Spray Combustion of Liquefied CO\textsubscript{2} Mixed Fuel for NO and Soot Simultaneous Reduction

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ABSTRACT

The authors propose a new concept on the simultaneous reduction of NO and soot emission in Diesel engine exhaust. This concept should be realized by flash boiling process of injected fuel oil with liquefied CO\textsubscript{2} dissolved. Thus, selective flash boiling effect of CO\textsubscript{2} component of this mixed two component solution is believed to improve the spray atomization due to prompt cavitation bubble generation. When, the mixed fuel is injected from high-pressure to low-pressure of chamber pressure, CO\textsubscript{2} gas should be generated through the flash boiling process or just gas separation process. Therefore, we can get rapid evaporation spray, and NO emission should be reduced due to "spray-internal EGR effect" of this CO\textsubscript{2} gas.

Further, soot particles believed to be reduced with the effect of reburning by OH radicals formed with thermal dissociation of CO\textsubscript{2}. In this study, characteristics of the evaporative mixed fuel spray were examined by shadow photography and flame characteristics were measured by direct photography applying two-color method. Also exhaust gas emissions, such as NO, soot, CO, CO\textsubscript{2} and THC were detected. From the results, it is revealed that the Diesel fuel-liquefied CO\textsubscript{2} mixed fuel can successfully reduce NO and soot emissions in Diesel combustion process with keeping or improving the combustion efficiency.

INTRODUCTION

In Diesel engines, the trade-off relation for reducing both soot (Particulate Matter) and NO emissions can not be avoided. Accordingly, several combustion systems are proposed to reduce exhaust emission with keeping the thermal efficiency in recent years. High-pressure fuel injection system was tried to apply into engines with retarded injection timing to reduce soot emission. However, the application of this injection system would be subject to the increase in NO emission as well as greater driving force. Further, NO was not decreased well even in the case of micro-hole nozzle injection with higher fuel injection. On the other hand, novel combustion system by use of early stage in-cylinder injection has been proposed to reduce markedly NO\textsuperscript{1(2)}. In this system, they intend to realize the rapid burning of the lean-homogeneous mixture prepared in the cylinder with early stage fuel injection. Thus, NO emission is decreased remarkably with keeping low soot emission in the condition of light load (air excess ratio \(\lambda > 2.5\)). However, CO and HC emissions increase and the load range for NO reduction is limited as \(\lambda > 2.5\), in this system.

Figure 1 shows the illustration of A/F limitation for NO reduction in the case of lean-homogeneous mixture combustion. In Diesel combustion process, NO emission seems not to be decreased in the case of lean combustion region, since the formation of fuel rich mixture can not be unavoidable. On the contrary, NO emission must be decreased under the lean mixture combustion due to fully homogeneous mixture. Then, in the case of lean-homogeneous mixture combustion system for Diesel application by use of in-cylinder injection, it seems to be impossible to avoid the fuel rich region even in the case of overall lean mixture condition. Accordingly, this kind of technique can not apply to Diesel combustion process for high load conditions.

Therefore, there is a limitation for both reduction of NO and soot in single stage combustion process of lean-homogeneous mixture such as described above. It seems to suggest that the application of some kinds of additive to control the combustion process or combination of single stage combustion

\[\text{Fig. 1 Images of NOx profile with A/F ratio in lean-homogeneous mixture combustion}\]
and two stage combustion system to reduce effectively both emissions in high load conditions are required. The authors propose the new fuel injection system by use of Diesel fuel oil with liquefied CO₂ dissolved to reduce both soot and NO simultaneously. This concept reaches to improvement of spray atomization and evaporation, and to control the combustion process by the effect of separated or flash boiled CO₂ gas.

CONCEPT FOR LOW EMISSION COMBUSTION

Phase Change in CO₂ - n-Tridecane Mixed Fuel

For the pure substance, liquid region and vapor region can be separated accurately by a saturated vapor pressure p, line in Pressure-Temperature diagram. Here, when the liquid with single component is decompressed to the lower pressure below p, the liquid should be flash boiled promptly. In this flash boiling spray, it was revealed that the spray atomization was remarkably promoted with a large spray angle and smaller droplet diameter. As a result, we could realize a prompt vaporizing spray. However, for the several components of Diesel light gas oil the decompression process through the fuel injection from the nozzle condition to the chamber ambient could not down across the vapor pressure line.

Figure 2 shows a P-T diagram of two components solution by two kinds of liquid whose saturated vapor pressures are different in each other. The critical point is depending on the critical pressure, the critical temperature and the molar fraction and etc. of each component. It is peculiar that there appears the "two phase region" where liquid and vapor phases are mixed in. The upper boundary between two phase region and liquid phase region is called as a saturated liquid line and the lower one between that and vapor phases as a saturated vapor line. Both lines reach the critical point.

Figure 3 shows the effect of the mole fraction X₇₉ of CO₂ on P-T diagram in case of the two components solution of n-Tridecane and CO₂ used in the experiments. The locus of critical points corresponding to each X₇₉ was estimated according to methods of Chueh-Prausnitz and Krglewski-Kay, and the two phase region was decided by the corrected equation of Benedict-Webb-Rubin. As shown in Fig. 3, locus of the critical point and the profile of two phase region depend on the mole fraction of CO₂. Thus, we could optimize the two phase region for the injection process by controlling CO₂ mole fraction. Also, the fuel solution conditions of inside the nozzle and in-cylinder of Diesel engines are indicated in the figure.

As mentioned above, flash boiling process does not occur for Diesel injection process for a pure substance of n-Tridecane. However, in the case of mixed two component solution such as n-Tridecane & CO₂ system, the spray quality should be improved through the injection as follows:

(i) Higher CO₂ mole fraction case: It is suggested that a part of mixed fuel of n-Tridecane and liquefied CO₂ could be vaporized promptly owing to the flash boiling effect, since the pressure drop with the injection reaches to the two phase region.

(ii) Lower CO₂ mole fraction case: The pressure drop through the injection does not reach to the two phase region. However, slight improvement of the spray atomization is expected by the gas separation of supersaturated CO₂ component. According to Henry's law, saturated solubility of CO₂ for n-Tridecane is assessed to be 0.4 in CO₂ mole fraction at the chamber pressure. Thereafter, the fuel state is going across the two phase region by heating up due to the heat transfer from the hot state ambient, as a result, the flashing process should be occurred.

Low Emission Concept

In this study, the mixed fuel of liquefied CO₂ and n-Tridecane is applied to Diesel engine combustion system in order to reduce simultaneously both NO and soot emissions under keeping or improving thermal efficiency.

Concept:

(1) Application of low pressure fuel injection system to keep or improve thermal efficiency.

(2) Formation of rapid evaporation spray due to flashing or separation of CO₂ component.

(3) Capability for controlling combustion process and formation process of chemical species by an additive such as CO₂, which should be supplied through injection process.
**NO Reduction.** Figure 4 shows the effect of CO\(_2\) fraction in ambient on NO formation estimated by chemical equilibrium analysis. In the calculation, dissolved CO\(_2\) component in the fuel was assumed to separate to the ambient. In the figure, NO concentration is represented by normalized one with NO concentration at X\(_{CO2}=0.0\). And NO formation was assessed with extended Zeldovich mechanism by considering CO\(_2\) effect. As shown in the figure, NO concentration decreases markedly with increasing CO\(_2\) mole fraction owing to the increase in heat capacity of the ambient and CO\(_2\) thermal dissociation with endothermic reaction. And NO concentration is expected to reduce up to 60% in the case of X\(_{CO2}=0.8\). Accordingly, "spray-internal EGR effect" could reduce NO emission through the decrease in flame temperature due to the CO\(_2\) heat capacity and CO\(_2\) thermal dissociation.

**Soot Reduction.** Soot emission is expected to be reduced in this mixed fuel injection system as follows;

(i) Soot formation: Selective CO\(_2\) flash boiling process or CO\(_2\) separation process in this mixed fuel injection system results to avoid the fuel rich mixture region. It can reduce the soot formation.

(ii) Soot Oxidation or Soot Reburning: In general, it is believed that soot particles are burnt by O\(_2\) molecules or O radicals. In this CO\(_2\) mixed fuel injection system, CO\(_2\) is expected to dissociate to CO and O radical under high temperature field. Moreover, previous studies have reported that CO\(_2\) component could reduce soot emission directly\(^{[10]}\) in Diesel combustion field. This reaction of C + CO\(_2\) = 2CO is called as Boudouard reaction\(^{[11]}\). Accordingly, soot particles might be reburnt by CO\(_2\) dissociation effect and Boudouard reaction.

**EXPERIMENTAL APPARATUS AND PROCEDURE**

**Combustion Experiments**

For the combustion experiments, a Rapid Compression & Expansion Machine (RCEM) with 100 mm bore was used. The chamber shape is a flat disk type with a side injection system. The temperature of a cylinder wall is adjusted to a predetermined one by supplying the hot water into a water jacket. Air is charged in the cylinder through a pressure regulator from an air bomb. And, NO, CO, CO\(_2\), and THC concentration in burst gas are detected with chemiluminescence analyzer, NDIR analyzer and FID analyzer after the gas is gathered into a sampling bag. For a test fuel, n-Tridecane (CO\(_2\) mole fraction is zero), and the mixed fuel of liquefied CO\(_2\) and n-Tridecane (CO\(_2\) mole fractions are 0.4, 0.6, 0.8) are used.

**Fuel Injection System**

Figure 5 shows a schematic diagram of the fuel injection system used here. An oil pressure booster was applied for this mixed fuel injection system instead of jerk type fuel injection pump, since liquefied CO\(_2\) may vaporize when the line pressure reaches below the saturated vapor pressure of CO\(_2\). Here, compressed air was used to pressurize the fuel in the booster. And another booster can operate a needle of the injection nozzle as being independent for the fuel line. The pressurized liquefied CO\(_2\) of about 10 MPa is going to the booster with quasi-steady state. n-Tridecane (n-C\(_{13}\)H\(_{28}\)) as a standard fuel in a fuel tank is also fed into the booster. And, an agitator is operated in order to obtained well-stirred homogeneous mixed fuel.

**Experimental Conditions**

Table 1 shows experimental conditions. Single hole
nozzle (dₙ=0.18 mm, l/dₙ=4.17), which is set at top side, was used with the injection pressure of 16 MPa. The injected fuel quantity of n-Tridecane was the same as 10 mg/st. for both standard injection of only n-Tridecane (X_CO₂=0.0) and mixed fuel injection (X_CO₂=0.4, 0.6, 0.8). Then, the injection period is 3.6 ms for standard injection of n-Tridecane (X_CO₂=0.0), and 3.8 ms for X_CO₂=0.4, 4.5 ms for X_CO₂=0.6 and 6.5 ms for X_CO₂=0.8. The fuel was injected perpendicularly into the chamber. The distance between nozzle tip and the lower side cylinder wall is 96 mm. The overall excess air ratio is 25. For the operation of RCEM with compression ratio of 15, the ambient atmosphere in the cylinder reaches 750 K in temperature and 3.2 MPa in pressure at the time of injection, that is 5.0 deg. before TDC.

A quartz glass window is installed in the cylinder head to allow taking spray and flame photography by 16 mm high-speed camera (nac E-10). In this experiment, shadow photography for vaporizing spray and combustion flame were taken with Ar⁺ laser light of 514.5 nm in wavelength. Photographing speed is 6000 fps and a color negative film (Kodak VISION200T) is used. Further, two color method was applied to direct photograph images in order to assess flame temperature and KL factor inside the combustion flame.

SPRAY COMBUSTION PHENOMENA

Shadow Photography

Figure 6 demonstrates the temporal changes in typical shadowgraph photographs of the spray and the frame for each CO₂ mole fraction. At time t=1.00 and 1.33 ms, fuel concentration seems to be diluted in the spray downstream region for X_CO₂=0.6 and X_CO₂=0.8. At the timing around 1.67 ms, the visible flame appears near the mixing region at the tip of the main liquid jet for X_CO₂=0.0, while it appears near the downstream region or the spray tip region for larger CO₂ mole fraction conditions. In the case of X_CO₂=0.0, 0.4 and 0.6, the

Fig. 6 Temporal change in spray and flame shape under each mole fraction
visible flames cover the whole spray region during the main combustion period, thereafter the flame is mainly spreading near the wall. On the contrary, though the remarkable change in the intensity gradation is recognized over the whole spray region, the visible flame with lower intensity just observed near the central region of the spray in the case of $X_{CO_2}=0.8$. And it should be noticed that the flashing of the wall-wetted fuel film might be occurred near the wall in the case of $X_{CO_2}=0.6$ and $X_{CO_2}=0.8$.

Consequently, it seems to suggest that the non-visible combustion like a blue flame is activated around the visible flame region for the larger CO$_2$ mole fraction case. Further, it is found that the visible flame continuation term becomes shorter with increasing CO$_2$ mole fraction.

**Two Color Method Results**

In this study, flame temperature and KL factors are indicated with 256 gradation as a relative value with an arbitrary unit. The temporal changes in area mean flame temperature is represented in Fig. 7. The area mean value is defined by the ratio of sum of area temperature multiplied with flame area and sum of flame area as shown in the figure. In the flame of the CO$_2$ mixed fuel, relative flame temperature is apparently lower than that of n-Trimdecane for all crank angles. Therefore, it is derived that formation of thermal NO should be suppressed during the combustion process for CO$_2$ mixed fuel injection system.

With regard to KL factor, accumulated KL factor over the flame define by summation of KL multiplied with flame area $A_i$ is assessed in Fig. 8. From this figure, it is revealed that the accumulated KL factor decreases with increasing CO$_2$ mole fraction in this mixed fuel injection system. This result seems to be attributed to the fact that soot formation is suppressed as confirmed in non-visible flame combustion due to the decrease in fuel rich mixture as well as soot particles are reburnt with O radicals or Boudouard reaction.

**COMBUSTION PERFORMANCE**

**Combustion Characteristics**

Combustion characteristics of the typical combustion cycle are compared in Fig. 9 for $X_{CO_2}=0.0$, 0.6 and 0.8 injection cases. There is no remarkable difference in the ignition delay for all injection cases. Here, the latent heat of liquefied CO$_2$ is 121.8 kJ/kg at atmospheric conditions and it is enough smaller than that of n-Trimdecane of 359.5 kJ/kg. Then, the temperature drop due to the CO$_2$ vaporizing in the spray is derived to be negligible factor for the ignition delay. In rate of heat release diagram, the mixed fuel spray has an active combustion in the diffusion burning period and it is burnt out within the short term.

In total heat release diagram, the total heat release increases with an increase in CO$_2$ mole fraction. Thus, combustion efficiency for the injected fuel amount must be getting better in higher CO$_2$ mole fraction case. Accordingly, from the consideration mentioned above, the activated burning in the non-visible flame region and the burning of the wall-wetted fuel film due to the flashing might contribute the complete combustion process with keeping the lower exhaust emissions.
Fig. 10 Comparison of exhaust gas concentration at each mole fraction of CO₂

Exhaust Emission Results

Figure 10 shows the comparison of exhaust gas concentrations, which are averaged for typical 5 events.

In relation to NO emission, 48% reduction and 57% reduction could be achieved for X_{CO₂}=0.6 and 0.8 respectively, comparing with the case of X_{CO₂}=0.0. Also, concerning soot emission, 33% reduction and 49% reduction in Bosch smoke unit could be obtained for X_{CO₂}=0.6 and 0.8 respectively. Consequently, it is revealed that simultaneous reduction of NO and soot could be achieved by use of the liquefied CO₂ mixed fuel injection system. Thus, this novel injection system has a potential to break through the trade-off relation in NO and soot emission.

Further, THC concentration is also decreased in CO₂ mixed fuel injection. In the normal fuel case of X_{CO₂}=0.0, the fuel film might be formed on the wall and the quenching of the flame by the wall might be increased as shown in Fig. 6 owing to remained flame near the wall. These phenomena might provide the higher HC emission. On the contrary, CO concentration increases with increasing CO₂ mole fraction. This result seems to be attributed to thermal dissociation of CO₂ component, soot reburning by O radicals O₂ and Boudouard reaction.

CONCLUSIONS

A new concept on the simultaneous reduction of NO and soot emissions in Diesel engines was realized by injecting the mixed fuel of liquefied CO₂ and n-Tridecane. And, the following conclusions are drawn from this study.

(1) Pressure drop through the injection process in liquefied CO₂ mixed fuel can provide the gas separation of supersaturated CO₂ component. Thereafter, the mixed fuel should be flash-boiled by crossing the two phase region due to heating up process, leading to the improvement of spray evaporation.

(2) With increasing CO₂ mole fraction, we could obtain the novel combustion mechanism, where non-visible flame burning is dominant, with improving the combustion efficiency.

(3) By use of CO₂ mixed fuel injection system, simultaneous reduction of NO and soot could be achieved with breaking through the NO-soot trade-off relation.

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