Improvements in Thermal Efficiency and Exhaust Emissions with Ozone addition in a Natural Gas-Diesel Dual Fuel Engine

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Abstract

Here, ozone (O_3) was introduced into the intake air in a natural gas fueled engine ignited by diesel fuel, a natural gas – diesel dual fuel engine, to utilize the reactive O-radicals decomposed from the O_3 for the promotion of the ignition and for improvements in the thermal efficiency and exhaust emissions. The engine experiments were performed over a range of equivalence ratios of the natural gas in a single cylinder engine. The timing of the pilot injection of the diesel fuel was varied from early in the compression stroke to near top dead center to examine the changes in the effects of the O_3 addition on the ignition and combustion with the pilot injection timing while varying the O_3 concentration. The results showed that the combination of the O_3 addition and the early pilot injection is a means to improve the thermal efficiency and unburned emissions with a small amount

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of O_3. Further, the improvement in the thermal efficiency and the reduction of the unburned hydrocarbons with the O_3 addition are more pronounced for lower equivalence ratios of natural gas, while the O_3 addition has a limited effect on the thermal efficiency and the unburned hydrocarbons for higher equivalence ratios of the natural gas.

Keywords: Dual Fuel Engine, Ozone, Natural Gas, Diesel fuel, Pilot injection, Thermal Efficiency, Exhaust Emissions

Nomenclature:

CA50	Mass burned at 50% crank angle [°CA ATDC]
$(dp/d\theta)_{max}$	Maximum rate of pressure rise [MPa/°CA]
Q_{burn}	Energy released with chemical reactions [J]
Q_{cool}	Energy lost due to cooling [J]
Q_{fuel}	Total fuel energy supplied [J]
V_c	Clearance volume at the top dead center [m^3]
V_h	Displacement volume [m^3]
V_θ	Volume of combustion chamber at crank angle θ

Greek symbols:

φ_{cool}	Cooling loss [%]
φ_{gas}	Equivalence ratio of natural gas [-]
θ	Crank angle [°CA]
θ_{pilot}	Pilot injection timing of diesel fuel [°CA ATDC]
η_i	Indicated thermal efficiency [%]
η_{glh}	Degree of constant volume heat release [%]
η_{comb}	Combustion efficiency [%]
η_u	Unburned loss [%]

1. Introduction

Natural gas fueled engines ignited by diesel fuel, natural gas – diesel dual fuel engines in the following, can help to reduce the environmental effect of internal combustion engines, as it may provide higher thermal efficiency with lower exhaust emissions, and the methane, which is the primary constituent of natural gas, should be a candidate among carbon neutral fuels as it can be generated through carbon dioxide (CO_2)-free hydrogen derived from renewable energy sources and the CO_2 emitted from processes such as biomass power generation.

The drawback of such engines is that the unburned methane emissions which are released into the atmosphere have a warming potential many times that of carbon dioxide. The previous research reduced unburned methane emissions with optimization of the injection strategy of the diesel fuel and combustion chamber geometry, and by intake gas throttling [1-5]. Further improvements, however, would be needed as lean burn operation with supercharging, which are expected to be an effective means to increase thermal efficiency, may cause increases in the unburned methane emissions.

Another possible way to address the problem of increased methane release could be the addition of ozone (O_3) to the intake air of engines. The O_3 addition is promising in terms of rapid response and low energy consumption as O_3 can be produced with nonequilibrium plasma. The decomposition of O_3 to O-radicals occurs at temperatures around 500 K to 600 K [6-9]. Together with the O_3 decomposition, a recombination reaction of the O-radicals is initiated to reduce them to oxygen molecules (O_2), while the O-radicals react with hydrocarbons when there are coexisting hydrocarbons, enhancing the oxidation reaction [9-11].

The O_3 addition has been utilized to control the ignition timing in homogeneous charge compression ignition (HCCI) engines where hydrocarbons are premixed in the cylinder and the ignition of the hydrocarbons is enhanced by the reaction with the O-radicals produced via the ozone decomposition [12-15]. The ignition enhancement effects due to the O_3 addition have also been utilized in gasoline compression ignition (GCI) engines employing a two-stage direct injection strategy, in which the first injection is implemented before the O_3 decomposition to make the first injected fuel react with the O-radicals, and the ignition delay of the second injection is controlled by the temperature increase and the chemical species generated due to the first fuel injection [9, 16-17].

Nishida et al. [18] introduced O_3 into the intake air together with natural gas and injected diesel fuel directly into the cylinder near top dead center. That report showed that an O_3 concentration of 1000 ppm or more was needed to enhance the ignition [18]. This O_3 concentration is considerably higher than that used to enhance the combustion of premixed gasoline components, that is less than 100 ppm [10, 11, 15-17], and considerable energy amounts are consumed to generate the O_3 concentration above 1000 ppm [19]. The differences in the required O_3 concentration between the gasoline components and the natural gas would suggest that the oxidation reactions of larger hydrocarbons are more likely to be affected by the O-radicals.

The purpose of the present study is to develop a means to improve the thermal efficiency and exhaust emissions of natural gas-diesel dual fuel engines by utilizing the ignition enhancement effects of the O_3. To achieve this, an experimental study was carried out with a single cylinder engine. To examine the effects of the O_3 addition on the ignition of diesel fuel which consists of larger hydrocarbons, the pilot injection timing of the diesel fuel was varied from the early in the compression stroke to top dead center while varying the seeded O_3 concentration. Further, the engine performance and exhaust emissions were examined over a range of engine loads to elucidate the changes in the requirement of the O_3 concentration with the equivalence ratio of the natural gas.

2. Experimental Setup

The specifications of the test engine are detailed in Table 1. The test engine was a single cylinder engine equipped with a common-rail fuel injection system. A commercially available injector (DENSO, G4S) having an 8-hole nozzle with the nominal hole diameter of 0.125 mm and with the umbrella angle of 155º mounted on the cylinder head. The bore and stroke are 98 mm and 110 mm, and the displacement volume is 830 cm^3, the compression ratio is 17.6. A graphic of the piston is shown in Fig.1. The piston has a toroidal-shaped cavity which has a diameter of 62.1 mm. The engine was connected to an eddy current electric dynamometer (Tokyo Koki, W-130) to absorb the engine output. The test engine has a low pressure EGR pathway and a roots type blower (OGURA CLUTCH, TX04) for supercharging, but all the experiments were performed with naturally aspirated engine operations here.

An illustration of the experimental setup is shown in Fig.2. The piezoelectric pressure sensor (KISTLER, 6125B) was installed in the cylinder head, and the electric charge was converted into a voltage signal with a charge amplifier (KISTLER, 5011B). The voltage signal proportional to the in-cylinder pressure was recorded with a transient memory board at a resolution of 0.2°CA for 150 cycles. It may be possible to examine the effect of the ozone (O_3) addition on the cycle-to-cycle variation with the data recorded for 150 cycles. This is, however, outside the scope of the present study and will be examined in the future. In the present study, cycle-averaged profiles of pressure and rate of heat release are used to examine the combustion characteristics. Natural gas was delivered from a gas cylinder into the intake pipe (diameter: 52.7 mm), located 450 mm upstream of the intake port with a mass flow controller (ALICAT, MCR-50SLPM-D). The composition of the natural gas could be varied from gas cylinder to gas cylinder, and the gas composition is detailed in Table 2, measured with a thermal conductivity detector (TCD) for one cylinder used as the reference in the present study.

Ozone (O_3) was produced with an ozonizer (EcoDesign, ED-OG-S4AD) while introducing pure oxygen (O_2) from a gas cylinder, and it was delivered into the intake pipe, 450 mm upstream of the intake port. It is possible to produce O_3 from air as demonstrated in the previous study [9], but O_3 was made from O_2 to supply higher concentration of O_3 to the engine in the present study. The O_2 flow rate was measured with a rotameter embedded in the ozonizer. The O_3 concentration was measured with a UV ozone monitor (EBARA, EG-600) before the ozone-containing oxygen was introduced into the intake pipe. The volume-based ozone concentration in the intake air was determined with the measured O_3 concentration and the flow rates of the oxygen and the intake air which was measured using a differential pressure type flowmeter.

The concentrations of the total hydrocarbon (THC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), and oxygen (O_2) were measured at the intake and exhaust pipes with an exhaust gas analyzer (Best Sokki, BEX-5100D). The smoke emissions were measured with a Bosch-type smoke meter (ZEXEL, DSM-20AN). As only insignificant smoke emissions were detected, no smoke data are presented in this paper.

3. Experimental Results and Discussion

3.1. Effects of the ozone addition on the combustion, engine performance, and exhaust emissions at various pilot injection timings for a φ_{gas} of 0.42

First, the effects of the pilot injection timing of the diesel fuel on the rate of heat release (ROHR) were investigated for the fixed equivalence ratio of the natural gas, φ_{gas}, of 0.42.

The experimental conditions are detailed in Table 3. The injection quantity of the diesel fuel was maintained constant at the heat value of the injected diesel fuel formed 11 HV% of the total energy supplied. The pilot injection timing, θ_{pilot}, was varied from -39°CA ATDC to 1°CA ATDC except where the maximum rate of pressure rise exceeded 1.2 MPa/°CA and the rotation speed could not be maintained at 1200 rpm due to misfiring. The O_3 concentration was increased from 0 ppm to 560 ppm unless the indicated thermal efficiency begun to decrease with the increase of the O_3. As the O_2 was supplied to generate the O_3, the intake O_2 concentration was increased to 21.5 vol.%. No EGR and no supercharging were employed in the experiments.

Figure 3 shows the changes in the profiles of the in-cylinder pressure and the ROHR with the pilot injection timing of the diesel fuel, θ_{pilot}. The traces shown in Fig.3 (a) are for the late pilot injections, and those shown in (b) are for the early pilot injections. The number of the traces was reduced for simplicity, and the intermediate pilot injection timing, θ_{pilot}, of -19°CA ATDC was included in Fig.3 (a) and (b). Note that the combustion phase with the other pilot injection timings, not included in Fig.3, is in the order of the pilot injection timing.

At the late pilot injection timings, θ_{pilot}, of 1°CA ATDC, -4°CA ATDC, and -9°CA ATDC, two-stage combustion takes place: the first is a heat release by a mixture of the diesel fuel and natural gas, and the second is a heat release by the natural gas which is not mixed well with the diesel fuel. The advance of the pilot injection timing from 1°CA ATDC to -9°CA ATDC advances the start of the first-stage combustion and increases the ROHR in the second-stage combustion. At the pilot injection timing, θ_{pilot}, of -19°CA ATDC, single-stage combustion occurs, followed by a lower ROHR due to the late combustion after 10°CA ATDC. This change in the ROHR pattern from θ_{pilot} = -9°CA ATDC to θ_{pilot} = -19°CA ATDC arises as the early pilot injection makes the diesel fuel become leaner and mixed well with the premixed natural gas. This type of combustion can be seen in the reactivity controlled compression ignition (RCCI) strategy in which the early pilot injection of more reactive fuel is implemented directly into the cylinder where low reactive fuel is distributed [20-21]. Further advances of the pilot injection timing from -19°CA ATDC cause retardations of the combustion phase as the diesel fuel mixture becomes much leaner, something that prolongs the ignition delay and combustion duration.

Second, the effects of the O_3 addition were investigated for the fixed equivalence ratio of the natural gas, φ_{gas}, of 0.42 while changing the O_3 concentration and the pilot injection timing, θ_{pilot}. Figure 4 shows the effects of the O_3 concentration on the fuel mass burned at the 50% crank angle, CA50. The addition of the 80 ppm O_3 can prevent the misfiring caused by the early pilot injection. The CA50 advances with the increase of the O_3 concentration, and this is noticeable at pilot injection timings earlier than -19°CA ATDC. At pilot injection timings later than -9°CA ATDC, the O_3 addition has a smaller influence on the CA50, and the higher O_3 concentration is needed to advance the CA50 compared to the early pilot injection timings. This reason will be discussed in Fig.5.

Figure 5 shows the changes in the profiles of the in-cylinder pressure and the rate of heat release (ROHR) with the O_3 concentration. Here, the two pilot injection timings, θ_{pilot}, of (a) -4°CA ATDC and (b) -34°CA ATDC were chosen as late and early injection timings.

The traces of all the O_3 concentrations are not shown in Fig.5 for simplicity, and it was confirmed that the combustion phase with the other O_3 concentrations, not included in Fig.5, was in the order of the O_3 concentration.

At the late θ_{pilot} of -4°CA ATDC, the O_3 addition has a limited effect on the ROHR in the first-stage combustion, while the O_3 addition increases the ROHR in the second-stage combustion. This may be because the recombination reaction of the O-radicals which are produced by the decomposition of O_3 early in the compression stroke reduces O-radical concentration until late in the compression stroke [7, 9], and the O-radicals cannot enhance the first-stage combustion which is caused by the mixture of the diesel fuel and the natural gas. The premixed natural gas can react with the O-radicals, immediately after the O_3 decomposition, and the second-stage combustion which is mainly caused by the natural gas can be enhanced with O_3 of the order of hundreds of ppm.

At the early pilot injection timing, θ_{pilot}, of -34°CA ATDC, the ignition of the single-stage combustion which strongly depends on chemical reactions of the diesel fuel is enhanced with the 50 ppm O_3, and overall the combustion is advanced. This may be because the O_3 can remain undecomposed until the timing of diesel fuel injection, and the O-radicals produced from the O_3 would enhance the ignition of the diesel fuel which is mixed well with the premixed natural gas. A more detailed elucidation of the mechanism of the detailed ignition processes is outside the scope of the present study, and the mechanism will be examined in future work.

Figure 6 compares the effects of the O_3 addition on the THC and NO_x emissions between the θ_{pilot} of -4°CA ATDC and -34°CA ATDC. Without the O_3 addition (0 ppm), the early pilot injection at -34°CA ATDC discharges the higher ratios of THC emissions than the late pilot injection at -4°CA ATDC. The O_3 addition reduces the THC emissions, and the reduction of the THC emissions becomes more remarkable with the early pilot injection. The primary reason of the reduction of the THC emissions may be the advanced combustion phase. The combustion phase is advanced with the O_3 addition for the early pilot injection at -34°CA ATDC as can be seen in Fig.5. At the late θ_{pilot} of -4°CA ATDC, the O_3 addition increases the ROHR and decreases the duration in the second-stage combustion. As the cylinder pressure falls during the expansion stroke, the temperature of the unburned mixture decreases, and the unburned mixture remains unconsumed due to quenching of the oxidation process.

The nitrogen oxide (NO) formation rate depends on the flame temperature which is influenced by the local equivalence ratio in the combustion chamber. The NO formation rate changes with the combustion phase since the mixture which burns earlier in the cycle increases the peak cylinder pressure, and the higher peak cylinder pressures result in higher flame temperatures and higher NO formation rates. Further the increased residence time in high flame temperatures affects the amount of the NO formation. The late pilot injection at -4°CA ATDC forms a locally rich mixture where NO_x is generated. The NO_x emissions increase with the increase of the O_3 concentration due to the advanced combustion phase. At the θ_{pilot} of -34°CA ATDC, only low NO_x emissions are discharged due to the combustion of a leaner mixture of the diesel fuel, and the lower NO_x emissions are maintained when the O_3 concentration increases.

Figure 7 is a comparison of the effects of the ozone addition on the indicated thermal efficiency, η_i, the degree of constant volume heat release, η_{glh}, the combustion efficiency, η_{comb}, and the ratio of cooling loss, φ_{cool}, at the late and early pilot injection timings. The indicated thermal efficiency, η_i, is expressed by [22]

$$\eta_i = \eta_{th}\eta_{glh}(1 - \eta_u - \varphi_{cool}) \tag{1}$$

Here, η_{th} is the theoretical thermal efficiency for the Otto Cycle. The unburned loss, η_u, is defined as η_u =1-η_{comb}, and the combustion efficiency, η_{comb}, can be determined with the measured exhaust emissions. The degree of constant volume heat release, η_{glh}, can be calculated by the following equation with the consideration of the profile of the apparent rate of heat release, $dQ/d\theta$:

$$\eta_{glh} = \frac{1}{\eta_{th} \cdot Q} \int \left\{1 - \left(\frac{V_h + V_c}{V_\theta}\right)^{1-\kappa}\right\} \frac{dQ}{d\theta} d\theta \tag{2}$$

Here, κ is the ratio of specific heat, V_h is the displacement volume, V_c is the clearance volume at the top dead center, and V_θ is the volume of the combustion chamber at crank angle θ. The ratio of cooling loss, φ_{cool}, which is defined as $\varphi_{cool} = Q_{\mathrm{cool}}/Q_{\mathrm{fuel}}$ where Q_{cool} is the energy lost due to cooling, and Q_{fuel} is the total fuel energy supplied, can be calculated with Eq.(1) as the indicated thermal efficiency, η_i, and the unburned loss, η_u, can be determined in the experiments. A similar approach for calculating the ratio of cooling loss, φ_{cool}, is proposed in a reference [23] in which the ratio of cooling loss is defined as $\varphi_{cool} = Q_{\mathrm{cool}}/Q_{\mathrm{burn}}$ where Q_{burn} is the energy released by the chemical reaction, and the validity of the calculated ratio of cooling loss was assessed.

At the θ_{pilot} of -34°CA ATDC, the indicated thermal efficiency increases with the increase of the O_3 concentration, and the excess of O_3 decreases the indicated thermal efficiency. This is because with the increase of the O_3 concentration, the degree of constant volume heat release, η_{glh}, and the combustion efficiency increase, η_{comb}, while the cooling loss, φ_{cool}, increases due to the advanced combustion phase. Further, the degree of constant volume heat release decreases with the excess amounts of the O_3, higher than 170 ppm. At the θ_{pilot} of -4°CA ATDC, the indicated thermal efficiency increases with the increase in the O_3 concentration, as the increase of the O_3 concentration increases the degree of constant volume heat release and the combustion efficiency. With the late pilot injection, the higher O_3 concentration is needed to improve the indicated thermal efficiency above that with the early pilot injection.

Figure 8 shows the indicated thermal efficiency, η_i, CA50, the THC and NO_x emissions, and the O_3 concentration, at which the best indicated thermal efficiency can be achieved. The test results without the O_3 addition are shown for reference. The indicated thermal efficiency is improved with the O_3 addition for all the pilot injection timings. At the θ_{pilot} of -30°CA ATDC, the indicated thermal efficiency without the O_3 addition becomes close to that with the O_3 addition. Without the O_3 addition, the degree of constant volume heat release decreases due to the retardation of the CA50, and the combustion efficiency decreases as seen in the increase of the unburned emissions, but the retardation of the CA50 decreases the cooling loss. This result suggests that there is an optimal CA50 at which the indicated thermal efficiency is increased.

The higher O_3 concentration is needed to achieve the best indicated thermal efficiency at the later pilot injection timings, while the best indicated thermal efficiency can be achieved at pilot injection timings earlier than -20°CA ATDC with lower O_3 concentrations. The O_3 addition reduces the THC emissions and increases the NO_x emissions for all the pilot injection timings, but the lower NO_x emissions can be achieved with the early pilot injection. Overall, the O_3 addition with the early pilot injection is advantageous in terms of the lower O_3 concentration needed to achieve higher thermal efficiency, and low THC and NOx emissions.

3.2. Variations in ozone concentration and pilot injection timing, and optimization of indicated thermal efficiency over a range of equivalence ratios of natural gas

Operating conditions achieving the best thermal efficiency were investigated over a range of equivalence ratios of natural gas while varying the O_3 concentration and the pilot injection timing of diesel fuel.

The experimental conditions are detailed in Table 4. The equivalence ratio of natural gas, φ_{gas}, was varied from 0.33 to 0.53 while the pilot injection quantity of the diesel fuel was fixed. Due to a failure of the injector used in section 3.1, a different injector equipped with a nozzle with nominal specifications identical to the nozzle used in section 3.1 was used. There were, however, differences in the injection quantity between the injectors. As a result, the pilot injection quantity of the diesel fuel was slightly larger in this experiment. No EGR and no supercharging were employed in the experiments to examine the effects of the equivalence ratio without any complexity.

As explained in section 3.1, a higher O_3 concentration is needed to enhance the combustion at the later pilot injection timings, while the combustion is enhanced with a lower O_3 concentration at the early pilot injection timings. Considering this, the O_3 concentration was varied from 0 ppm to 280 ppm at the pilot injection timings from -69°CA ATDC to -29°CA ATDC, and from 0 ppm to 520 ppm at the pilot injection timings from -19°CA ATDC to 1°CA ATDC. The O_3 concentration was increased unless the indicated thermal efficiency begun to decrease with the increase of the O_3. A larger flow rate of O_2 was needed to produce a higher concentration of O_3, however it was difficult to control the O_3 concentration precisely with the larger flow rate of O_2. To overcome this, the flow rate of the O_2 was changed with the pilot injection timings. As a result, the intake O_2 concentration was 20.6 vol.% at the pilot injection timings from -69°CA ATDC to -29°CA ATDC, and 21.5 vol.% at the pilot injection timings from -19°CA ATDC to 1°CA ATDC. The differences in the intake O_2 concentrations have a limited effect on engine performance and exhaust emissions, since it was confirmed that the experimental results for the various pilot injection timings show a similar tendency to that obtained in section 3.1.

In the following experiments, first, the engine performance and the pilot injection timings encountering the occurrence of knocking and misfiring were examined without the O_3 addition. Figure 9 compares the indicated thermal efficiency, η_i, with the equivalence ratios of the natural gas, φ_{gas}. The limit of the operations due to the misfiring and knocking are superimposed. The operation with the φ_{gas} of 0.33 results in a low indicated thermal efficiency, and the late and early injections are limited by misfiring due to the combustion of the lean fuel-air mixture. With the higher φ_{gas} at 0.39 and 0.45, the indicated thermal efficiency increases primarily due to the improvement in the combustion efficiency, and the pilot injection without misfiring can be advanced. In analogy with the trend in Fig.8, the higher indicated thermal efficiency can be achieved at the earlier pilot injection timings with the φ_{gas} of 0.39 and 0.45. For the φ_{gas} of 0.53, the pilot injection timing is limited to the late crank angles due to knocking. The indicated thermal efficiency for the φ_{gas} of 0.53 is higher than the 0.39 and 0.45 φ_{gas} at the late pilot injection timings of -4°CA ATDC and 1°CA ATDC, while the highest thermal efficiency of the φ_{gas} of 0.39 and 0.45, which can be achieved at the earliest pilot injection timings, is almost equivalent to the thermal efficiency of the φ_{gas} of 0.53.

Second, the O_3 was introduced, and the pilot injection timing was varied within the range where no knocking and misfiring occur. Figure 10 shows the effects of the O_3 concentration on the fuel mass burned at the 50% crank angle, CA50. With the pilot injection timing, θ_{pilot}, later than -9°CA ATDC, the O_3 addition has a limited effect on the CA50 at all the equivalence ratios of the natural gas, φ_{gas}. For the φ_{gas} of 0.33 and 0.45, advances of the θ_{pilot} from -29°CA ATDC cause retardations of the CA50, and the CA50 is advanced with the increase of the O_3 concentration. In the present study, it was possible to operate the engine at the θ_{pilot} of -69°CA ATDC with the aid of the O_3 for the φ_{gas} at 0.33, while it was not possible to establish conditions under which the θ_{pilot} earlier than -49°CA ATDC could be set without causing misfiring and knocking for the φ_{gas} of 0.45. Further, with the θ_{pilot} earlier than -4°CA ATDC was limited by knocking with the φ_{gas} of 0.53.

Figure 11 shows the indicated thermal efficiency, η_i, the degree of constant volume heat release, η_{glh}, the combustion efficiency, η_{comb}, and the cooling loss, φ_{cool}, for the φ_{gas} of 0.33. Without the O_3 addition, the lower indicated thermal efficiency is mainly due to the lower combustion efficiency that is caused by the combustion of the lean natural gas mixture. The O_3 addition improves the combustion efficiency and the degree of constant volume heat release noticeably with the θ_{pilot} earlier than -49°CA ATDC due to the combustion promotion effect. The excess of O_3, however, decreases the indicated thermal efficiency with the θ_{pilot} at -49°CA ATDC since the CA50 is advanced, and the cooling loss is increased. With the θ_{pilot} at -69°CA ATDC, a simultaneous higher combustion efficiency and lower cooling loss is obtained with the O_3 addition because the θ_{pilot} of -69°CA ATDC allows the moderately late CA50 that reduces the cooling loss. As a result, the highest indicated thermal efficiency of 41.6% is attained at the θ_{pilot} of -69°CA ATDC with the 140 ppm O_3. Figure 12 shows the indicated thermal efficiency, η_i, and the factors related to the thermal efficiency for the φ_{gas} at 0.45. Unlike the φ_{gas} at 0.33, the higher indicated thermal efficiency can be achieved at the θ_{pilot} of -69°CA without the O_3 addition due to the better combustion efficiency. With an increase of the O_3 concentration to around 50 ppm, the indicated thermal efficiency increases due to the improvements in the combustion efficiency and the degree of constant volume heat release increase while maintaining the lower cooling loss. The further increase of the O_3 concentration, however, increases the cooling loss. As a result, the highest indicated thermal efficiency of 41.7% is attained at the θ_{pilot} of -49°CA ATDC with the 30 ppm O_3. Figure 13 shows the indicated thermal efficiency, η_i, and the factors related to the thermal efficiency for the φ_{gas} at 0.53. The pilot injection timings are limited to -4°CA ATDC and 1°CA ATDC. At the late pilot injection timings, the O_3 addition slightly increases the degree of constant volume heat release and the cooling loss due to the advanced CA50, and the O_3 addition has a limited effect on the indicated thermal efficiency.

Figure 14 shows the effect of the O_3 concentration on the maximum rate of pressure rise, $(dp/d\theta)_{max}$, over the range of equivalence ratios of the natural gas, φ_{gas}. The increase in the $(dp/d\theta)_{max}$ with the O_3 addition is more remarkable for the pilot injection timings, θ_{pilot}, earlier than -29°CA ATDC for (a) the φ_{gas} of 0.33 and (b) the φ_{gas} of 0.45. This is because the O_3 addition advances the combustion phase of the single-stage combustion at the early pilot injection, while the O_3 addition with the late pilot injection has a limited effect on the first stage combustion which determines the maximum rate of pressure rise, as can be seen in Fig.5. For (c) the φ_{gas} of 0.53, the $(dp/d\theta)_{max}$ increases with the increase of the O_3 concentration at the late pilot injection of the θ_{pilot} of -9°CA ATDC as the ROHR at second stage combustion becomes large and increases the maximum rate of pressure rise.

The early pilot injections with the O_3 addition lead to the lower $(dp/d\theta)_{max}$ compared to the θ_{pilot} of -9°CA ATDC for (a) the φ_{gas} of 0.33, and for (b) the φ_{gas} of 0.45, the early pilot injections with the O_3 addition cause too much advanced CA50 as seen in Fig.10 and lead to the higher $(dp/d\theta)_{max}$. This result suggests that the combination of the early pilot injection and the O_3 addition can be used with an acceptable level of the maximum rate of pressure rise at lower equivalence ratio of the natural gas while achieving an optimal CA50.

Figure 15 shows the indicated thermal efficiency, η_i, the THC and NO_x emissions, the pilot injection timing, θ_{pilot}, and the O_3 concentration, at which the best indicated thermal efficiency can be achieved. The test results without the O_3 addition are shown for reference. The improvements in the indicated thermal efficiency and the THC emissions with the O_3 addition are most remarkable for the equivalence ratio of natural gas, φ_{gas}, of 0.33, where the θ_{pilot} is advanced to -69°CA ATDC, and the O_3 concentration is at 140 ppm. Without the aid of the O_3, it is difficult to implement the early pilot injection due to misfiring. With the increase of the φ_{gas}, the best pilot injection timing is retarded, the best O_3 concentration decreases, and the differences with and without the O_3 addition become small. For the φ_{gas} 0.53, the best indicated thermal efficiency is obtained without the O_3 addition at the θ_{pilot} near top dead center. There are no remarkable differences in the NO_x emissions with and without the O_3 addition over a range of φ_{gas}.

4. Conclusions

To improve the thermal efficiency and exhaust emissions of natural gas fueled engines ignited by diesel fuel (natural gas – diesel dual fuel engines) with the ignition enhancement effects of O_3, an experimental study was carried out in a single cylinder engine while varying the O_3 concentration at the intake port and the pilot injection timing of the diesel fuel. Further, the equivalence ratio of the natural gas was varied from 0.33 to 0.53 to elucidate the changes in the requirement for the O_3 concentration. The conclusions may be summarized as follows:

1. In the natural gas – diesel dual fuel engines, a two-stage heat release takes place with

the late pilot injection. The first stage is a heat release by the mixture of the diesel fuel and the natural gas, and the O_3 addition has little influence on the rate of heat release. The second stage is a heat release by the natural gas which is not mixed well with the diesel fuel, and O_3 of the order of several hundred ppm is needed to increase the rate of heat release. With the early pilot injection, a single-stage heat release takes place, and the ignition timing and the combustion phase are advanced with the O_3 concentration lower than 100 ppm.

2. With the O_3 addition, the unburned hydrocarbons decrease, the NO_x emissions increase, and the early injection timing can be advanced without misfiring.
3. The O_3 concentration needed to achieve the best indicated thermal efficiency can be reduced more with the early pilot injection, compared to the late pilot injection. In addition, the lower unburned hydrocarbons and NO_x emissions can be achieved with the combination of the O_3 addition and the early pilot injection.
4. The O_3 addition increases the maximum rate of pressure rise notably for the early pilot injection. The operation with an acceptable level of the maximum rate of pressure rise, however, can be achieved at lower equivalence ratio of the natural gas while achieving optimal combustion phase.
5. The improvement in the indicated thermal efficiency and the reduction of the

unburned hydrocarbons with the O_3 addition are more pronounced for lower equivalence ratios of the natural gas, while the O_3 addition has a limited effect on the indicated thermal efficiency and the unburned hydrocarbons for higher equivalence ratio of the natural gas. This would suggest that the combination of the O_3 addition and supercharging which reduces the equivalence ratio and decreases the cooling loss is a means to improve the thermal efficiency and emissions at higher engine loads. Further, the use of EGR along with the O_3 addition may improve the indicated thermal efficiency due to the decrease in the cooling loss while avoiding misfiring caused by the dilution of mixtures.

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5. References

[1] Shioji, M., Ishiyama, T., Ikegami, M., Mitani, S. and Shibata, H., "Performance and Exhaust Emissions in a Natural-Gas Fueled Dual-Fuel Engine," JSME International Journal, B, 44(4):641-648, 2001, doi: 10.1299/jsmeb.44.641.

[2] Ogawa, H., Shibata, G., Goto, J. and Jiang, L., "Performance Improvements in a

Natural Gas Dual Fuel Compression Ignition Engine with 250 Mpa Pilot Injection of Diesel Fuel as an Ignition Source," SAE Technical Paper 2016-01-2306, 2016, doi: 10.4271/2016-01-2306.

[3] Wang, B., Li, T., Ge, L. and Ogawa, H., "Optimization of Combustion Chamber Geometry for Natural Gas Engines with Diesel Micro-pilot-induced Ignition," Energy Conversion and Management, 122(15), pp.552-563, 2016, doi: 10.1016/j.enconman.2016.06.027.

[4] Li, Y., Li, H., Guo, H., Li., Y. and Yao, M., "A Numerical Investigation on Methane Combustion and Emissions from a Natural Gas-Diesel Dual Fuel Engine Using CFD Model," Applied Energy, 205(1):153-162, 2017, doi: 10.1016/j.apenergy.2017.07.071.

[5] Lerin, C., Edwards, K. D., Curran, S. J., Nafziger, E. J., Moses-DeBusk, M., Kaul, B. C., Singh, S., Allain, M. and Girbach, J., "Exploring the Potential Benefits of High-efficiency Dual-fuel Combustion on a Heavy-duty Multi-cylinder Engine for SuperTruck I," Int. J. Engine Research, 23(6), pp.1082-1099, 2022, doi: 10.1177/14680874211006943.

[6] Yamada, H., Yoshii, M. and Tezaki, A., "Chemical Mechanistic Analysis of Additive Effects in Homogeneous Charge Compression Ignition of Dimethyl Ether," Proc. the Combustion Institute, Vol.30, Issue 2, pp.2773-2780, 2005, doi: 10.1016/j.proci.2004.08.253.

[7] Ekoto, I. and Foucher, F., "Mechanism of Enhanced Reactivity with Ozone Addition for Advanced Compression Ignition," SAE Technical Paper 2018-01-1249, 2018, doi: 10.4271/2018-01-1249.

[8] Seignour, N., Ekoto, I., Foucher, F. and Moreau, B., "Measurements and Modeling of Ozone Enhanced Compression Ignition in a Rapid Compression Machine and Optically-accessible Engine," SAE Technical Paper 2019-01-2254, 2019, doi: 10.4271/2019-01-2254.

[9] Kobashi, Y., Wang, Y., Shibata, G., Ogawa, H. and Naganuma, K., "Ignition Control in a Gasoline Compression Ignition Engine with Ozone Addition Combined with a Two-stage Direct-injection Strategy," Fuel, 249, pp.154-160, 2019, doi: 10.1016/j.fuel.2019.03.101.

[10] Foucher, F., Higelin, P., Mounaïm-Rousselle, C. and Dagaut, P., "Influence of Ozone on the Combustion of n-heptane in a HCCI Engine," Proc. the Combustion Institute, 34, pp.3005-3012, 2013, doi: 10.1016/j.proci.2012.05.042.

[11] Masurier, J.-B., Foucher, F., Dayma, G. and Dagaut, P., "Homogeneous Charge Compression Ignition Combustion of Primary Reference Fuels Influenced by Ozone Addition," Energy and Fuels, 27(9), pp.5495-5505, 2013, doi: 10.1021/ef401009x.

[12] Nishida, H. and Tachibana, T., "Homogeneous Charge Compression Ignition of Natural Gas/Air Mixture with Ozone Addition," J. Propulsion and Power, 22(1), pp.151-157, 2006, doi: 10.2514/1.14991.

[13] Mohammadi, A., Kawanabe, H., Ishiyama, T., Shioji, M. and Komada, A., "Study on Combustion Control in Natural-gas PCCI Engines with Ozone Addition into Intake Gas," SAE Technical Paper 2006-01-0419, 2006, doi: 10.4271/2006-01-0419.

[14] Schönborn, A., Hellier, P., Aliev, A. E. and Ladommatos, N., "Ignition Control of Homogeneous-charge Compression Ignition (HCCI) Combustion through Adaptation of the Fuel Molecular Structure by Reaction with Ozone," Fuel, 89, pp.3178-3184, 2010, doi: 10.1016/j.fuel.2010.06.005.

[15] Truedsson, I., Rousselle, C. and Foucher, F., "Ozone Seeding Effect on the Ignition Events in HCCI Combustion of Gasoline-ethanol Blends," SAE Technical Paper 2017-01-0727, 2017, doi:10.4271/2017-01-0727.

[16] Pinazzi, P. M. and Foucher, F., "Potential of Ozone to Enable Low Load Operations of a Gasoline Compression Ignition (GCI) Engine," SAE Technical Paper 2017-01-0746, 2017, doi: 10.4271/2017-01-0746.

[17] Kobashi, Y., Da, D. D. T., Inagaki, R., Shibata, G. and Ogawa, H., "Optimization of Gasoline Compression Ignition Combustion with Ozone Addition and Two-stage Direct-injection at Middle Loads," Int. J. Engine Research, 23(2), pp.232-242, 2022, doi: 10.1177/1468087420984574.

[18] Nishida, H., Ishii, T., Hirashima, S. and Tachibana, T., "Effect of Ozone on Combustion of a Dual Fuel Engine," Trans. the Japan Society of Mechanical Engineers Series B, 70(695) (in Japanese), pp.1884-1889, 2004, doi: 10.1299/kikaib.70.1884.

[19] Inoue, T., Tamida, T., Hashimoto, T., Wada, N., Nakagawa, A., Sakashita, T., Wada, K. and Honda, T., The Development of Intake In-line Type Ozonizer for Application to HCCI Combustion, Trans. Society of Automotive Engineers of Japan, 48(4), pp.827-832, 2017, doi: 10.11351/jsaeronbun.48.827.

[20] KokJohn, S. L., Hanson, R. M., Splitter, D. A. and Reitz, R. D., "Fuel Reactivity Controlled Compression Ignition (RCCI): a Pathway to Controlled High-Efficiency Clean Combustion," Int. J. Engine Research, 12(3), pp.209-226, 2011, doi: 10.1177/1468087411401548.

[21] Nieman, D., Dempsey, A. and Reitz, R., "Heavy-Duty RCCI Operation Using Natural Gas and Diesel," SAE Technical Paper 2012-01-0379, 2012, doi: 10.4271/2012-01-0379.

[22] List, H., Thermodynamik der Verbrennugskraftmaschine, Julius Springer, p.71, 1939, doi: 10.1007/978-3-7091-5345-1.

[23] Shudo, T., Nabetani, S. and Nakajima, Y., Analysis of the Degree of Constant Volume and Cooling Loss in a Spark Ignition Engine Fuelled with Hydrogen, Int. J. Engine Research, 2(1), pp.81-92, 2001, doi: 10.1243/1468087011545361.

APPENDIX

Here, the electric energy consumption needed to produce the ozone (O_3) is calculated. The ozonizer used in the present study (EcoDesign, ED-OG-S4AD) is not manufactured specifically for the use in internal combustion engines, and its energy consumption may not be suitable for the evaluation. Instead, data of an intake in-line type ozonizer manufactured for gasoline engines, which can be found in Ref.[19], were employed to determine the energy consumption.

According to Ref.[19], the electric energy consumption of 60 W is needed to produce the O_3 concentration, $[O_3]$, of 50 ppm with the flow rate of air at 0.2 m^3/min with the intake in-line type ozonizer using dielectric-barrier discharge. For simplicity, the present calculation assumed that the electric energy consumption is proportional to the produced O_3 concentration and to the flow rate of air. Further, assuming that the volumetric efficiency of the engine is unity, the electric energy consumption, E [W], needed to produce $[O_3]$ [ppm] is expressed as follows:

$$E\ [\mathrm{W}] = 60\ [\mathrm{W}] \times \frac{V_\mathrm{h} \cdot n \cdot i\ [\mathrm{m^3/s}]}{0.2\ [\mathrm{m^3/s}]} \times \frac{[\mathrm{O_3}]\ [\mathrm{ppm}]}{50\ [\mathrm{ppm}]} \qquad \text{(A1)}$$

Here, V_h is the stroke volume [m^3], n is the engine rotation speed [rpm], and i is 1/2 for four stroke-cycle engines.

The power output, N_p, [W] is expressed with the following relation:

$$N_\mathrm{p}\ [\mathrm{W}] = p_\mathrm{me}\ [\mathrm{Pa}] \cdot \left(V_\mathrm{h} \cdot \frac{n}{60} \cdot i\right)\ [\mathrm{m^3/s}] \qquad \text{(A2)}$$

Here, p_me is the mean effective pressure [Pa].

The ratio of the energy consumption due to the O_3 production, γ, is defined as follows:

$$\gamma\ [\%] = \frac{E}{N_\mathrm{p}} \times 100 = \frac{3600}{0.2 \times 50} \frac{[\mathrm{O_3}]}{p_\mathrm{me}} \times 100 \qquad \text{(A3)}$$

The calculated ratio of the energy consumption, γ, versus the mean effective pressure, p_me, with the variation of the O_3 concentration is shown in Fig.A-1. The ratio of the energy consumption, γ, increases with the increase of the O_3 concentration, and the energy consumption is significant at the lower brake mean effective pressure.