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# Formaldehyde and Methanol Emissions from a Methanol/Gasoline-Fueled Spark-Ignition (SI) Engine

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With a three-cylinder spark-ignition (SI) engine, formaldehyde (HCHO) and methanol (CH<sub>3</sub>OH) emission characteristics as well as the three-way catalytic converter (TWC) conversion efficiency were investigated when it ran on gasoline, M10, M20, and M85 (gasoline blended with 10, 20, and 85% of methanol in volume), respectively. HCHO and CH<sub>3</sub>OH were detected by gas chromatography (GC) with a pulsed discharge helium ionization detector (PDHID). Experimental results show that HCHO emission increases with engine speed, while CH<sub>3</sub>OH emission from a methanol/gasoline blend-fueled engine decreases with it. HCHO emission from a gasoline-fueled engine varies in a “U” curve with the engine torque. The addition of 10% methanol in gasoline doubles the HCHO emission. The increasing methanol fraction greatly improves HCHO and CH<sub>3</sub>OH emission; their concentrations are both approximately linear to the amount of cyclically supplied fuel methanol. CH<sub>3</sub>OH can be totally removed by lightened-off TWC. However, the HCHO concentration may increase rather than decrease via the conversion of TWC at high engine speeds.

## 1. Introduction

Methanol, known as methyl alcohol, has been used as a fuel for automotive engines in many countries. Its excellent combustion properties have made it the strongest choice of the automotive industry,<sup>1,2</sup> and its low emission characteristics and improvement of engine power and thermal efficiency have generated considerable interest.<sup>3–8</sup> All of the advances as well as the abundant sources, such as natural gas, coal, and extensive biomass resources, meet the concerns on energy security, future oil supply, and environmental protections and also make methanol one of the most attractive alternative fuels for spark-ignition (SI) engines. However, more toxic formaldehyde (HCHO) and unburnt methanol (CH<sub>3</sub>OH) are emitted.<sup>9–11</sup> Formaldehyde plays an important role in photochemistry; it is also classified as a probable human carcinogen by the United States Environmental Protection Agency (U.S. EPA). The International Agency for Research on Cancer (IARC) has

determined that there is “sufficient evidence” that occupational exposure to formaldehyde causes nasopharyngeal cancer in humans.

It is proven that the hydrocarbon detector, flame ionization detector (FID), hardly has a response on HCHO.<sup>12,13</sup> The CARB method 1004 (ASTM method D5197 and U.S. EPA methods TO-11A and 8315) is commonly used to monitor aldehyde emissions from engines. In this method, samples are first collected in a absorbent cartridge impregnated with 2,4-dinitrophenylhydrazine (DNPH), where aldehydes will be converted to the corresponding 2,4-dinitrophenylhydrazone derivatives. They can be detected by high-performance liquid chromatography (HPLC) with an ultraviolet (UV) detector<sup>14</sup> or gas chromatography (GC) with FID.<sup>15</sup> However, except for the sampling time, it takes over 1 h for the operation of derivation, elution, extraction, and detection of the DNPH hydrazone. The complex sample pretreatment is not endurable, especially when a lot of testing points are needed.

Restricted by the detecting method, limited monitor points of engine-out HCHO were investigated in the literature.<sup>10,11</sup> The HCHO emission characteristics cannot be precisely reflected. Over the past few years, a fast chromatographic method with the pulsed discharge helium ionization detector (PDHID) was developed, which is capable of monitoring low levels of formaldehyde and with a simple sampling process in several minutes.<sup>12,13,16</sup> The presence of PDHID makes it much easier to investigate engine-out HCHO emission characteristics in a wide range of engine speeds and torque.

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In this study, HCHO and CH<sub>3</sub>OH were detected by PDHID in selective Ar–PDHID mode to improve the response and selectivity by eliminating the interference of water and permanent gases.<sup>13</sup> Their emission characteristics as well as the three-way catalytic converter (TWC) conversion efficiencies were experimentally investigated on the three-cylinder SI engine fueled with gasoline and three kinds of methanol/gasoline fuel blends. To obtain the maps of formaldehyde and methanol emissions, a series of engine experiments were carried out; that is, the engine speed varied from 2000 revolutions/min to the rated speed (where the engine obtains the maximum power) of 5500 revolutions/min at the interval of 500 revolutions/min, and the engine torque varied from 7 N m to wide open throttle (WOT) at the interval of 7 N m. Then, their emission characteristics can be clearly seen, and the influences, such as methanol fraction, exhaust temperature, and engine-operating conditions, on formaldehyde and methanol emissions can be known.

## 2. Experimental Section

A three-cylinder, electronic-controlled fuel injection, JL368Q<sub>3</sub> SI engine (bore, 68 mm; stroke, 72 mm; total displacement, 0.796 L; compression ratio, 9.4) was used for the investigation. There is no special retrofit on the engine, except the increase of cyclic fuel delivery quantity when M85 is applied, to keep its power. The exhaust temperature was tested 20 cm away from the outlet of the exhaust port with a thermal couple. Commercial 93 gasoline is used as the base fuel. First-grade industrial methanol with the purity of 99.9% was mixed in fractions of 10, 20, and 85% in volume, and the fuel blends were thus named M10, M20, and M85, respectively. To prevent the problems of miscibility (e.g., methanol in the blends absorbs water vapor from air), all of the blends were prepared just before each experiment, where the room temperature was above their dissolving temperature. Therefore, no additives were required and used.

HCHO and CH<sub>3</sub>OH were detected by GC (GC-2010, Shimadzu, Japan) consisting of a Gs-OxyPLOT capillary column (10 m × 0.53 mm inner diameter × 10 μm, Agilent Technologies) and a pulsed discharge ionization detector [PDHID, model D4-I-SH-17R, VICI (Valco Instrument Co., Inc.)]. The detector was performed in Ar–PDHID mode by doping with 2% argon (99.999%) into the discharge gas helium (99.999%). The carrier gas was also helium (99.999%). The discharge flow was 30 mL/min (at 6 psi) maintained by a calibrated restrictor (TGA-R-30F60P, VICI Valco, Switzerland). Because a stringent purity is required in the system, the high-purity carrier gas helium and discharge gas were both “cleaned” by gas purifiers (HP2, VICI Valco, Switzerland). The method has been introduced in detail in our previous work;<sup>17</sup> thus, it is briefly described here.

The exhaust gas was first sampled in the bags made of fluoropolymer–ethylene–propylene (FEP). Then, the bags were kept in a thermostat at 80 °C to prevent water from condensing. The detection procedures are as followings. First, the sample gas in the FEP bag was drawn into the six-way switch, a stainless-steel quantitative loop (volume of 100 μL), at the speed of about 200 mL/min via a vacuum pump. Then, the trapped gas in the loop was switched into the Gs-OxyPLOT capillary column with the help of the carrier gas, where it was separated according to the polarity of the gaseous components. Finally, the separated sample was detected by Ar–PDHID. To obtain a better resolution and shorter analyzing time, the carrier gas flow and split ratio were set to be 100 cm/s and 5, respectively. The programmed column temperature was developed as 90 °C for 1 min and then up to 170 °C at 20 °C/min. The total analysis time is 5 min. The detection limits of formaldehyde and methanol are  $28.2 \times 10^{-9}$  and  $89.3 \times 10^{-9}$  g/L,

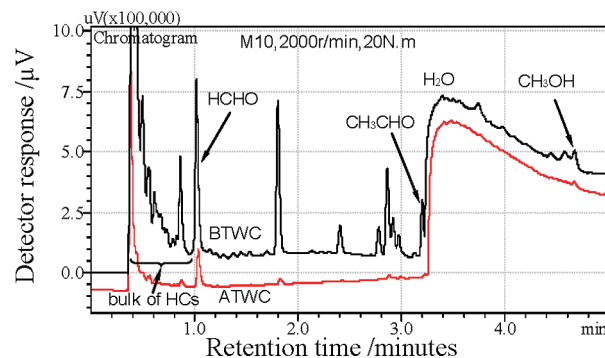


Figure 1. Chromatogram of exhaust gas before and after TWC.

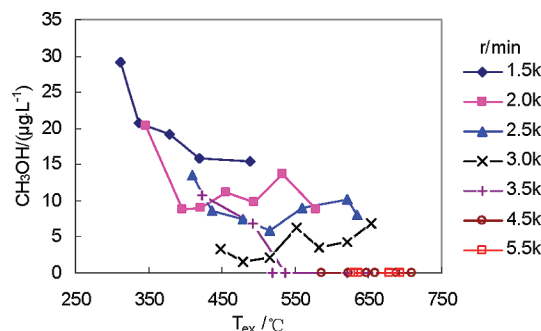


Figure 2. Characteristics of methanol emissions from the M10 engine.

respectively. One of the chromatograms is shown in Figure 1. The separation and response of formaldehyde on the GC system indicates that this method is competent for the detection of formaldehyde within engine exhaust gases.

## 3. Results and Discussion

Under stable operating conditions, the SI engine was run on gasoline, M10, M20, and M85 at a given engine speed and load, respectively. The exhaust HCHO and CH<sub>3</sub>OH were detected as well as the exhaust temperatures. The engine speeds, such as 1500 revolutions/min, 2000 revolutions/min, etc., are shortened as 1.5k r/min, 2.0k r/min, etc. on the right-hand side margins of the figures.

### 3.1. Unburned Methanol Emission from the M10 Engine.

Although the literature shows that methanol can also be produced from isooctane, hexane,<sup>10</sup> and MTBE,<sup>18</sup> for oxidation from a recombination of a CH<sub>3</sub> and OH radical or CH<sub>3</sub>O and H (free or abstraction of a hydrocarbon), no methanol was detected from the gasoline engine in our experiments. Exhaust methanol comes from the unburned fuel methanol. Figure 2 gives the methanol emission characteristics of the M10 engine. Methanol emission decreases with the engine speed and load in general. No methanol was detected when the engine speed was over 4500 revolutions/min. It seems that CH<sub>3</sub>OH emission affected exhaust temperature and engine speed rather than the air/fuel ratio. Figure 3 shows the maps of methanol emission characteristics. It is clear that methanol mainly exists under the low-speed and low-load conditions, especially when the temperatures are lower than 530 °C.

Although the methanol supply was increased with the increase of the engine torque cyclically, the air/fuel ratio was kept around a unit. Even if the concentration of methanol left unburnt was the same, the oxidation was enhanced because of the higher exhaust temperature. On the other hand, the quantity of unburnt

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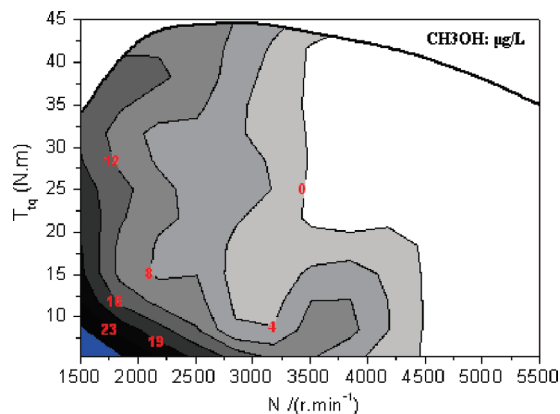


Figure 3. Map of methanol emission from the M10 engine.

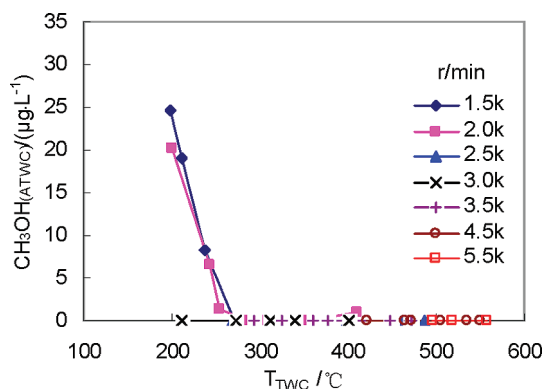


Figure 4. Characteristics of after-TWC methanol emission from the M10 engine.

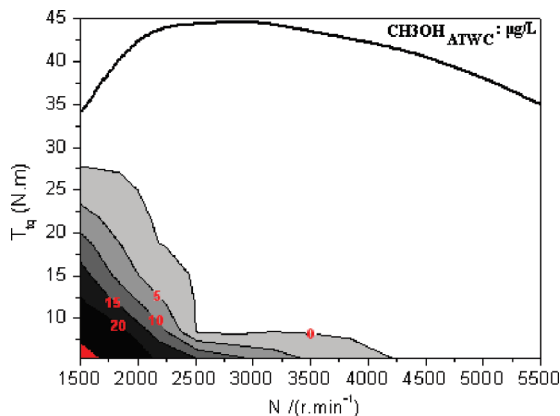


Figure 5. Map of after-TWC methanol emission from the M10 engine.

methanol from the crevice storage was reduced at the increasing engine speed conditions.<sup>19</sup> Meanwhile, at the increase of the engine speed, the exhaust temperature was also increased, which enhanced the post-flame oxidation of unburned methanol in both the cylinder and exhaust port and pipe. Therefore, methanol emission decreased with the engine torque.

Results indicate that methanol oxidizes rather fast, with the period of the exhaust gas staying in the cylinder, and the tailpipe has a negligible effect on methanol oxidation compared to the exhaust temperature.

Figure 4 presents the measured methanol emissions at different constant engine speeds after TWC, and Figure 5 shows the map of the methanol emission transferred from Figure 4.

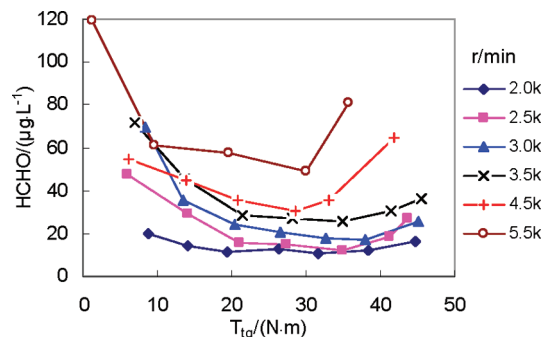


Figure 6. Characteristics of formaldehyde emission from the gasoline engine.

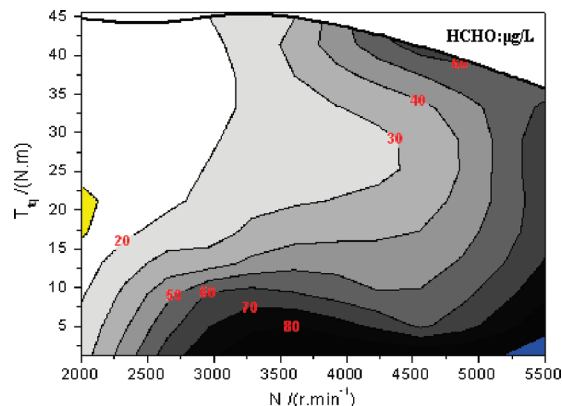


Figure 7. Map of formaldehyde emission from the gasoline engine.

Although much methanol is emitted into the atmosphere because of the high methanol concentration in the tailpipe and low TWC conversion efficiency, no detectable methanol is emitted when TWC is warmed up at around 270 °C.

**3.2. Formaldehyde Emission Characteristics.** **3.2.1. Formaldehyde Emission from the Gasoline Engine.** Formaldehyde is an important intermediate product of hydrocarbon (HC) oxidation. The processes of formaldehyde generation and oxidation are influenced by the temperature and residence time of HCs in the exhaust.<sup>10,20–22</sup> That is why there is formaldehyde emitted from the gasoline engine. It can be seen from Figure 6 that formaldehyde emission increased with the engine speed. To a given speed, at the two ends of high- and low-load conditions, the emission of formaldehyde increases a little. It can be considered rich in the air/fuel mixture at the two ends. Thus, there is a U-shaped curve of formaldehyde emission.

Engine speed affects HCHO emission in two ways: exhaust temperature and the residence time that exhaust gas stays in the hot environment of the cylinder and exhaust port and pipe. Experiments prove that it takes about 10 ms for the consumption of formaldehyde at the conditions of 1095 K, equivalence ratio of 0.93, and atmosphere pressure.<sup>23</sup> The test conditions str similar to the conditions in the cylinder when the exhaust valve opens. Thus, the residence time, i.e., the engine speed, controls the concentration of formaldehyde in the exhaust to some extent.

Figure 7 is the map of formaldehyde emission from the SI engine. It is clear that more formaldehyde will be emitted at three extreme conditions of high engine speed and low load,

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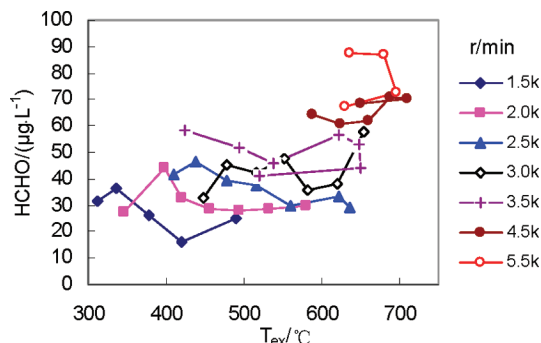
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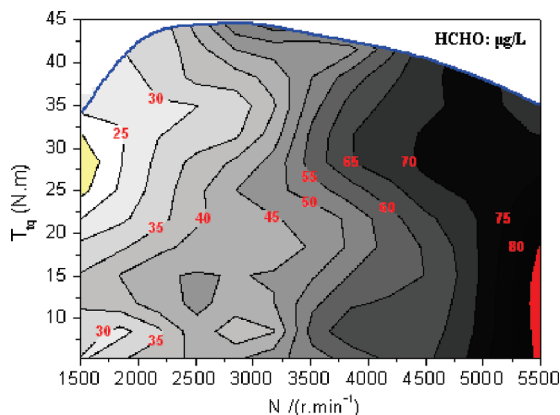
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**Figure 8.** Characteristics of formaldehyde emission from the M10 engine.



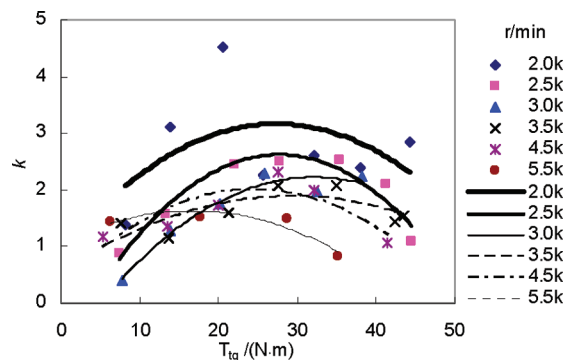
**Figure 9.** Map of formaldehyde emission from the M10 engine.

especially at wide open throttle (WOT) conditions. In this study, the highest formaldehyde emission is as much as 80  $\mu\text{g/L}$  or more.

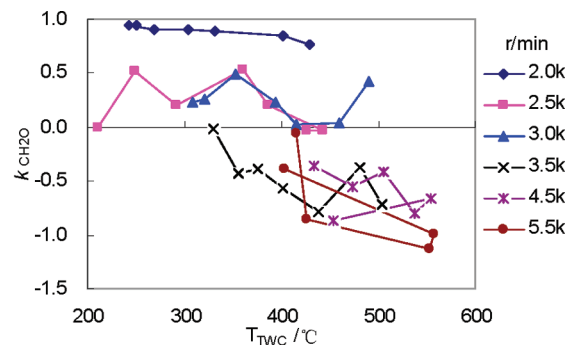
**3.2.2. Formaldehyde Emission from the M10 Engine.** However, when methanol is added into the fuel of gasoline, the oxidation of HCs may have less of an effect; the paths of HCHO generation and oxidation are quite changed. Alzueta et al.<sup>24</sup> found that the oxidation of methanol was initiated at above 1000 K and becomes rapid over 1250 K, which is much easier than that of HCs. It can be derived that the formed formaldehyde will be frozen for the exhaust temperatures lower than 1000 K. In this case, the M10 engine-out formaldehyde is from the methanol oxidation rather than the oxidation of HCs. The characteristic of formaldehyde emission is shown in Figures 8 and 9. HCHO emission increases with the engine speed and exhaust temperature, rises almost in parallel lines along the engine speed, and obtains its maximum value of 85  $\mu\text{g/L}$  at the rated speed.

There exist two effects of HCHO. On one hand, HCHO can be oxidized to CO (consumption), while on the other hand,  $\text{CH}_3\text{OH}$  and HCs can be oxidized to HCHO (generation), where the key points are the temperature and the space speed of the exhaust flow. Temperature determines the generation and consumption speed of HCHO pool, while space speed determines the reaction time, thus affecting the amount of residual HCHO.

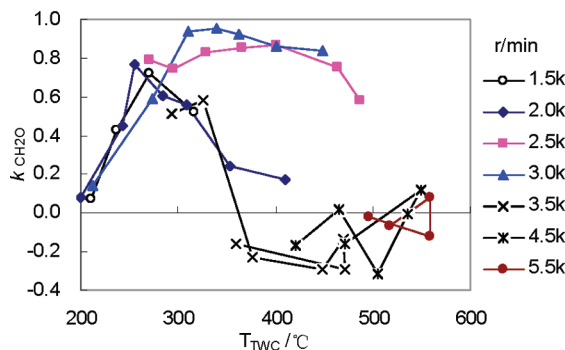
Figure 10 compares Figure 8 to Figure 6 and shows the formaldehyde concentration rates of M10- versus gasoline-fueled engines, where  $k = C_{\text{M10}}/C_{\text{gasoline}}$ , where  $C_{\text{M10}}$  and  $C_{\text{gasoline}}$  are the concentrations of M10 and gasoline engine-out formaldehyde, respectively. M10 engine-out formaldehyde is elevated to 1–3 times as much approximately, and the elevation becomes



**Figure 10.** Formaldehyde concentration rates of M10- versus gasoline-fueled engines.



(a) Gasoline



(b) M10

**Figure 11.** Characteristics of the TWC conversion effect on formaldehyde emission.

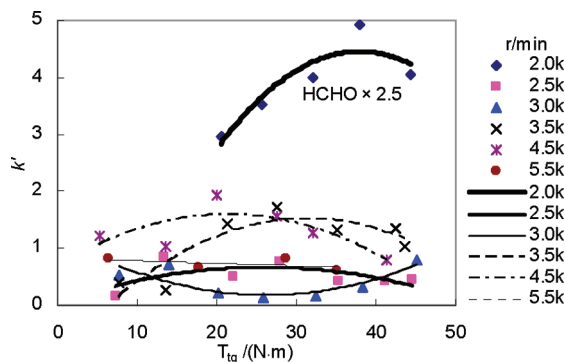
weakened with the increasing engine speed because of the decrease of the remaining methanol in the exhaust.

**3.2.3. TWC Conversion Efficiencies.** From Figure 5, it is safe to say that  $\text{CH}_3\text{OH}$  can be effectively removed when TWC is lightened off. Thus, only HCHO conversion efficiency is focused here.

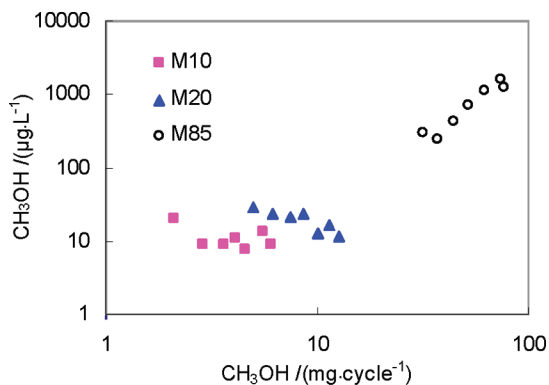
Figure 11 shows a group of the measured conversion efficiencies ( $k_{\text{HCHO}}$ ) of TWC on HCHO under different engine speeds. The effects of TWC conversion on gasoline and M10 engine-out HCHO are quite similar but different from the removal of the regulated emissions, such as carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxides ( $\text{NO}_x$ ). HCHO emission may increase via the conversion of TWC at high engine speeds, where the HCHO generation speed is larger than its consumption speed. The TWC temperature and space speed are also the two controlling factors.

Although there are different conversion ratios on formaldehyde when the engine fuels with gasoline and M10 fuel blend, the absolute emission of formaldehyde from the M10 engine is

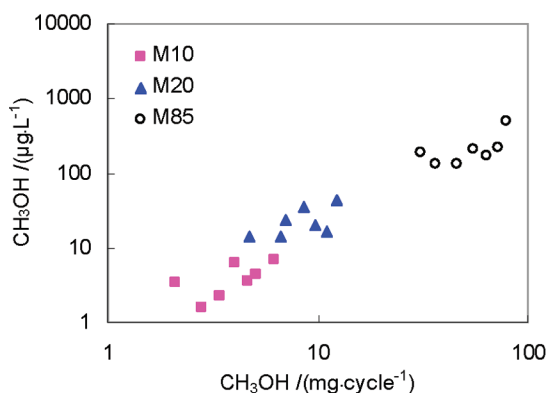
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**Figure 12.** After-TWC formaldehyde concentration rates of the M10 versus gasoline engine.



(a) 2000r/min

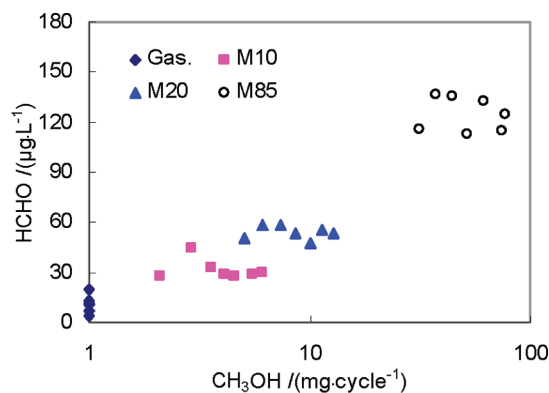


(b) 3000r/min

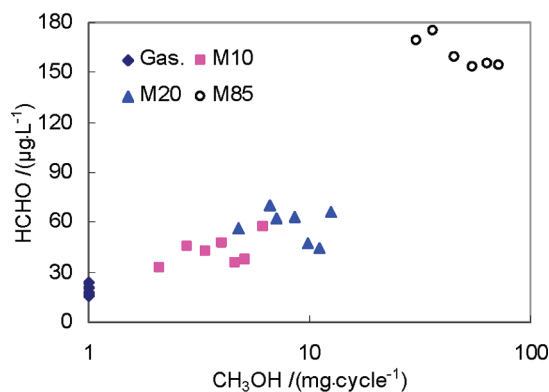
**Figure 13.** Relationship between the methanol emission and cycle-supplied methanol.

not always larger, as seen in Figure 12, where  $k'$  is the HCHO concentration rate of the M10 versus gasoline engine at the TWC outlet. The highest formaldehyde emission is emitted at WOT conditions, where the gasoline engine emits around  $120 \mu\text{g/L}$ , while the M10 engine emits less than  $90 \mu\text{g/L}$ .

**3.3. Effects of the Methanol Fraction on Formaldehyde and Methanol Emissions.** As mentioned above, no detectable  $\text{CH}_3\text{OH}$  was found in the exhaust when the engine was fueled with gasoline in our study.  $\text{CH}_3\text{OH}$  emission is actually the unburned fuel methanol. It proves that, the higher the methanol fraction in fuel blend, the more  $\text{CH}_3\text{OH}$  will be emitted. As seen in Figure 13, it is approximately linear to the amount of cyclic-supplied fuel methanol. As much as  $1000 \mu\text{g/L}$  of  $\text{CH}_3\text{OH}$  was emitted when the engine was fueled with M85 fuel blend, which is almost 100 times that from M10 when the engine ran



(a) 2000r/min



(b) 3000r/min

**Figure 14.** Relationship between the formaldehyde emission and cycle-supplied methanol.

at 2000 revolutions/min. In addition, the higher the engine speed, the lower the methanol emission.

Formaldehyde is the simplest aldehyde and can be produced from alcohols and paraffin.  $\text{CH}_3\text{OH}$  oxidizes to HCHO following the path of  $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH}/\text{CH}_3\text{O} \rightarrow \text{HCHO}$ ,<sup>20</sup> and paraffin produces formaldehyde by the oxidation of final access methyl radical ( $\text{CH}_3$ );<sup>21,22</sup> thus, the generation path from  $\text{CH}_3\text{OH}$  is shorter than that from HCs. Moreover, the initial temperature of methanol oxidation is lower than most hydrocarbons; meanwhile,  $\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{O}$  radicals are more active than  $\text{CH}_3$ . Thus, the generation of  $\text{CH}_2\text{O}$  from  $\text{CH}_3\text{OH}$  oxidation is easier than from HCs. As a result, blending methanol in gasoline caused the increase of formaldehyde emission. As shown in Figure 14, HCHO emission characteristics are similar to  $\text{CH}_3\text{OH}$  emission and also approximately linear to the amount of cyclic-supplied fuel methanol.

#### 4. Conclusions

The formaldehyde and methanol emission characteristics from gasoline and methanol/gasoline blends as well as the TWC conversion efficiency were studied on a three-cylinder SI engine. Formaldehyde emission characteristics from the gasoline and M10 engines were compared, and the effect of the blending ratio of methanol in fuel blends on formaldehyde and methanol emissions were also investigated.

Methanol emission is the unburnt fuel methanol. The exhaust temperature determines the emission via controlling its oxidation (consumption), and any operation that may promote the tem-

perature will decrease methanol emission, for instance, increasing the engine speed and torque. Moreover, the increasing fraction of methanol in the fuel blend apparently enhances methanol emission as well. Zero methanol emission is available after TWC is lightened off at over 270 °C.

There exist two effects of formaldehyde: oxidation (consumption) and its formation from methanol and HC oxidation, where the key point is the temperature and the residence time that the exhaust gas stays in the hot environment, i.e., cylinder, exhaust port and pipe, and TWC. The engine speed controls the formaldehyde emission to some extent. The higher the engine speed, the larger the formaldehyde concentration. The addition of methanol in gasoline results in an increase of the formaldehyde emission as well. Similar to methanol emission, the larger the methanol fraction in the fuel blend, the larger the formal-

dehyde concentration and its concentration is also approximately linear to the amount of cyclically supplied fuel methanol.

The effect of TWC on the formaldehyde conversion is quite different from the removal of the regulated emissions, such as CO, HC, and NO<sub>x</sub>. The interesting thing is that minus conversion efficiencies appear at high engine speeds. It seems that some formaldehyde is produced by the TWC rather than removed, which makes the TWC-out formaldehyde from the gasoline engine even more than that from the M10 engine at some operating conditions.

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