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Fundamental Studies on Effect of Ozone Injection to the Internal-Combustion Engine - FTIR Spectrum of Hydrocarbon Compound Reformulated by Ozone -

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Abstract. The mixture gas composed of hydrocarbon compounds and air/O₂ exposed to discharge was analysed by FTIR. The emission spectroscopy of combustion in the enriched condition of O₂ and O₃ was not very different because it was assumed that the consumption of O atoms required for combustion was consistent. The spectrum around 1750 cm⁻¹ of the mixture gas, which did not appear before discharge, was detected by FTIR. The generation rate of the by-product around 1750 cm⁻¹ strongly relates with O₃ concentration. It was suggested that O₃ is the major molecule reacting with vaporised hydrocarbon compounds. A candidate for the by-product was supposed to be C₈H₁₆O or/and C₈H₁₆O₂ from the reference absorption spectra of FTIR. The by-product was produced with thin O₃ concentration, which was 0.62 g/m³ in the test, although O₃ was emitted as extra when injected O₃ was more than approximately 2 g/m³.

1. Introduction

Alternative energy sources against a fossil fuel for automobile, such as hydrogen, bio-diesel fuel (BDF), dimethyl ether (DME) and ethanol, are widely studied and some of them have been developed to a practical level recently [1-3]. Simultaneously, effective and practical uses of a fuel for an internal-combustion engine, that great majority of these automobiles are currently in use, also have been progressed. It is reported that cetane number improved when O₃ was injected to a compression ignition engine [4]. Moreover, it is proposed that the automobiles that have the discharge reactor placed at the air inlet increased fuel efficiency, and also the rate of CO, NO and CH was decreased [5-7]. However, the mechanisms of O₃/discharged air to the engine for improvement of the fuel consumption and cleanness of automobile exhaust gas are not cleared yet.

In a four-stroke cycle engine, the vaporised hydrocarbon compounds was blended with air in induction stroke. Air through the discharge reactor installed before an inlet of engine has the possibility to change the composition of vaporised hydrocarbon compounds in induction stroke. We analysed the emission spectroscopy of HC compounds flame in the enriched condition of O₂ or O₃ and the FTIR spectrum of the mixture gas composed of vaporised hydrocarbon compounds and air/O₂ exposed to discharge.
2. Experimental procedure

2.1 Ozone generator
Ozone was generated from O\textsubscript{2} or air with discharge that was generated on the surface of a discharge element placed in the discharge reactor. The surface discharge element was made of thin-gritted tungsten electrode fixed on BaTiO\textsubscript{3} plate. The discharge voltage was generated by high AC voltage power supply (Logy Electroc Co., LHV-13AC) and varied from 8.0 to 13.0 kV (with 9 ~ 11 kHz in frequency).

2.2 Emission spectroscopy of HC compounds flame
Emission spectroscopy of hydrocarbon compounds flame in the enriched condition of O\textsubscript{2} or O\textsubscript{3} was measured by emission spectrometer (Hamamatsu, PMA-C8808). The flame was generated by the burner (MSR, DragonFly) using hydrocarbon compounds (commercial use, Octane number: 90~92), as shown in Fig. 1. The O\textsubscript{3} was prepared from O\textsubscript{2} through the discharge reactor and the concentration of it was maintained 7.3 g/m\textsuperscript{3}. The flame burned with O\textsubscript{3} or O\textsubscript{2} that occupied the surroundings of the burner. The gas flow was kept 1 L/min consistently.

2.3 FTIR spectrum of the mixture gas
Induction stroke of a four-stroke cycle engine was simply composed of an inverted jar as a reactor for a mixture gas of discharged air/O\textsubscript{2} and vaporised hydrocarbon compounds in this study, as shown in Fig. 2. The beaker filled with 50 mL of hydrocarbon compounds, that was commercially available (octan number 90 ~ 92), was located in the centre of the jar. Air or O\textsubscript{2} exposed to discharge (the reactor mentioned above was used) was sent into the jar and was mixed with vaporized hydrocarbon compounds. The hydrocarbon compounds were spontaneously vaporised in the inverted jar and the density of it was kept around 5 ppm on condition that atmospheric pressure was 1022 hPa (±2 hPa) and temperature was 17 °C (±1.0 °C). The concentration of O\textsubscript{3} made of O\textsubscript{2} was varied from 0.62 g/m\textsuperscript{3} to 8.8 g/m\textsuperscript{3}, and O\textsubscript{3} made of air was varied from 0.76 g/m\textsuperscript{3} to 2.7 g/m\textsuperscript{3}.

The mixture gas was analysed by FTIR (Shimadzu, FTIR-8900) with 24 m long-path distance gas cell. Flow rate of the sample gas was kept on 12 L/min consistently. The experiment was carried out under the conditions of an atmospheric pressure and temperature around 25 °C. The mixture gas analysed by FTIR was emitted to the air through an active charcoal filter.

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Fig 1. A schematic of the experimental apparatus for measurement of emission spectroscopy of HC compounds flame.
3. Results and discussion

The emission spectroscopy of combustion in the enriched condition of O$_2$ and O$_3$ was not very different because it was assumed that the consumption of O atoms required for combustion was consistent. It was indicated that the hydrocarbon compounds were totally decomposed by high temperature of burning itself, and then each atom such as C and H reacted with O. However, the effect of O$_3$ injection was not clear from the analysis of the emission spectroscopy of combustion with the burner.

The atmosphere in the jar became clouded from transparent immediately after injection of air and O$_2$ that were exposed to discharge. It was suggested that H from vaporised hydrocarbon compounds and O from decomposed O$_3$ made moisture and a saturated vapour appeared in the jar.

The spectra at around 1750 cm$^{-1}$, which was not observed before discharge, were detected in the case of both air and O$_2$ as shown in Fig. 3. Also, around 890cm$^{-1}$ and 970cm$^{-1}$ were disappeared after discharge. It is found that the composition of the vaporised hydrocarbon compounds was chemically changed by reacting with the discharged air or O$_2$. A candidate for the by-product detected at around 1750 cm$^{-1}$ is C$_8$H$_{16}$O or/and C$_8$H$_{16}$O$_2$ because they indicate similar FTIR spectra [8] with the by-product.

Ozone could be one of the main molecules of inducing chemical changes in the hydrocarbon compounds. The O$_3$ concentration closely relates with the generation of the by-product at 1750 cm$^{-1}$ as shown in Fig. 4. The generation rate of the by-product at around 1750 cm$^{-1}$ rises quickly until approximately 2.5 g/m$^3$ in the case of O$_2$ and approximately 4.0 g/m$^3$ in the case of air, and then both stay constant. The air exposed to discharge tended to easily produce the by-product. Other gases in the discharged air such as NO, NO$_2$ and other excited gases maybe assist to generate the by-product.

The by-product observed at around 1750 cm$^{-1}$ was generated when 0.62 g/m$^3$ that is the thinnest O$_3$ produced from O$_2$ in the test was injected. The concentration of injected O$_3$ is important for reforming vaporised hydrocarbon compounds in the jar. Moreover, unconsumed O$_3$ was observed at around 1050 cm$^{-1}$, 2100 cm$^{-1}$ and 2350 cm$^{-1}$ when injected O$_3$ was more than approximately 2 g/m$^3$. Hydrocarbon compounds are effectively vaporised in induction stroke by fuel injector or carburetor of practical internal-combustion engine. It is certain that the density of hydrocarbon compounds is much higher than the case of this study, which was approximately 5 ppm. Therefore, in high density condition of hydrocarbon compounds, it is suggested that unconsumed ozone detected by FTIR could completely react to hydrocarbon compounds and simultaneously production rate of by-product could be increased.
The composition of vaporised hydrocarbon compounds was chemically changed with O$_3$ and the by-product at 1750 cm$^{-1}$ was generated after injecting air/O$_2$ exposed to discharge. It was found that relatively low density of O$_3$ such as around 2 g/m$^3$ is enough to change the composition of the hydrocarbon compounds in the test. Moreover, air through the discharge reactor could easily generate the by-product at 1750 cm$^{-1}$ in comparison with O$_2$.

Fig 3. Typical FTIR spectra of the mixture gas of vaporized HC compounds and discharged air/O$_2$ analyzed with 24 m long-path distance gas cell.

Fig 4. The generation rate of the by-product detected at around 1750 cm$^{-1}$.

**4. Conclusions**

The composition of vaporised hydrocarbon compounds was chemically changed with O$_3$ and the by-product at 1750 cm$^{-1}$ was generated after injecting air/O$_2$ exposed to discharge. It was found that relatively low density of O$_3$ such as around 2 g/m$^3$ is enough to change the composition of the hydrocarbon compounds in the test. Moreover, air through the discharge reactor could easily generate the by-product at 1750 cm$^{-1}$ in comparison with O$_2$.

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