Emission Characteristics of OH and C₂ Radicals under Engine Knocking*

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Emission from the area of autoignition in an actual S. I. engine is observed under knocking operation using optical fibers. The difference in emission intensity observed between knocking and nonknocking operation is mainly due to the emission intensities of the OH and C₂ radicals. The emission intensity from these two species increases sharply when autoignition occurs. In addition, emission intensity from the C₂ radical shows two peaks in some cycles. Since the first peak is due to the autoignition reaction, the second peak is thought to be caused by soot formation in some cycles under knocking operation. This second peak corresponded to shadowlike matter seen in high-speed shadowgraphs taken during the expansion stroke.

**Key Words:** Internal Combustion Engine, Knocking, Optical Fiber, Autoignition, Radical, Soot

1. Introduction

In a previous report\(^1\), the authors described a method for detecting the location of autoignition using several optical fibers inserted through the head gasket into the combustion chamber of a spark ignition engine. With this method, emission intensities were obtained from several regions where autoignition frequently occurs near the cylinder wall on the opposite side from the spark plug, and compared under knocking and nonknocking operation. In addition, a monochromator was employed to investigate which species contributed to differences in emission intensities under these two operating conditions. It was found that the emission intensities of the OH and C₂ radicals accounted for such differences. Emission time histories of these species in relation to the crank angle were then compared for two A/F ratios. These species are assumed to be intermediates and combustion products related to autoignition, flame propagation and other aspects of combustion. Thus, they are thought to differ from other components which are involved in pre-autoignition reactions and display weak emission intensities.

In the emission spectrum of the C₂ radical, there are 36 spectral lines of varying intensities in the Swan system that is observable in the flame. Among the ones produced by an emission as a result of electron transition, there are three sequential groups having a difference of 0, 1 and 2, respectively, between the vibrational quantum number of upper and lower excited states. The heads of bands of these groups which means the sharp "heads" or edges of the band spectra, are 516.5 nm \((v'=0, v''=0)\), 563.5 nm \((0, 1)\) and 619.1 nm \((0, 2)\), where the primes ' and '' refer to the upper and lower electronic states, respectively and \(v'\) and \(v''\) value corresponds to the initial and final vibrational quantum numbers, respectively. The order of their emission intensity is \(v'\), \(s\) and \(v''\), with the emission intensity being the weakest at 619.1 nm. It was found that only this wavelength showed a large difference in emission intensity between knocking and


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nonknocking operation. It should be noted that \( C_2 \) is generally recognized as being a precursor of soot\(^{(3)} \).

There have been many reports to date by different researchers concerning the mechanism causing soot formation in diesel engines, and several theories have been proposed to explain the causes of soot\(^{(4)} \sim \(^{(6)} \). In general, it is known that soot forms during diffusion combustion of a gas-liquid fuel mixture. Akamatsu et al.\(^{(7)} \) visualized the locations of emission from OH and \( C_2 \) radicals in the flame of a burner for varying mixture conditions of a gas-liquid fuel. They reported that large quantities of \( C_2 \) and soot were generated under a poor mixture condition and that the \( C_2 \) radical was observed in the rearward direction from the OH radical, which was produced in the reaction zone at the flame front.

On the other hand, Furutani et al.\(^{(8)} \) used the transmission attenuation characteristics of He–Ne laser light injected into a rapid compression machine to detect the formation of soot when \( n \)-heptane fuel autoignited as a result of compression. At the same time, they also observed emission at 680 nm, which was assumed to be emission from soot precursors. Based on those observations, they concluded that soot and soot precursors are formed even with a lean mixture when autoignition occurs in a low-temperature regime.

The above-mentioned studies and others carried out to date, however, have not been conducted with an engine based on the actual spark-ignition internal combustion engine. One point of particular interest that is still not understood is the relationship between the occurrence of knocking and the formation of soot. To shed some light on this issue, the potential for the formation of soot during knocking operation of an actual engine using gasoline as the fuel was examined in this research by investigating the cycle-to-cycle emission behavior of the \( C_2 \) and OH radicals.

2. Experimental Equipment and Procedure

The experimental equipment used in this work was basically the same as that described in our previous report\(^{(9)} \). It is shown schematically in Fig. 1, and the areas observed via the optical fibers are indicated in Fig. 2. All of the optical fibers were made of ultraviolet-ray-transmitting quartz and had a core diameter of 200 \( \mu \)m and a secondary covering diameter of 1 mm. An area within the full angle of 20° was observed with each of the optical fibers.

An effort was made to introduce into the monochromator the emission signals accompanying autoignition in the final combustion region as much as possible. To accomplish this, a bundle of optical fibers (denoted as no. 17, fiber I in Fig. 1) was provided perpendicular to the direction of flame propagation. One of the fibers in this bundle was introduced into a photomultiplier tube and the other six optical fibers were introduced into the monochromator (no. 16). The fiber bundle was passed through a fairly thick tube, and the space around the fiber bundle was cooled with nitrogen gas. The area observed by fiber bundle I at top dead center (TDC) of the compression stroke was a circle about 10 mm in diameter, the center of which is indicated by the black dot in Fig. 2.

The monochromator used was Model CT50 produced by Nihon Bunko Kogyo K.K., and a mechanically cut diffraction grating was used which provided 1 200 lines/mm. The photomultiplier tube (Model 931A made by Hamamatsu Photonics K.K.) employed to detect the total emission in the visible

![Fig. 1 Configuration of experimental equipment](image-url)
radiation region was sensitive to emission in a wavelength range of 300–650 nm. The photomultiplier tube (Model R955 equipped with the C659-S cooling unit) used with the monochromator had a wavelength sensitivity range of 160–930 nm. The incidence slit of the monochromator was set at a width of 2 mm, which provided a wavelength resolution of 3 nm. Before measurements were made, the wavelength of the monochromator was calibrated using a low-pressure mercury lamp.

The wavelength transmission characteristics of the light receiving system, consisting of the optical fibers and the photomultiplier tubes, are shown in Fig. 3 along with the linear characteristic of the output voltage in relation to the intensity of the incident light.

The engine operating parameters were a compression ratio \( e \) of 9.5:1, engine speed \( N_e \) of 1200 rpm, charging efficiency \( \eta_c \) of 80%, \( A/F \) ratios of 12.0:1 and 13.75:1 and ignition timing \( \theta_i \) of 15(5), 19, 22 and 25 BTDC, corresponding to knocking intensities of nonknocking, trace, light and heavy knocking, respectively. The fuel used was regular gasoline having an octane number of 91.0. Fuel was supplied by an EGI system with port face injection when the intake valve was closed. With this injection timing, the injected fuel strikes the intake valve and heat from the port walls and other areas promotes premixing. In the case of uniform premixing, it is known that soot typically forms when the mixture is richer than the \( A/F \) ratio of 2-3. Although the \( A/F \) ratios used in the present work were considerably leaner than that, there is a possibility that nonuniform mixing could cause soot to form. However, with an \( A/F \) ratio similar to those used in this study, it has been observed that the fuel is vaporized in the vicinity of TDC of the compression stroke. Consequently, as long as the fuel is not unevenly distributed, it can safely be assumed that a mixture as rich as an \( A/F \) ratio of 3 would not be formed.

3. Experimental Results

3.1 Location of emission accompanying autoignition

Figure 4 shows the knocking intensities obtained in approximately 15 cycles of operation for each of three different ignition timings. Knocking intensity was defined as the maximum pressure oscillation amplitude of the high-frequency components above 3 kHz, among the pressure signals detected by pressure pickup No.1 (Fig.1.), which was located near the region having the highest incidence of autoignition. The data plots show that the knocking intensity varied considerably from cycle to cycle and that the average intensity tended to increase as the ignition timing was advanced. Examination of the results for each cycle reveals that when the ignition timing was set on the advanced side, there were also cycles that showed lighter knocking intensities than when it was set on the retarded side.

In Fig. 5, the emission intensities detected with five optical fibers that were used to observe areas near the cylinder wall are shown in relation to the four knocking intensity levels. The emission intensities are given as cumulative values for fifty cycles of the
peak intensities detected in each cycle. The observed areas denoted as A, B, C, D and E correspond to the areas within the full angle of 20° that were observed with the optical fibers numbered 7, 6, 5, 2, and 1, respectively.

Optical fiber No. 4 differed from the other fibers in that the area it was used to observe also included a portion of the combustion chamber near the center of the cylinder in addition to the vicinity of the cylinder wall. For that reason, the results obtained with optical fiber No. 4 have been omitted here. The results for optical fiber No. 3 have also been omitted because of a signal acquisition problem caused by deposits on the optical fiber.

The results shown in Fig. 5 for an ignition timing of 15° BTDC (nonknocking operation) indicate that the emission intensity decreased with increasing distance from observed area D. With this ignition timing, pressure in the combustion chamber rose as the flame propagated and reached approximately its maximum value at the time when flame propagation was completed. Consequently, the peak emission intensity occurred at the time the flame passed in front of the end of optical fiber No. 2 that was used to observe area D, the final region of flame propagation.

The results for trace knocking operation (ignition timing of 19° BTDC) also show virtually the same tendencies. The reason for this can be understood with reference to the data in Fig. 4. Statistically, the knocking intensity at this ignition timing was still very slight and the frequency of knocking was low. In addition, the emission intensities were not significantly different from the results seen for nonknocking operation. These results indicate that trace knocking in an actual engine is within an allowable intensity range.

As the ignition time was advanced to 22° and 25° BTDC, the emission intensity from observed area D rose sharply. In addition, the regular ranking of the observed areas in terms of emission intensity that was seen for ignition timings of 15° and 19° BTDC became ambiguous. In the case of light knocking, only observed area D showed strong emission intensity, suggesting that autoignition occurred with a high frequency in certain specific locations. In contrast, strong emission intensities are seen in all observed areas in the case of heavy knocking, indicating that the location of autoignition extended into the unburned end-gas region. This observation was also substantiated by shadowgraphy results.

The foregoing results show that emission intensities increased substantially when autoignition occurred. It was seen that the area with the statistically strongest emission intensities was the observed area D, which constituted the region of final combustion under non-knocking operation.

As the next step in this study, the behavior of the OH and C2 radicals around the time autoignition occurred was analyzed by emission spectroscopy. This was accomplished using fiber bundle I, which was placed perpendicular to the flame propagation path to observe an area within an angle of 20° near the cylinder wall in the center of observed area D. As mentioned earlier, a comparison was first made of the emission intensities of different species under knocking and nonknocking operation. The OH and C2 radicals were identified as two species whose emission intensities differed greatly between the two conditions. An analysis was then made of the emission time histories of these two intermediates in relation to the crank angle.

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![Fig. 5 Emission intensities detected with five optical fibers under different knocking intensity levels](image-url)
3.2 Emission spectrum analysis

Figures 6 and 7 show the emission intensities of the OH radical (characteristic spectrum of 306.4 nm) and C₂ radical (characteristic spectrum of 619.1 nm) under nonknocking operation and knocking operation, respectively.

The signal waveforms shown in the figures in relation to the crank angle are for the cylinder pressure detected by pressure pickup No. 1, which was the closest to the location of autoignition, the total emission intensity obtained with fiber bundle I for all visible radiation wavelengths, the emission intensities obtained with the monochromator for the OH and C₂ radicals and the visible radiation emission intensity obtained with optical fiber No. 4. The signal for fiber No. 4 was used in comparison with that of fiber bundle I for the purpose of understanding flame propagation and the occurrence of autoignition.

Under nonknocking operation, both the OH and C₂ radicals showed virtually no strong emission intensity. The emission waveforms of these two radicals under knocking operation, in contrast, showed their first sharp peaks when autoignition occurred. The waveform of the OH radical did not show a second peak in any of the cycles. On the other hand, there were some cycles in which the C₂ emission showed an appreciably large second peak, which was not observed for the OH emission.

There were even some cases when three peaks were observed, as indicated by the fiber bundle I waveform in Fig. 7(a). The timing of the second peak in this figure was close to the occurrence of autoignition. Therefore, it is assumed that autoignition occurred at two different locations in the area.

![Fig. 6 OH and C₂ emission intensities under nonknocking operation](image)

![Fig. 7 OH and C₂ emission intensities under knocking operation](image)
under observation at slightly different times. Accordingly, in the case of Fig. 7(a), the second peak discussed below refers to the third peak.

The output waveform of fiber No. 4, which included a wide range of visible radiation wavelengths, indicates the detection of emission with differing characteristics even before autoignition occurred. This is attributed to the fact that this fiber detected the propagating flame, as was described in our previous report\(^{(4)}\). In contrast, the output waveform of fiber bundle I, which was used to observe the final combustion region, indicates that it detected only the emission from autoignition, detecting no appreciable emission from the propagating flame. These results show that fiber bundle I made it possible to observe only the emission accompanying autoignition without the emission from the propagating flame.

The results thus obtained using fiber bundle I indicate that the C\(_2\) emission differed from the OH emission and that there were also cycles after autoignition in which the emission intensity of the C\(_2\) radical increased.

### 3.3 C\(_2\) emission behavior for different A/F ratios

The OH emission intensities at the first peak and the C\(_2\) emission intensities at the first and second peaks are shown in Figs. 8 and 9, respectively, as functions of the crank angle at which the emission peak occurred. The OH emission data are for an A/F ratio of 13.75 : 1 and the C\(_2\) emission data are for ratios of 12.0 : 1 and 13.75 : 1.

It has been reported that the concentration of the OH radical shows strong temperature dependence\(^{(9)}\). In addition, we have observed that the OH emission intensity at the time of autoignition shows the same tendency as the correlation between the occurrence of autoignition and the knocking intensity\(^{(10)}\). Therefore, it can be assumed that as the temperature rises with increasing knocking intensity, a higher OH concentration will result.

The C\(_2\) radical, on the other hand, showed higher emission intensity with an A/F ratio of 13.25 : 1, near the stoichiometric level, than with a ratio of 12.0 : 1. It is seen in Fig. 9 that the closer the first emission was in time to TDC of the compression stroke, the higher the peak intensity became. This indicates that the emission intensity of the C\(_2\) radical became stronger under a condition of stronger knocking intensity\(^{(10)}\), which is thought to be indicative of temperature dependence. In contrast, cycles showing a second peak intensity were divided into two groups, one of which was characterized by weak emission intensity (Group A) and the other considerably strong emission intensity (Group B). It is thought, however, that the temperature was not so high at the time when the second peak intensity occurred.

The Group A data plots show little difference in emission intensity between the two A/F ratios. It is assumed that this type of second peak intensity pattern resulted from a combination of two factors, both
of which were due to the progression to the expansion stroke. One was a decline in the density of the luminescent species and the other was an increase in the depth of the area under observation. This same reason is thought to explain the occurrence of the second peak seen in the fiber I waveform (total emission intensity at all wavelengths) in Fig. 6 for non-knocking operation.

On the other hand, the number of cycles showing strong emission intensity (Group B) was larger with an $A/F$ ratio of $13.75:1$ than with a ratio of $12.0:1$. With either $A/F$ ratio, however, the number of cycles showing a second emission intensity peak ($A+B$) was only around 50% of the total number of cycles. The proportion of the cycles showing the Group B pattern of strong emission intensity was less than one-half of that figure. From this small ratio therefore, it is inferred that the conditions supporting the formation of a high $C_2$ concentration in the burned gases are limited to certain temperature and pressure conditions. It is possible, however, that $C_2$ might be transformed to a quasi-stable species in a different energy state from that of a short-lived radical, or to soot or some other substance having large molecular weight. From the standpoint of heat release, as indicated by the pressure waveform, it is also clear that the emission came from the burned gases, since flame propagation was already completed by the time the second peak occurred.

Furthermore, it is seen in Fig. 7 that the emission intensity shows many repetitions over time, suggesting that the luminescent species were unevenly distributed spatially. Figure 10 shows Schlieren shadowgraphs obtained under knocking operation in a study prior to the present work. Some shadowlike matter with varying degrees of gradation is seen in the shadowgraph of the expansion stroke. The matter appears to be moving in a clockwise swirl, and this is assumed to indicate variation in emission intensity accompanying the movement of luminescent species having a concentration distribution.

4. Conclusions

An optical fiber technique was used to conduct an emission spectroscopic analysis of species involved in autoignition reactions at the time knocking occurs. The results of this study are summarized below.

1. Compared with normal combustion, emission intensities were found to be higher when knocking occurred. This is attributed to large increases in the emission intensities of such species as the OH and $C_2$ radicals.

2. When autoignition occurred, the emission intensities of the OH and $C_2$ radicals increased according to the knocking intensity. This behavior is thought to be due to temperature dependence.

3. When the $A/F$ ratio was varied from the overly rich side ($12.0:1$) toward a stoichiometric mixture ($13.75:1$) while keeping the ignition timing constant, the $C_2$ emission increased in the cycles in which autoignition occurred. This is attributed to an increase in knocking intensity.

4. Cycles were observed in which the $C_2$ radical showed a second emission intensity peak distinct from the peak associated with the occurrence of autoignition. It is assumed that some of these cycles are related to the formation of soot.

References

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