Homogeneous Charge Compression Ignition of Natural Gas/Air Mixture with Ozone Addition

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Controlling the ignition and the combustion of a homogeneous charge compression ignition (HCCI) engine has been attempted by partially ozonizing the intake gas in a natural gas premixed compression engine. It was experimentally proved that ignition timing can be controlled by changing the ozone concentration. To understand the phenomenon, an investigation using a numerical analysis has been carried out, and it was found that controlling the HCCI operation with ozone addition becomes feasible by generating OH via H_2O_2, that the influence of ozone addition to ignition angle is about the same as that of direct injection of an O radical, and that its addition is one order of magnitude more effective than addition of an OH radical.

I. Introduction

HOMOGENEOUS charge compression ignition (HCCI) engines have been proposed[1] for purifying the exhaust gas from a diesel engine while maintaining their high efficiency; hence, effects such as remarkable reductions of exhaust smoke and NOx have been reported.[2] However, because ignition timing and combustion duration of HCCI are governed by chemical reactions, and are independent of physical factors such as the turbulence intensity of the premixed charge, a supercharging mechanism and an intake gas preheating mechanism are currently applied for controlling ignition timing and combustion duration. There are drawbacks in that improper supercharging or preheating lead to nonignition and knocking and that controlling the additional mechanisms is complex.

With the objective of solving these issues, it has been attempted to control ignition and combustion by partially ozonizing the intake gas in a natural gas premixed compression engine. This method has been conceived from research on the application of ozone to combustion conducted by the authors of Ref. 3, whereas the addition of ozone to enhance HCCI combustion was originally proposed in a patent[4] and the use of ozone as an additive was recently analyzed as reported in Ref. 5. This method has enabled HCCI operation without using a supercharging mechanism or an intake gas preheating mechanism. Therefore, to understand the phenomenon, an investigation using a numerical analysis has been carried out focusing on the influence of reactions caused by ozone addition on the HCCI. The mechanisms controlling ignition timing and combustion duration have been elucidated and are described in this report.

II. Experiments on HCCI Operation

A. Experimental Apparatus and Conditions

Figure 1 shows a schematic of the experimental apparatus. The test engine used was a direct injection diesel engine, with an air-cooled four-stroke-cycle single cylinder, a displacement of 276 ml, bore × stroke equal to 72×68 mm, a compression ratio of 20.5, a rated power of 4.6 kW, and injection timing during diesel operation

of 18 deg before top dead center (BTDC) as listed in Table 1. For the HCCI operation, a venturi mixer was attached to the intake gas system, and natural gas and air were premixed for supply to the engine. Exhaust gas was sampled from the exhaust pipe using a probe, and each emission concentration of NOx, black smoke, hydrocarbons (HCs), and CO was measured. The natural gas used was city gas 13A with the composition shown in Table 2.

Experiments were carried out with diesel operation in the conventional manner for comparison and by HCCI operation using a natural gas/air premixed charge. In the latter operation, a gas with the same oxygen/nitrogen ratio as air made by adding nitrogen to oxygen (5 l/min), partially ozonized by passing it through an ozonizer, was supplied together with a premixed charge.

Brake mean effective pressure was fixed at 450 kPa (torque equal to 9.8 N · m), and flow rates of diesel fuel and the natural gas were adjusted so that revolutions stay at 1500 rpm in each operation. Ignition and combustion conditions are studied from measured cylinder pressure changes (a P–θ diagram), with heat release rate and thermal efficiency calculated from them.

B. Experimental Results and Discussions

Figure 2 shows changes in the cylinder pressure and the heat release rate with changes in ozone concentration in HCCI operation. The heat release rate curve for the operating condition with an ozone concentration of about 600 ppm in the combustion chamber indicates that more sluggish combustion is occurring than in the diesel operation because heat is generated even at about 40 deg after top dead center (ATDC). When the ozone concentration is raised in the combustion chamber, an increase in peak cylinder pressure due to combustion is observed in comparison with cases of a lower concentration. The heat release rate also indicates that the heat-generation peak is located closer to the top dead center. Generally, controlling ignition timing is vital for the efficient operation of a reciprocating engine, and the case in which timings of peak cylinder pressure occurrence are at 10–15 deg ATDC is claimed to be the optimum. Timings of peak cylinder pressure occurrence are optimized by controlling ignition timings: spark ignition timing in spark ignition engines represented by gasoline engines and diesel fuel injection timing and combustion duration in compression ignition engines represented by diesel engines. The methods applied in conventional engines, however, cannot be employed to ignition and combustion in HCCI operation; therefore, it is difficult to control ignition timing and combustion duration. However, the heat release rate graph indicates that the ignition timing can be controlled by changing the ozone concentration in the combustion chamber. The peak cylinder pressure rises with an increase in ozone concentration, and when

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Table 1   Engine specifications used in the experiment

Engine geometric parameters	Conditions and values
Type	Not assisted (direct injection diesel engine)[a] air-cooled four stroke-cycle single cylinder
Displacement	276 ml
Bore × stroke	72 × 68 mm
Compression ratio	20.5
Rated power[a]	4.6 kW
Injection timing[a]	18 deg BTDC

[a]Applicable only during diesel operation.

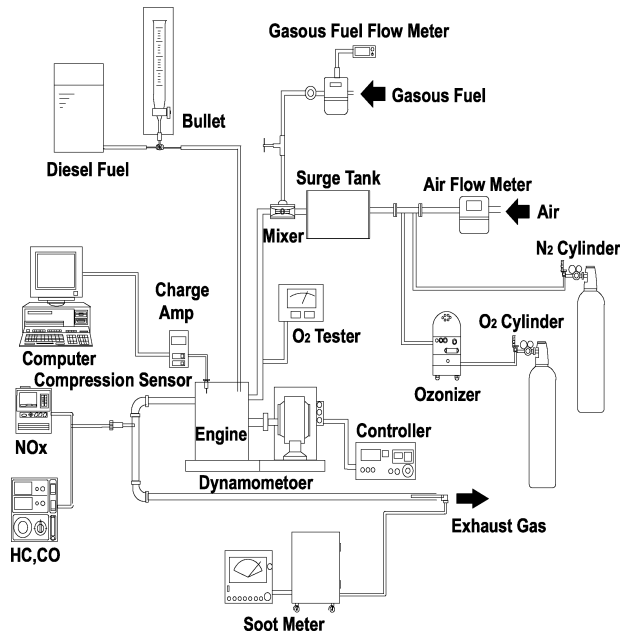**Table 2   Composition of the natural gas used in the experiment**

Gas	Composition, vol %
CH_4	88.2
C_2H_6	7.0
C_3H_8	1.8
C_4H_{10}	3.0

Fig. 1   Experimental apparatus.

Fig. 2   Effects of ozone concentration in parts per million in HCCI operation.

Table 3   Emissions

Composition	Diesel	HCCI[a]
NOx, ppm	890	12
CO, %	0.04	0.12
HC, %	0.016	0.386
Bosch smoke, %	9	0

[a]Added O_3 700 ppm.

Table 4   Gas fuel composition used in the numerical analysis

| Gas	Composition, vol %
CH_4	88.2
C_2H_6	7.0
C_3H_8	4.8
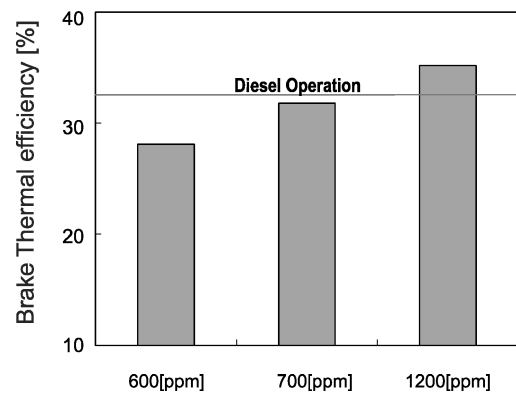
Fig. 3   Variation of thermal efficiency in HCCI operation, ozone concentration in parts per million.

700 ppm of ozone are added, the peak cylinder pressure appears at about 10 deg ATDC. Observation of changes in thermal efficiency with changes in ozone concentration for HCCI operation shows that when the ozone concentration is low, such as 600 ppm, efficiency is significantly lower due to sluggish combustion than in diesel operation. However, when combustion was carried out with ideal ignition timings by increasing the ozone concentration to 700 ppm, the same thermal efficiency was obtained with diesel operation (Fig. 3).

A comparison of diesel operation and HCCI operation with an ozone concentration of 700 ppm, as shown in Table 3, suggests that the combustion gas temperature in HCCI operation does not rise as much with combustion of a lean homogeneous premixed charge. Therefore, regardless of a higher oxygen concentration in the combustion chamber than in diesel operation, HCCI operation generates extremely small amounts of NOx. Furthermore, because diffusion combustion of diesel fuel does not occur, and only premixed combustion of natural gas takes place, no black smoke is generated in HCCI operation. On the other hand, HC and CO increase in HCCI operation in comparison with the diesel operation, although they can be reduced by raising the ozone concentration in the combustion chamber.

III.   Reaction Analysis of Ozone and Natural Gas/Air Mixture Using Numerical Calculation

Reaction calculations were performed to study the influence of ozone on the combustion of natural gas and air. The composition of natural gas is shown in Table 4. Ignition delay times obtained by reaction analyses with ozone added to a natural gas/air mixture are compared to that for the case without ozone addition. As for the reaction model of the natural gas/air mixture, GRI-Mech 3.0 (Ref. 6) was used, and the following reaction equations were added for the ozone
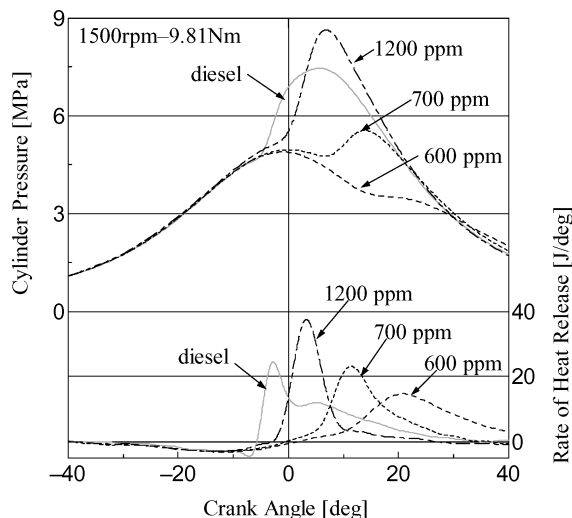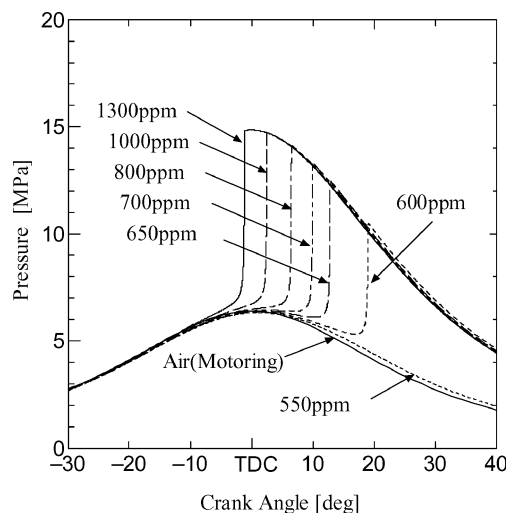
Fig. 4 Calculated ignition delay for different ozone concentrations.

reaction[7,8]:

$$R326 : O_3 + M \leftrightarrow O + O_2 + M$$

$$R327 : O_3 + O \leftrightarrow O_2 + O_2$$

$$R328 : O_3 + CH_3 \leftrightarrow O_2 + CH_2O + H$$

$$R329 : O_3 + H \leftrightarrow O_2 + OH$$
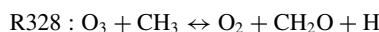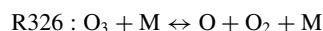
More specifically, 329 elementary reaction equations and the following 54 chemical species were considered: H_2, H, O, O_2, OH, H_2O, HO_2, H_2O_2, C, CH, CH_2, $CH_2(S)$, CH_3, CH_4, CO, CO_2, HCO, CH_2O, CH_2OH, CH_3O, CH_3OH, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, $HCCO$, CH_2CO, $HCCOH$, N, NH, NH_2, NH_3, NNH, NO, NO_2, N_2O, HNO, CN, HCN, H_2CN, $HCNN$, $HCNO$, $HOCN$, $HNCO$, NCO, N_2, AR, C_3H_7, C_3H_8, CH_2CHO, CH_3CHO, O_3.

Calculations were performed for an adiabatic compression–expansion cycle with a compression ratio of 20.5, and 1500 rpm. It was assumed that there are no spatial distributions of temperature, pressure, and concentration. The ignition timing is defined as the timing when the temperature rise becomes 400 K higher than that estimated as adiabatic compression. A self-ignition promotion effect by ozone was evaluated by comparing ignition timings for various ozone addition amounts.

A. Influence of Added Ozone Concentration

Figure 4 shows differences in the cylinder pressure histories for cases with and without ozone added to the natural gas/air mixture and for various amounts of ozone added at an initial temperature of 298 K, an initial pressure of 1 atm, and an equivalence ratio of 0.5. Very steep rises in pressure differing from the experiment are observed, which, as already described, are considered to be attributed to assuming no spatial distributions of temperature, pressure, and concentration and to not considering heat loss in the calculations. Self-ignition was observed when 600 ppm ozone was added, at which operation became possible in the experiment as well.

Figure 4 shows that ignition timing is advanced when ozone addition is further increased beyond 600 ppm, with self-ignition observed at 19 deg ATDC. When 1300 ppm of ozone are added to the natural gas/air mixture, ignition is advanced to 1 deg BTDC. Thus, it was found that, without preheating the intake gas and changing the compression ratio, self-ignition with compression of the natural gas premixed charge becomes possible by adding ozone and that the ignition timing can be controlled by changing the amount added.

B. Influence of Chemical Species Generated by Ozone Addition on Reactions

Studies are presented in this section on what chemical species are generated by ozone addition and on the influence of those chemical
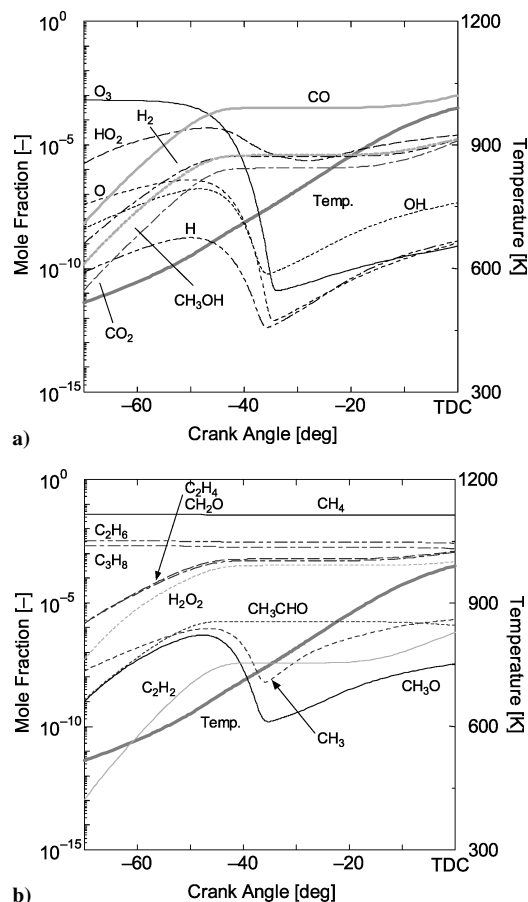

a)

b)

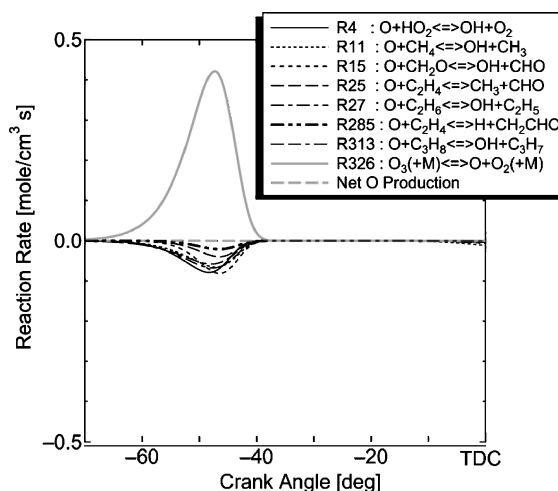**Fig. 5 Calculated initial ozone reactions.**

Fig. 6 Calculated reaction rates of major reactions including O.

species on the self-ignition under compression of the natural gas premixed charge. From the viewpoint of the timing of peak cylinder pressure occurrence in diesel engines as described, the influence of chemical species was studied from calculations for an addition of 650 ppm of ozone.

Figure 5 shows changes in the mole fractions of notable species where a steep drop in ozone concentration is observed at about 40 deg BTDC. This is caused by the dissociation reaction R326, $O_3 + M \leftrightarrow O + O_2 + M$, as shown in Fig. 6. The generated O radical is promptly consumed and generates H_2, CO_2, CH_3OH, CH_3CHO, CH_2O, C_2H_4, C_2H_2, and H_2O_2 with little heat generation. Concentrations of OH, O, and H, which are said to be relevant to ignition, decrease. Because this phenomenon is not observed when ozone is not added, the chemical species generated here are
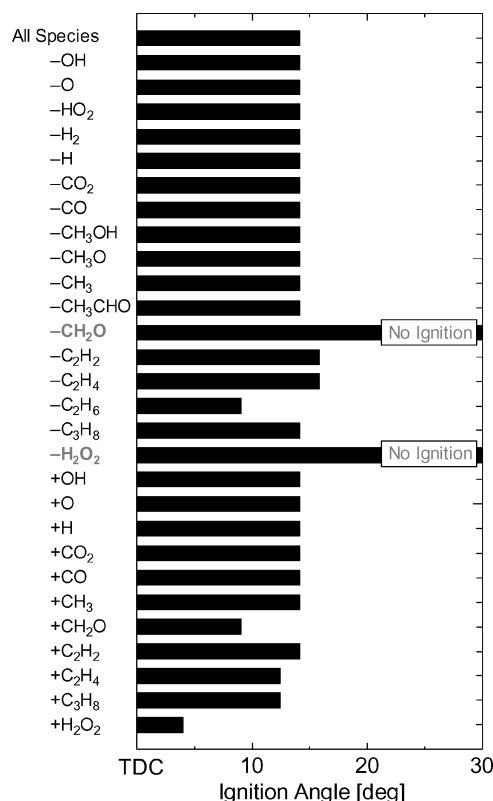
Fig. 7   Variation of ignition time in HCCI operation.

Fig. 8   Calculated ignition reactions.

considered to have some influence on the self-ignition promotion effect.

Therefore, to study the influence of individual chemical species on self-ignition, ignition times by crank angles were numerically calculated by individually setting the concentration of species at zero (indicated by a minus sign in Fig. 7) and at doubled values (indicated by a plus sign in Fig. 7) at the point of 35 deg BTDC, where the reaction of ozone decomposition is nearly completed. The results of this sensitivity analysis are shown in Fig. 7 with the baseline ignition angle of 13 deg BTDC when all species are included.

Figure 7 shows that even when chemical species of OH, O, and H, which are said to be relevant to ignition, are not present, the ignition timing does not change, that when C_2H_2 and C_2H_4 are eliminated, a delay in ignition timing is observed, and that when CH_2O or H_2O_2 is not present, ignition does not occur. It also shows that when C_2H_6 is not present, ignition timing tends to be advanced.

On the other hand, the chemical species OH, O, and H did not influence ignition timing, even when the concentrations of these chemical species were doubled. When the concentrations of C_2H_4 or C_3H_8 were doubled, the ignition timing showed a tendency to be a little advanced. H_2O_2 or CH_2O, which had a crucial influence when not present, was observed to advance ignition timing for crank angles over 10 or 5 deg, respectively, when its concentration was doubled. These results indicate that ozone addition is considered to influence the self-ignition timing of the natural gas through H_2O_2 and its supplier CH_2O.

C.   Mechanism of Compression Ignition Promotion by Ozone Addition

Changes in the mole fractions of major chemical species at the self-ignition are shown in Figs. 8a and 8b, which show that OH concentration rapidly increases immediately before self-ignition. A major reaction route from the generation of O radical due to ozone decomposition described in the preceding section through generation of CH_3 to the ignition is shown in Fig. 9. More specifically, reactions from decomposition of O_3 up to generation of H_2O_2 occur at 40–30 deg BTDC, and reactions do not much proceed subse-
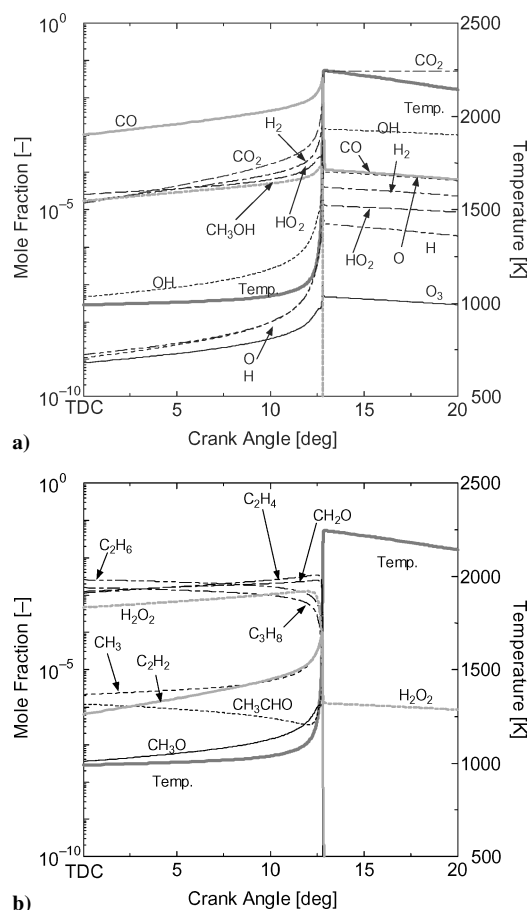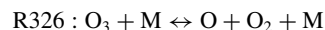
quently up to 15 deg BTDC. It is speculated that OH is generated afterward at about 10 deg BTDC by the reaction R85, $2OH + M \leftrightarrow H_2O_2 + M$, as shown in Fig. 10a; reactions proceed to reaction R98, $OH + CH_4 \leftrightarrow CH_3 + H_2O$, which generates CH_3; and finally to the ignition at around 15 deg BTDC.

To extract a major reaction route among these, the influence of whether or not each reaction equation takes place on self-ignition reactions was studied as shown in Fig. 11. When the nonexistence of a specific reaction equation incurs no ignition reaction, the reaction is regarded as a major route of a series of self-ignition reactions. Reaction routes from O_3 up to H_2O_2 are listed in time series as follows.

The decomposition of O_3 through generation of H_2O_2 (at 40–30 deg BTDC) encompasses the following reactions.

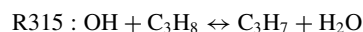Decomposition of O_3 and generation of O:

$$R326 : O_3 + M \leftrightarrow O + O_2 + M$$

Decomposition of CH_3:

$$R98 : OH + CH_4 \leftrightarrow CH_3 + H_2O$$

Generation of OH:

$$R119 : HO_2 + CH_3 \leftrightarrow OH + CH_3O$$

Generation of C_3H_7:

$$R315 : OH + C_3H_8 \leftrightarrow C_3H_7 + H_2O$$

Generation of CH_2O and C_2H_5:

$$R324 : HO_2 + C_3H_7 \leftrightarrow OH + C_2H_5 + CH_2O$$

Generation of HO_2:

$$R175 : C_2H_5 + O_2 \leftrightarrow HO_2 + C_2H_4$$
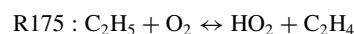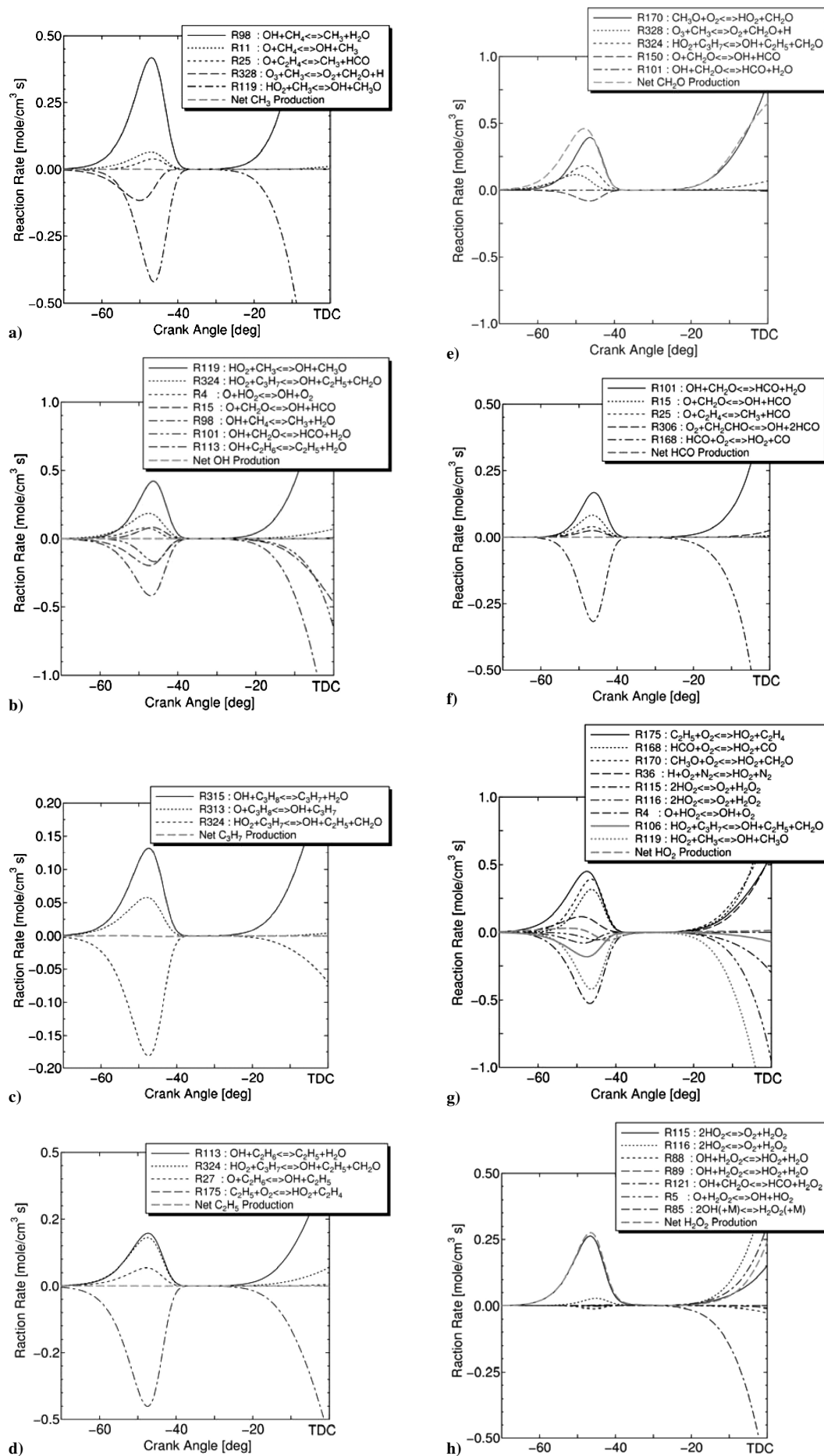
Fig. 9   Calculated initial reaction including a) CH$_3$, b) OH, c) C$_3$H$_7$, d) C$_2$H$_5$, e) CH$_2$O, f) HCO, g) HO$_2$, and h) H$_2$O$_2$.
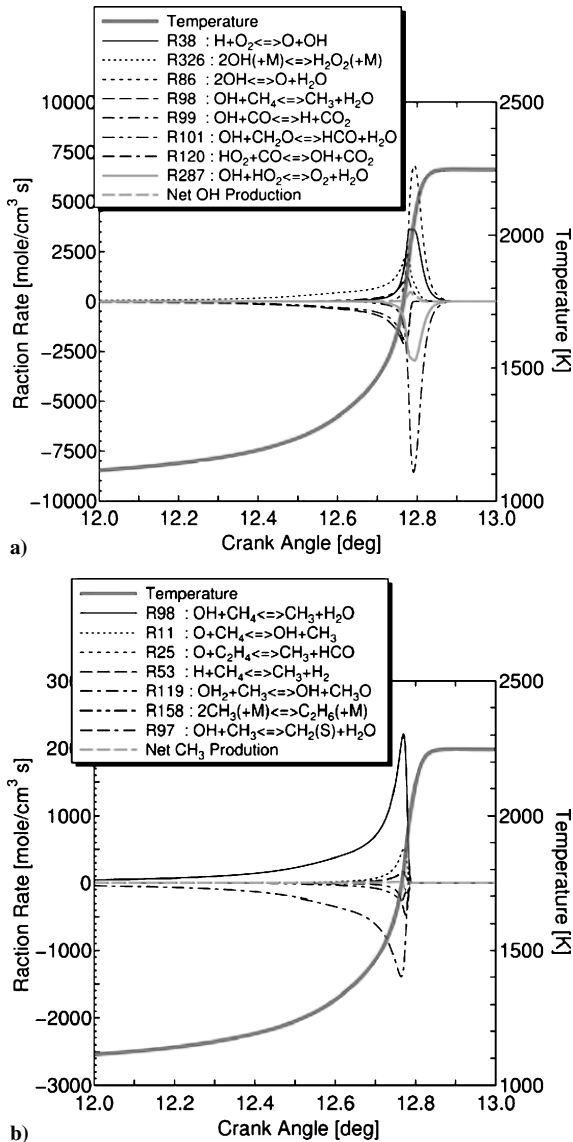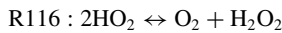
Fig. 10 Calculated ignition reaction including a) OH and b) CH_3.

Generation of H_2O_2:

$$R121 : HO_2 + CH_2O \leftrightarrow HCO + H_2O_2$$

$$R115 : 2HO_2 \leftrightarrow O_2 + H_2O_2$$

$$R116 : 2HO_2 \leftrightarrow O_2 + H_2O_2$$
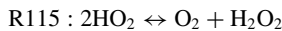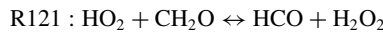
The decomposition of H_2O_2 through ignition (at 10–15 deg BTDC) includes the following reactions.

Generation of OH:

$$R85 : 2OH(+M) \leftrightarrow H_2O_2(+M)$$
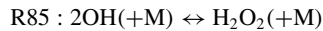
Generation of CH_3, ignition:

$$R98 : OH + CH_4 \leftrightarrow CH_3 + H_2O$$

More specifically, although the chemical species OH, O, and H, which are said to be relevant to ignition, are generated by ozone addition, most of them are converted once into H_2O_2 through a series of reactions, are preserved until immediately before ignition, and revert to OH, O, and H, which finally leads to ignition. The importance of the H_2O_2 decomposition reaction on ignition for HCCI operation has been reported.[9] In the present study, the details of the causal correlation and some additional reaction pathways are clarified.

Figure 12 shows the relationship between H_2O_2 concentration and ignition timing when O_3, O, and OH are added at 35 deg BTDC at which crank angle the reaction of the ozone decomposition is nearly
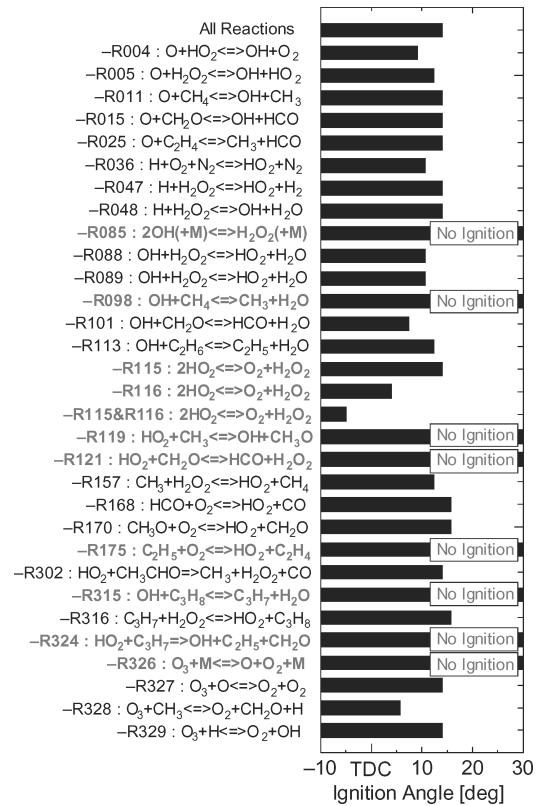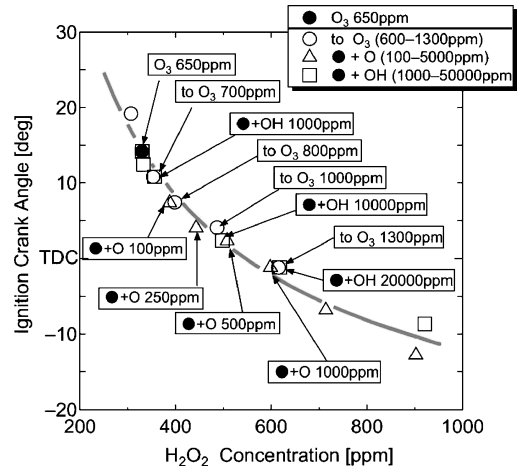

Fig. 11 Variations of ignition time with various reactions.

Fig. 12 Calculated ignition crank angle with various H_2O_2 concentrations or equivalent cases with O_3, O, OH, and their combination.

completed, as described earlier. We can glean from Fig. 12 that the ignition (crank angle) is advanced as H_2O_2 is increased (shown as a solid curve slanting to the right), whereas H_2O_2 concentration, in turn, is equivalent to some concentration of O_3, O, OH, or their combination. One example is that the effect of 600 ppm H_2O_2 is nearly equivalent to that of 1300 ppm O_3, 650 ppm O_3 plus 20,000 ppm OH, or 650 ppm O_3 plus 1000 ppm O. This result is in agreement with the idea that three components are preserved as H_2O_2 and control ignition.

The effect obtained by a 650 ppm increase of ozone addition from 650 to 1300 ppm is equivalent to those of 1000 ppm O and 20,000 ppm OH. Although it is difficult to supply such high concentrations of radicals even by using a device such as an O_2 plasma-jet, it is fairly easy using ozone and its decomposition mechanism. This is the main advantage of this method. The ozone addition shows a slightly greater effect than direct injection of an O radical, and its addition is one order of magnitude more effective than the addition of an OH radical.

IV. Conclusions

To clarify the effects of ozone addition for natural gas HCCI operation, experimental and numerical analyses were conducted. As a result, the following conclusions were obtained, when natural gas was used as fuel for HCCI operation.

1) It was experimentally proved that HCCI operation is made possible by ozone addition and that ignition timing can be controlled by changing the ozone concentration.

2) Controlling HCCI operation by adding ozone becomes feasible by generating OH via H_2O_2.

3) It was found that the influence of the ozone addition on ignition angle is slightly greater than direct injection of an O radical and is one order of magnitude more effective than adding an OH radical.

Acknowledgments

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