ignition of an air-fuel mixture, a direct-injection diesel engine equipped with a common-rail type of injection system was employed. It is because, unlike an HCCI engine, it can expose a mixture only to a limited range of the in-cylinder temperature before the ignition, and therefore, can separate low-temperature and high-temperature parts of interaction of CH₂O, that is, parts interacting with cool-flame reaction.
and blue-flame reaction. Vapor of CH$_2$O was added to the intake air. The ignition was induced at different fuel-injection timings, compression ratios and intake-air temperatures, that is, at different in-cylinder temperatures. Light emission spectra at the ignition timing were detected.

When low-temperature oxidation starts at a temperature above 900 K, there are cases that the CH$_2$O addition advances the ignition timing. Below 900 K, to the contrary, it always retards the timing. In case of the remarkable retardation, the CH$_2$O completely eliminates the OH radical emission. After all, the experimental results of the ignition timing are consistent with those using an HCCI engine in Fig. 1. This means that in case of the advancement of the HCCI timing, the interaction of CH$_2$O with cool-flame reaction is negligible for the timing.

The opposite effects of the CH$_2$O on the ignition delay were most simply modeled. Above 900 K, a part of the CH$_2$O is changed into CO and H$_2$O$_2$, and the latter acts as an OH radical generator in the final stage of low-temperature oxidation. Below 900 K, on the other hand, the CH$_2$O itself acts as an OH radical scavenger against cool-flame reaction, from the beginning of low-temperature oxidation.

Then, the engine was modified for its extraordinary function as a gasoline-knocking generator, in order that an effect of CH$_2$O on knocking could be discussed. The CH$_2$O retards the onset of auto-ignition of an end gas. Judging from a large degree of the retardation, the ignition is probably triggered below 900 K.

References