Unburned Methanol and Formaldehyde in Exhaust
Gases from a Methanol Fueled S.I. Engine

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With the aid of a derivative spectrophotometer, emission characteristics of formaldehyde from a methanol fueled S.I. engine were obtained. Formaldehyde and unburned methanol were measured at several distances along the exhaust tube for various air-fuel equivalence ratios and ignition timings. Experiments show that dominant oxidation of unburned methanol in exhaust system is obtained at temperatures above 400 °C. However, formaldehyde levels were maintained during the exhaust movement for a fuel rich mixture. In fuel lean operation, formaldehyde increased in exhaust tube. This fact suggests that formaldehyde is formed by the oxidation of unburned methanol during the exhaust process, and the formation already begins in the cylinder. Careful experiments using a heated tube reactor set at engine exhaust port, and kept at a constant temperature range of 300-650 °C probe that formaldehyde accumulation occurs in exhaust system at a temperature range of approximately 400-600 °C.

Key words: Internal Combustion Engine, Combustion, Methanol, Formaldehyde, Spark Ignition Engine, Emission, Unburned Fuel, Oxidation.

1. Introduction

Recently, alcohol fuels such as methanol and ethanol have attracted special interest as an alternative to petroleum fuel[1]. Especially, ethanol is intended for an automobile spark ignition engine and has been already put to practical use in pure form since 1980 in Brazil. Also, an ethanol / gasoline blend fuel named gasohol has been widely marketed in several states of the United States. On the other hand, research on the use of methanol is underway in the United States, West Germany and Japan.

Judging from the present situation, nothing poses a substantial obstacle to using alcohol for an S.I. engine except the selection of engine materials[2]. However, in regard to exhaust emissions, the use of alcohol raises a peculiar problem. This is an increase of aldehydes. NOx emissions from alcohol operation can be considered to be slightly lower than those from gasoline operation, while the total unburned hydrocarbons are almost the same. Moreover, the amount of formaldehyde in methanol combustion and those of formaldehyde and acetalddehyde in ethanol combustion cannot be disregarded[3]. These aldehydes are well known as harmful air pollutants and can be considered to have some effects on the atmospheric environment when alcohol fuels are actually used in great quantities. It is necessary to investigate the formation mechanism of unburned methanol and formaldehyde in an S.I. engine and the influence of their emissions on the atmosphere because they have relatively high reactivity.

Much investigation has been reported on exhaust emissions from an alcohol fueled engine but no detailed study on the conditions and the mechanism of aldehyde formation has been performed. Iwai et al[5] examined the relation of emission characteristics between unburned methanol and formaldehyde under a restricted engine operating condition using methanol fuels, but the relation could not be clarified.

Browning et al[6] studied the aldehyde formation mechanism in a methanol fueled S.I. engine using a methanol reaction scheme which was proposed by Bowman[7] and Westbrook et al[8]. However, the calculated aldehyde concentrations were approximately an order of magnitude lower than measured values. This difference could be caused by insufficient consideration of the reaction process. The purpose of this paper is to elucidate the formation mechanism of formaldehyde included in the exhaust gases of neat methanol combustion in an S.I. engine. To achieve this object, the effects of engine variables on unburned methanol and formaldehyde emissions were examined. Moreover, the concentration changes of these emission species along the exhaust tube were measured, because it can be expected that chemical reactions take place during gas movement in an exhaust system. To clarify the influences of the gas temperature and the residence time on the reactivity of exhaust gases, experiments on the exhaust gas oxidation at constant temperature were performed with a reactor tube set at the engine exhaust port. From these experimental results, it was found that the oxidation reaction of unburned methanol in exhaust system was characterized by an increase of formaldehyde produced from unburned methanol in a certain temperature range.
2. Experimental apparatus and procedures

2.1 Engine and its performance

The engine used was a water cooled, single cylinder, four stroke cycle spark ignition engine (Mitsubishi R-52-GW1). The stroke volume was 322 cc. Engine specifications are listed in Table 1. The engine was operated at a speed of 1500 rpm with a wide open throttle (WOT). Both ignition timing (IT) and air-fuel equivalence ratio ($\Phi_{AF}$) were varied. During the test program, the lubricating oil and coolant temperatures were kept at 80±2 °C. Methanol used in this study was of an industrial grade (CH₃OH; above 99.3 percent). Fig.1 shows the brake mean effective pressure (BMEP) and the specific energy consumption (SEC) of the engine as a function of $\Phi_{AF}$.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine type</td>
<td>1 cylinder, 4 cycle</td>
</tr>
<tr>
<td>Chamber type</td>
<td>wedge type</td>
</tr>
<tr>
<td>Bore/stroke</td>
<td>74 mm/75 mm</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>8.71</td>
</tr>
<tr>
<td>Carburetor</td>
<td>single barrel</td>
</tr>
<tr>
<td>Max. Power*</td>
<td>0.83 MPa/2000 rpm</td>
</tr>
<tr>
<td>Max. power*</td>
<td>8.82 kW/5500 rpm</td>
</tr>
</tbody>
</table>

- gasoline fueled operation

Fig. 1 Test engine performance operated at a speed of 1500 rpm with a WOT

2.2 Gas analysis

2.2.1 Sampling position

To examine the change of gas component concentration, exhaust gases were sampled, as shown in Fig.2, at six locations along the exhaust tube of the test engine with an original exhaust system. After this, a straight exhaust pipe (diameter 37 mm, length 2.2 m) with twenty sampling positions at intervals of 100 mm was provided to observe the effects of piston flow in the exhaust tube of the same single cylinder engine. Exhaust gas temperatures were also measured in the same sampling positions using CA thermocouples. The exhaust tubing was exposed to room air without heat insulator or cooling device.

2.2.2 Measurements of unburned methanol

Unburned methanol in exhaust gases was analysed by a gaschromatograph equipped with FID. Exhaust gases were sampled by a syringe which was held at 150 °C in temperature. The reason for holding the syringe at 150 °C was to avoid condensation of water and experimental error due to conversion of unburned methanol to methyl nitrite at low temperatures.

2.2.3 Formaldehyde determination

Trace analysis of formaldehyde is generally conducted by MBTH, 2-4DNPH and other wet chemical procedures because formaldehyde has no sensitivity to gaschromatographic analysis. An instrumental analysis using FID was attempted which measured a concentration of methane converted from formaldehyde. These procedures have good reproducibility and sensitivity, but they are complex techniques and very time-consuming for both gas sampling and gas analysis. In order to make a great number of measurements easily and exactly, an instrumental analysis of formaldehyde using a derivative absorption spectrophotometer was developed for this study. As shown in Fig.3, formaldehyde is well known to have a distinctive second order derivative spectrum within the wave range of 270-310 nm. Quantitative analysis was accomplished by observing the derivative intensity of 284 nm band which was proportional to formaldehyde concentration without the interference of other coexisting gas components.

The schematic of spectrophotometer used is shown in Fig.4. The measurements were continuously performed by introducing the exhaust gases into the sample cell of the spectrometer through the sampling probe. The sampling line was electrically heated to 150 °C and the sample cell was held at 170 °C. Because, at temperatures below 150 °C, gas-
ous formaldehyde was easily converted to trioxane\(^{(11)}\) which was not detected by the derivative spectrometry. The calibrations between a derivative spectral intensity and formaldehyde concentration were conducted by two methods; one was to check with MBTH and 2-4 DNP procedures and the other was to use a reference mixture whose formaldehyde concentration was known.

3. Experimental results and discussion

3.1 Emission characteristics near exhaust port

As is well known, unburned emissions in exhaust gases are considerably oxidized during the exhaust movement in the exhaust manifold\(^{(12)}\) because of their high temperatures of several hundreds degree Celsius. To understand the emission characteristics just after emission from the engine cylinder, exhaust gases were sampled at a distance of 75 mm downstream of the exhaust port. The results of unburned methanol (CH\(_3\)OH) and formaldehyde (H\(_2\)O) concentrations are shown in Fig.5 together with the exhaust gas temperature. The gas concentrations measured at this sampling position were nearly equal to the concentrations at the latter half of exhaust process rather than to the mean concentrations in the exhaust process. Details of this reason will be discussed later in 3.2.1.

In any ignition timing, unburned methanol concentrations became a minimum value at \(\phi_{AF} = 0.9-1.0\) and increased as the mixture became progressively richer or leaner. These emission characteristics of unburned methanol showed a similar tendency to those of unburned hydrocarbons emitted from a gasoline engine. The effects of ignition timing were remarkably sensitive to a richer mixture rather than to a leaner mixture. These phenomena could be explained as follows:

under fuel lean operation almost all unburned methanol was born at the piston crevice and the quench layers, while under fuel rich operation unburned methanol was also born spatially in the combustion chamber. In the case of \(IT=40^\circ\)CA which took a longer time from the ignition to the exhaust valve opening, unburned methanol reached a minimum value approximately at \(\phi_{AF}=0.9\). This mixture strength agreed well with that which gave the minimum quenching distance\(^{(19)}\).

Fig. 5 Emission characteristics of unburned methanol and formaldehyde at \(=75 \, \text{mm}

The emission characteristics of formaldehyde, as shown in Fig.5, were remarkably different from those of unburned methanol. Except the ignition timing of TDC, formaldehyde increased with increasing air-fuel equivalence ratio in the range of fuel rich mixtures, but it varied little with air-fuel equivalence ratio in the range of fuel rich mixtures. On the other hand, in case of TDC operation, formaldehyde concentration reached maximum at \(\phi_{AF}=1.2\), and then decreased in the range of \(\phi_{AF}\) 1.2. The unique emission characteristics observed in TDC operation was also very much in agreement with the results measured at the exhaust port (\(=0\)). From these experimental results, it was first surmised that formaldehyde emissions depended on the concentration of oxygen in exhaust gases. Judging from the decrease in formaldehyde concentration for a lean mixture with retarded timing, it could be surmised that other contributions to formaldehyde emission are of combustion period, exhaust gas temperature and other emissions. However, the influences on formaldehyde emissions were not conclusively clear from only these experimental results.

In comparison of unburned methanol with formaldehyde as a function of \(\phi_{AF}\), formaldehyde was low in fuel rich mixture, though unburned methanol was high. On the other hand, formaldehyde as well as unburned methanol increased with an increase of \(\phi_{AF}\) in fuel lean mixture. But they differed from each other in the rate of increase. To clarify the relation between unburned methanol and formaldehyde, the results rewritten from Fig.5 are shown in Fig.6 as a parameter of ignition timing.

Iwai et al.\(^{(5)}\) indicated that both unburned methanol and formaldehyde were produced at the same place in an engine cylinder due to a good correlation between unburned methanol and formaldehyde concentrations at the same mixture strength and the same sampling position. However, the re-
results as shown in Fig.6 did not always have adequate correlation for all operating conditions. Formaldehyde concentrations were barely proportional to unburned methanol concentrations only in case of a relatively advanced timing and leaner mixture operation. However, it was difficult to find a simple correlation for all conditions. Accordingly, it can be considered that formaldehyde concentrations are basically independent of methanol concentrations.

3.2 Changes of exhaust gas concentrations along the exhaust tube

3.2.1 Effects of pulsating exhaust gas flow

It is well known that unburned hydrocarbons in a gasoline engine are continuously oxidized during the exhaust movement in an exhaust system. Accordingly, it is, of course, expected that the oxidation of unburned methanol in a methanol engine occurs in an exhaust tube. To elucidate the oxidation rate, it is necessary to examine the concentrations of exhaust gas compositions along the exhaust tube. In these examination, however, special attention should be paid to where exhaust gases are pulsatingly emitted from an engine cylinder, therefore concentrations of unburned fuels are not uniform during the exhaust process. A stripped pattern, alternatively rich and lean in hydrocarbons, can be observed along the exhaust tube of a gasoline engine.

The phenomena can be explained by the occurrence of high hydrocarbon concentrations near the beginning and the end of exhaust process.

In this study, the pulsating exhaust gas flow effects are unavoidable due to the use of a single cylinder engine. Fig.7 shows the concentrations of unburned methanol and formaldehyde along the straight exhaust pipe together with the exhaust gas temperature. Unburned methanol concentrations showed the highest value at the exhaust port and a minimum at \( L=300 \) mm, and then increased with an increase of the distance from the engine until the first peak appeared at \( L=600 \) mm. The range of the concentration change became gradually less while repeating this rise and fall as the exhaust gases went farther away from the exhaust port. It could be distinctly recognized that the periodic concentration change occurred three times in an exhaust tube of 2 meters in length. The volume of exhaust gas movement during one working cycle of engine corresponds to the length from peak to peak of unburned methanol concentration along the exhaust tube. This distance, as shown in Fig.7, was calculated by gas temperature and stroke volume. Accordingly, the resulting three cycles change was clearly observed in this figure.

As seen in methanol concentrations of each cycle, it was found that unburned methanol in high concentration was emitted at early and late stages in the exhaust process and the maximum value in each cycle decreased, while the minimum value showed slightly increasing with time. The change of concentrations became less, due to mixing and diffusion.

On the other hand, the average concentration of unburned methanol was less in the second cycle than in the first cycle and it was almost unchanged after the second cycle. The decrease in the average concentrations resulted from an oxidation of unburned methanol. The exhaust gases emitted late in the exhaust process remained for a long time at a high temperature so that the oxidation rate became high. It can be considered that unburned methanol oxidation remarkably occurs at a temperature at about or above 400 °C and hardly occurs below this temperature.

The change of formaldehyde was by far less than that of unburned methanol. Although unburned methanol was considerably decreased by oxidation, formaldehyde was not decreased. It would be unreasonable to understand that formaldehyde could not be oxidized and could be stable in the exhaust tube from the resulting no change of formaldehyde concentration along the exhaust tube. It is preferable to consider that formaldehyde remained constant in its concentration in spite of active formation of formaldehyde by methanol oxidation.

3.2.2 Effects of engine operating conditions

Unburned methanol and formaldehyde concentrations along the original exhaust tube were examined for various \( \Phi_F \) and ignition timings. This original tube was curved and irregular in diameter. Accordingly, exhaust gas concentrations were easily averaged in the original tube than in the straight one. The experimental results of gas temperature.
measurements are shown in Fig.8. In any operating condition, unburned methanol concentrations attained the highest value near the exhaust port and then decreased rapidly after 250-400 mm downstream. A decrease in unburned methanol, namely, an oxidation of unburned methanol was observed in the exhaust gas temperature range of 400-500 °C. The decreasing rate of unburned methanol depended on the exhaust gas temperature and ignition timing, that is, it was remarkable at high temperature and at retarded timing.

Most of the results show that formaldehyde reaches the minimum at about $L=75$ mm, and then slightly increases downstream, and remains constant after $L=250$ mm. The tendency of increasing formaldehyde was extreme in lean operating conditions. In the case of $\phi_{AF}=1.4$ and $IT=TDC$, formaldehyde concentrations after $L=250$ mm were two times higher than the minimum value at $L=75$ mm. The change of formaldehyde concentrations occurred at a temperature above 500 °C and never occurred at a temperature below 400 °C.

Comparing the change of unburned methanol with that of formaldehyde, except $\phi_{AF} = 0.8$, the emission levels of formaldehyde became higher with an increase in unburned methanol oxidation. However, the relation depended on $\phi_{AF}$.

From these experimental results, it is obvious that formaldehyde and unburned methanol differ remarkably from each other in their behaviors. However, any quantitative relations cannot be recognized from these results. Moreover, it is difficult to judge whether the phenomena of rising and falling in formaldehyde concentration within 250 mm show the change of concentrations during the exhaust process, or the change of time-resolved concentrations. Anyway, it can be considered that unburned methanol oxidation takes place in the exhaust tube and formaldehyde, which is a main intermediate in methanol oxidation, rises and falls. In addition, formaldehyde itself may be also oxidized.

3.3 Oxidation of unburned methanol and formaldehyde under constant temperature

3.3.1 Reactor

The variations of unburned methanol and formaldehyde along the exhaust tube were observed in the pulsating exhaust gas flow, while temperature was lowered with an increase in tube distance. Accordingly, any reaction progress with time could not be observed in the exhaust gas measurements through the exhaust tube. The effects of gas temperature and residence time on unburned methanol reaction were examined using a quartz tube reactor, as shown in Fig.9, into which a part of exhaust gas was introduced. The lengths of the reactor tube L were 200, 400 and 600 mm, and inner diameter of each reactor tube was 4 mm. The drawing rate of sample gas was 1.5-4.5 l/min. The concentrations of unburned methanol and formaldehyde were measured at the inlet and the outlet of the reactor.

3.3.2 Oxidation of unburned methanol

To examine the effects of reactor temperature $T_r$, experiments were carried out for the sample gases of various $\phi_{AF}$ at a constant drawing rate. The experimental results are shown in Fig.10. An overall tendency, irrespective of $\phi_{AF}$, showed that the change of unburned methanol concentrations between the inlet and the outlet
hardly occurred in a temperature range of 350–400 °C. However, unburned methanol concentration gradually decreased with an increase of Tr above 400 °C, and unburned methanol was finally distinguished in a temperature range of 600–620 °C.

The dependency of residence time on methanol consumption is shown in Fig. 11. Approximately 30 percent of methanol was consumed during the residence time of 100 ms at Tr = 450 °C and 80 percent was consumed during 40 ms at Tr = 600 °C. The time required for methanol consumption was equivalent to that of one working cycle at the engine speed of 1500 rpm.

As seen from these reactor tube experiments, no change of unburned methanol concentrations takes place in the reactor tube at exhaust gas temperature below 400 °C. It can be expected that a rapid methanol consumption, namely, an extreme oxidation reaction occurs at higher temperatures of this experimental range.

3.3.3 Formation and destruction of formaldehyde

Fig. 12 shows the change of formaldehyde concentrations as a function of Tr. Formaldehyde concentrations, irrespective of $\phi_F$, hardly changed up to Tr=400 °C and gradually increased above 400 °C, and then reached the maximum value in the temperature range of 500–550 °C. The concentration sharply decreased over 500–550 °C, and at last, it became lower than that of the inlet at 580–600 °C.

The effects of the residence time on formaldehyde concentration are shown in Fig. 13. The dependences of reactor temperature on the concentration differed from those on unburned methanol. In the case of 621 °C, formaldehyde increased in a few milliseconds of residence time, and it became lower than initial concentration after 15 ms and was completely consumed at about 45 ms. This consumption time of formaldehyde could be equivalent to that of unburned methanol which was given by interpolating the results shown in Fig. 11. In the case of 568 °C, the maximum concentration of formaldehyde attained two times as much as the initial value. As the reactor temperature fell further, the tendency of formaldehyde to increase occurred in a longer residence time.

3.3.4 Reaction mechanism

In the temperature range of 400–600 °C, the decrease of unburned methanol and the increase of formaldehyde can be interpreted as follows; the formaldehyde formation reaction progressed in step with methanol oxidation reaction because formaldehyde was one of the main intermediate products in methanol oxidation. Moreover, formaldehyde itself was oxidized and decreased in this temperature range. Accordingly, the concentration of formaldehyde depended on the rates of formation and destruction. The formaldehyde concentration observed in the exhaust tube increased when the formation rate of formaldehyde was higher than the destruction rate.

At temperatures above 600 °C, methanol oxidation was rapid but formaldehyde concentrations were extremely low. This was due to a rapid formaldehyde oxidation. Of course,
the effects of gas temperature on formalde- 
yde concentrations depended on the residence 
time. Moreover, the reaction rate slightly 
depended on the air-fuel equivalence ratio. 
Therefore, it can be considered that the de-
struction of unburned methanol and formalde-
yde depended on other gas components, es-
pecially on oxygen and also on radical 
species.

A detailed reaction scheme of methanol 
oxidation and formaldehyde reaction was thor-
oughly examined in our other reports (17)(18). 
These experimental results agreed well with 
the theoretical results.

3.3.5 Comparison with the exhaust 
tube testing

The experimental results from the re-
actor tube can qualitatively explain the con-
centration changes of unburned methanol and 
formaldehyde in the exhaust tube. The resi-
dence time of exhaust gases staying in the 
range of temperatures over 500-600 °C was 
shorter than that of the time required for one 
working cycle of engine. Consequently, for-
maldehyde could not be completely oxidized 
during that time while unburned methanol was 
considerably oxidized. After that, exhaust 
gas temperature decreased while moving down-
stream, so that a decrease in formaldehyde 
was not observed. In a temperature range of 
400-500 °C, formaldehyde scarcely changed 
within a residence time of 100 ms and 
slightly increased with a longer residence 
time. From these results, the phenomena in 
the reactor tube are not contradictory to 
those in exhaust tube.

Consequently, unburned methanol has 
been oxidized in the exhaust tube and formal-
dehyde has been produced with the metha-
nol oxidation. From the experiments at a 
constant temperature using a reactor tube, 
it is found that unburned methanol was stead-
ily decreasing while formaldehyde was slight-
ly increasing rather than scarcely changing 
as in the exhaust tube.

4. Conclusions

In this paper, we dealt with an unburn-
ed fuel composition, especially formaldehyde 
among the exhaust emissions in a neat methanol 
fueled S.I. engine and examined the emission 
characteristics and the concentration changes 
along the exhaust tube. The results derived 
from this study are summarized as follows;

(1) Unburned methanol in exhaust emissions 
is considerably oxidized in an exhaust tube at 
temperatures above 400 °C, irrespective of 
air-fuel equivalence ratio and ignition tim-
ing. Therefore, its concentrations along the 
exhaust tube sharply decreases in the begin-
ing of exhaust event while increasing at a 
distance from engine at temperatures below 
400 °C, the concentrations remained constant 
due to the interruption of the reaction.

(2) Formaldehyde concentrations along the 
exhaust tube scarcely decreased except in a 
fuel lean condition, but gradually increased in 
the same condition. This was a reason why 
formaldehyde was produced by the oxida-
tion of unburned methanol and it was also 
oxidized at the same time. Therefore, form-
aldehyde concentrations in the exhaust tube 
depended on the difference of reaction rate 
between formation and destruction. Accord-
ing to the reaction studies in experiments, an increase 
of formaldehyde concentration could be ob-
served in the temperature range of 400-580 °C for 
the residence time of 40-100 ms.

(3) At temperatures above 600 °C, a similar 
phenomenon was observed in a short residence 
time (20-30 ms). In a longer residence time, however, unburned methanol as well as formalde-
yde was completely oxidized.

(4) The results mentioned above gave an 
important suggestion on formaldehyde forma-
tion in an engine. Namely, unburned methanol in a quench layer is mixed with a high tem-
perature burned gas and the oxidation reac-
tion proceeds during the exhaust stroke. 
Consequently, it can probably be considered 
that there exists a temperature condition 
which increases formaldehyde during the 
exhaust process. Moreover, considerable amount 
of formaldehyde has already existed in the 
cylinder when the residence time of exhaust 
gases kept at above 600 °C was not so long. 
Especially, there is a possibility of an in-
crease of formaldehyde at the latter half of 
the exhaust process.

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References

(2) Sato, A., JSME Symp. on Alcohol Fuel and 
Comb. (in Japanese), (1979-11), p63
(3) Heitland, H., et al., 2nd Symp. on LPFSD 
(1974), p35
(in Japanese), No.13 (1977-11)
(5) Iwai, N., et al., Trans. SAE Japan (in 
(6) Browning, L.H. and Pefley, R.K., SAE 
Paper 790676 (1979)
(7) Bowman, C.T., Comb. and Flame, Vol.25 
(1975), p343
Sci. Tech., Vol.20 (1979), p125
(9) Ito, K., et al., Preprint JSME (in Japan-
ese), No.813-4 (1981-7), p83
(10) Kachi, K., et al., Trans. SAE Japan (in 
Japanese), No.15 (1978-3), p44
(11) Yamamoto, T., Methanol and Formalin (in 
Japanese), (1962), p126, SEIBUNDO
(12) Takagi, T., et al., Trans. JSME (in Japan-
(13) Yano, T. and Ito, K., J. Fuel Soc. Japan 
(14) Nakagawa, Y., et al., Trans. SAE Japan 
(15) Sakai, Y., Comb. and Eims. of Auto. Engn. 
(in Japanese), (1973), p73, SANKAI DO
(16) Tabaczynski, R.J., et al., SAE Trans., 
Vol.81 (1972), p379 (Paper No. 720172)
(17) Yano, T. and Ito, K., Trans. JSME (in 
(18) Yano, T. and Ito, K., Trans. JSME (in 