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## Effects of Methanol/Gasoline Blends on a Spark Ignition Engine Performance and Emissions

Wei Yanju, Liu Shenghua,\* Li Hongsong, Yang Rui, Liu Jie, and Wang Ying

School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

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Three typical methanol–gasoline blends M10, M20, and M85 containing 10%, 20%, and 85% of methanol by volume, respectively, were used to investigate the effects of different methanol/gasoline ratios on engine power, thermal efficiency, and emissions, especially the exhaust methanol emission. A three-cylinder, port fuel injection engine was applied. Experimental results show that the engine power/torque ratio under the wide open throttle condition mainly depends on the amount of heat delivered to the engine. The addition of methanol significantly improves the brake thermal efficiency, while the methanol/gasoline ratio has a slight effect on it. Engine out CO and NO<sub>x</sub> emissions decrease with the increase of the methanol/gasoline ratio. The use of M85 leads to a reduction of CO and NO<sub>x</sub> by about 25% and 80%, respectively. A gas chromatograph is calibrated and used to measure the methanol emission. Measurement indicates that the addition of methanol in gasoline results in an increase of the unburnt CH<sub>3</sub>OH emission. And its concentration is nearly logarithmically proportional to the cyclically injected quantity. Because the response of the flame ionization detector to methanol is 40% that of hydrocarbon, the total hydrocarbon emission of the engine is revised. The nonmethanol hydrocarbons that resulted from gasoline are less affected by methanol addition, while the methanol emission is controlled independently by the cyclic quantity of fuel methanol injection.

### 1. Introduction

With ever increasing concerns on environmental pollution, energy security, and future oil supplies, the global community has been seeking nonpetroleum based environment friendly alternative fuels for the past decade. Methanol (CH<sub>3</sub>OH) can be produced from natural gas, gasification of coal, wood, straw, plant stalk, and even combustible trash. It can be easily synthesized from carbon monoxide (CO) and hydrogen (H<sub>2</sub>) via the reaction  $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ ,  $-91 \text{ kJ/mol}$ . That is, methanol conversion is feasible wherever H<sub>2</sub> and CO or C can be massively and cheaply obtained. This is very important to China because of the lack of oil and the availability of coal. China is the world's largest coal consuming country. The direct burning of coal has already caused serious air pollution. Methanol can be synthesized during coal gasification and clean application, such as in an integrated gasification combined cycle. Besides, the lack of grain to produce ethanol for automobiles makes the methanol path inevitable. The low price is also very attractive to the China market.<sup>1,2</sup> Actually, several provinces have conducted the fleet demonstration of the methanol/gasoline fuel blends.

Methanol has advantages to prove its attraction. Table 1 shows the properties of methanol and gasoline. It can be used as an additive or an alternative fuel for gasoline engines. With the addition of methanol into gasoline, the fuel economy and thermal efficiency are improved, and because of the high octane number, engines are allowed to operate under a higher compression ratio.

Table 1. Comparison of Fuel Properties

|  | methanol           | gasoline                       |
|--|--------------------|--------------------------------|
| molecular formula                        | CH <sub>3</sub> OH | C <sub>8</sub> H <sub>18</sub> |
| molecular weight                         | 32                 | 95–120                         |
| oxygen content (wt %)                    | 50                 |                                |
| density (kg/m <sup>3</sup> )             | 792                | 740                            |
| boiling point (°C)                       | 64.7               |                                |
| LHV (MJ/kg)                              | 20.0               | 44.3                           |
| octane number                            | 111                | >90                            |
| autoignition temperature (°C)            | 465                | 228–470                        |
| stoichiometric A/F ratio                 | 6.47               | 14.8                           |
| latent heat (kJ/kg)                      | 1103               | 305                            |
| LHV of stoi-mixture (MJ/m <sup>3</sup> ) | 3906               | 3810                           |

Compared with gasoline, the lower boiling point, faster flame propagation speed, high oxygen content (50 wt %), and simple chemical structure of methanol all help to reduce the CO and hydrocarbon (HC) emissions,<sup>3–10</sup> but NO<sub>x</sub> emis-

(3) Hu, T. G.; Wei, Y. J.; Liu, S. H.; Zhou, L. B. Improvement of Spark-Ignition (SI) Engine Combustion and Emission during Cold Start, Fueled with Methanol/Gasoline Blends. *Energy Fuels* **2007**, *21*, 171–175.

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\* To whom correspondence should be addressed. Telephone: +86 29 82663587. Fax: +86 29 82668789. E-mail: shenghua@mail.xjtu.edu.cn.

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Table 2. Specifications of the SI Engine

|                         |                     |
|-------------------------|---------------------|
| type                    | JL368Q <sub>3</sub> |
| bore (mm) × stroke (mm) | 68.5 × 72           |
| displacement (L)        | 0.796               |
| compression ratio       | 9.4                 |
| maximum power (kW)      | 26.5 (at 5500 rpm)  |
| maximum torque (N·m)    | 52 (at 3000 rpm)    |

sions do not always decrease; Andrey et al. observed an increase by 5–10%.<sup>11</sup> However, the addition of methanol may cause a slight power loss, a cold start problem in deep cold conditions, and the risk of a vapor block in hot weather. Power loss can be solved by prolonging the injection pulse width or by enlarging the injector's flow flux; the cold start and vapor block problems can be settled by providing particular methanol/gasoline blend fuels for summer and winter. Other disadvantages such as toxicity, separation from gasoline, erosion on plastic and rubber, and so on can be solved by strictly sealing the fuel supply system, adding additives in fuel blends, and changing to anti-erosion parts, respectively.

If gasoline is regarded as octane, it is estimated that methanol takes a 50% mole fraction in a fuel blend at about 30% volume fraction. Therefore, methanol combustion in an engine becomes dominant. The change of the engine combustion mechanism results in different characteristics of the engine performance and emission. This gives a good explanation of the reduction of the CO and HC emission. However, methanol emission may play a leading role, especially when a high fraction of the methanol/gasoline fuel is utilized. Study has shown that methanol addition into gasoline results in a reduction of the regulated emissions, and more unburnt methanol will be emitted.<sup>12</sup>

As is known, the response of methanol on a flame ionization detector (FID) is only 40% of the HCs,<sup>2</sup> while the HCs are evaluated by equivalent methane. So the measured value of methanol is far less than it theoretically is. The measurements of total HC (THC) will inevitably result in errors with an FID without special calibration, and the higher the methanol ratio in the fuel blend is, the worse the situation will be. However, most literature reports use an FID directly without attention to this.

In this paper, to investigate the effects of the methanol/gasoline ratio on spark ignition (SI) engine emission, especially THC emission, three typical methanol/gasoline blends of M10, M20, and M85 were tested. THC and methanol were measured with a HORIBA MEXA7100DEGR gas analyzer and a Shimadzu GC 2010, respectively. Gas chromatography (GC) methanol data was then used to correct the THC data.

## 2. Experimental Engine and Equipment

A three-cylinder, port fuel injection, four-stroke, electronic control SI engine was used for the investigation. The engine specifications are listed in Table 2. Figure 1 shows the schematic diagram of the test bench. A HORIBA MEXA7100DEGR emission analyzer (Horiba Ltd., Japan) was used to detect the regular CO, THC, and NO<sub>x</sub> emissions; a gas chromatograph (GC2010, Shimadzu Co., Japan) with a Porapak Q packed column ( $\varphi 3 \times 3\text{m}$ ) and an FID were adopted to analyze the unregulated CH<sub>3</sub>OH emission. All engine tests were conducted at the speed of 3000 rpm.

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(11) Andrey, N.; Vladislav, K.; Eran, S.; Ben, G. *The effects of oxygenates in motor fuel blends on the reduction of exhaust gas toxicity*; SAE Paper 940311; SAE 1994 World Congress: Detroit, MI, 1994.

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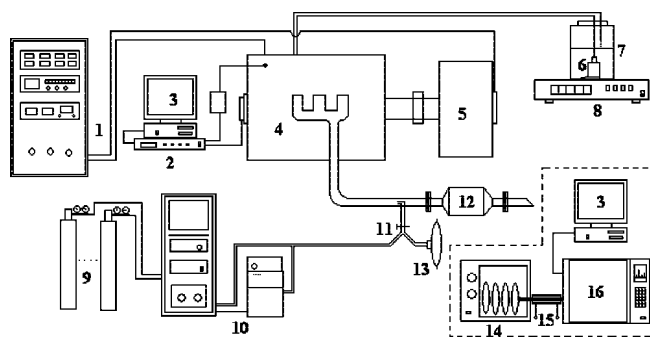


Figure 1. Schematic diagram of the SI engine test bench: (1) dynamometer controller; (2) combustion analyzer; (3) computer; (4) SI engine; (5) dynamometer; (6) fuel pump; (7) fuel bottle; (8) electronic balance; (9) standard gas bottles; (10) Horiba emission analyzer; (11) Y valve; (12) TWC; (13) sampling bag; (14) gas heater; (15) sampling pipe heater; (16) gas chromatograph.

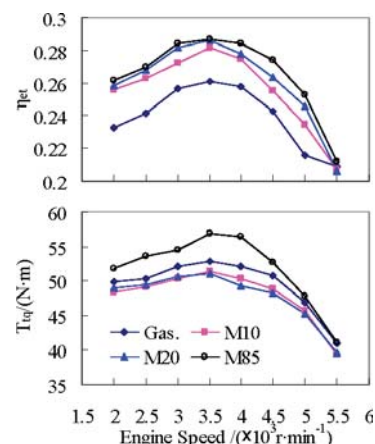


Figure 2. Engine performance under WOT condition.

Because methanol is prone to absorb water vapor from the air, which may cause the separation of the methanol–gasoline fuel blend, the M10, M20, and M85 fuel blends were prepared before each experiment. Although the lower heating value (LHV) of methanol is only 46% that of gasoline, experiments prove that the power output of an SI engine with M10 or M20 changes little. However, when fueled with M85, the engine theoretically remains merely 52% of its original power with its initial fuel delivery system. For the use of its original engine control system, three larger AXCA1.6 type, four-hole injectors were replaced, whose flow flux was 1.583 times (0.965 times the energy flux) that of the original one.

Methanol is detected by GC samples from 0.50 mL of exhaust gas via a quantitative ring on a six-way valve. If it is sampled directly from the tail pipe, the results will not be so repeatable because of the cyclic variation. In practice, the exhaust gas was first collected into sampling bags. That is, an average concentration of methanol was measured. A three-way switch was used to lead exhaust gas to the HORIBA gas analyzer or the sampling bag. The concentrations of CO, THC, and NO<sub>x</sub> were directly measured by the HORIBA gas analyzer. For the measurement of methanol, the bags were kept at a constant temperature of about 60 °C to prevent water from condensing.

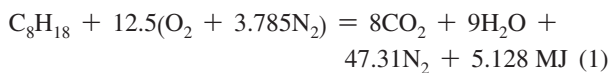
## 3. Results and Discussion

**3.1. Engine Torque and Brake Thermal Efficiency.** Figure 2 gives the torque and the brake thermal efficiency against the methanol ratio under wide open throttle (WOT) operating conditions. It shows that the engine torque decreases for M10 and M20 compared with that for gasoline. That is because the SI engine is in a  $\lambda$  open-loop control under WOT conditions; although the same volume of fuel blends is injected, the energy

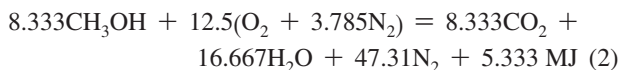
that M10 and M20 bring into the cylinder decreases. As to M85, although only 0.965 times the energy is injected with the new injectors, the engine torque increases by 4.75% because of the higher thermal efficiency. The laminar flame of methanol propagates faster than that of gasoline,<sup>13</sup> the combustion process occurs near top dead center (TDC), and the combustion heat is released in a shorter time and a smaller volume; as a result, the isometric effect is improved.

Moreover, it can be seen from the total combustion reaction formulas of gasoline (substituted by isooctane) and methanol with air, as shown in eqs 1 and 2. For the same amount of heat release, methanol has 49% more triatomic molecules in the combustion products than gasoline. This means that the burnt gas heat capacity of methanol is larger than that of gasoline; thus, the combustion temperature of methanol is lower than that of gasoline. The cooling heat loss via radiation and conduction is reduced, and, consequently, the thermal efficiency is improved.<sup>14</sup>

Gasoline:



Methanol:



The brake thermal efficiencies of M10, M20, and M85 are 6.67%, 8.88%, and 10.85% higher than that of the gasoline based operation, respectively.

### 3.2. Effects of Methanol on Combustion Characteristics.

The combustion parameters of the ignition delay and the combustion duration can be obtained by computing the heat release rate from the cylinder pressure–time data. The formula is as follows:

$$\Delta Q_i = \left( \frac{k}{k-1} \right) (p_{i-1} V_{i-1}^k - p_i V_i^k) \left( \frac{V_i - V_{i-1}}{V_{i-1}^k - V_i^k} \right)$$

where  $\Delta Q_i = \Delta Q_B - \Delta Q_W$ ,  $\Delta Q_B$  and  $\Delta Q_W$  are the net heat release and the cooling heat transfer in a step of the crank angle  $\varphi$ , and  $p$  and  $V$  are the sampled pressure and the calculated cylinder volume, respectively. The exponent  $k$  is the ratio of the specific heat of the gases in the combustion chamber. The ignition delay and the combustion duration are defined as the crank angle from the spark event to 10% and from 10% to 90% cumulative heat release, respectively.

Figure 3 shows a group of cylinder pressures. Under the same engine speed and torque conditions, the maximum cylinder pressure ( $p_{\max}$ ) increases with the increase of the methanol ratio. The  $p_{\max}$  of M85 is 17.6% higher than that of pure gasoline. Meanwhile, the crank angle when the  $p_{\max}$  occurs is advanced by about 4–5 °CA, as shown as in Figure 4. It is because the laminar flame propagation speed of methanol is faster than that of gasoline. As can be seen from Figure 5, the ignition delay and the combustion duration are advanced by 5 and 6 °CA, respectively, for M85 compared with those for gasoline. Under the same ignition timing strategy, the methanol/gasoline blends burn in a smaller chamber, and the heat is released in a shorter time; as a result, the  $p_{\max}$  of the methanol/gasoline blends becomes higher and occurs closer to TDC.<sup>4,5</sup>

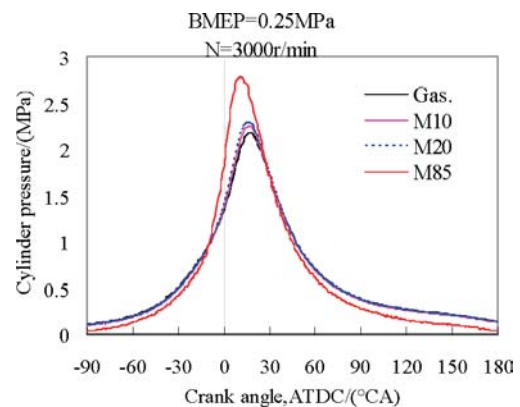


Figure 3. Comparison of cylinder pressure diagrams.

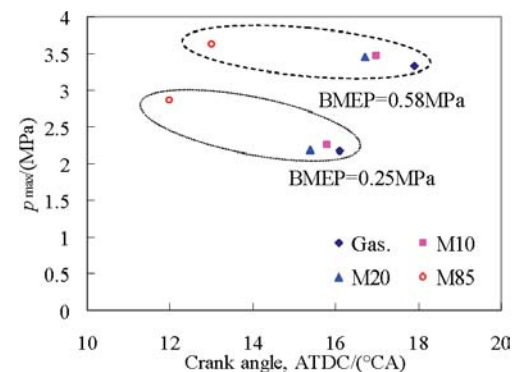


Figure 4. Maximum cylinder pressure characteristics.

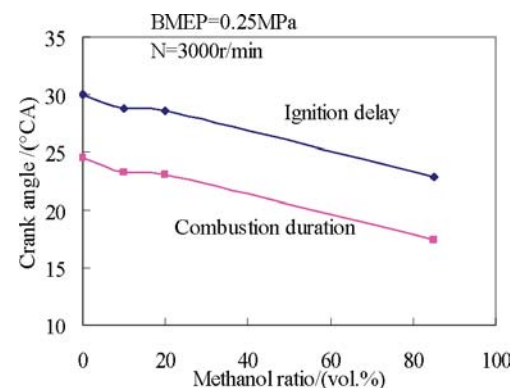


Figure 5. Effects of methanol ratio on ignition delay and combustion duration.

**3.3. Effects of Methanol on CO and NO<sub>x</sub> Emissions.** Figure 6 shows the effects of methanol ratio on the CO and NO<sub>x</sub> emissions. The CO emission decreases with the increase of the methanol ratio; similar results were found in refs 4, 7, 10, and 11. Methanol contains only about 44% carbon (gasoline contains 86%) and converts directly to CO during combustion, which quantitatively reduces the CO formation and emission. Moreover, CO emission is likely to be reduced because of the oxygen enrichment coming from methanol; this can be regarded as a “pre-mixed oxygen effect” to make the reaction go to a more complete state.<sup>15</sup> For NO<sub>x</sub> emission, owing to the fast flame propagation speed, the combustion temperature increases, which tends to increase the NO<sub>x</sub> emission. On the other hand, the high latent heat and the large gas heat capacity of the triatomic molecules reduce the peak combustion temperature, which causes the reduction of the NO<sub>x</sub> emission. Because of the above

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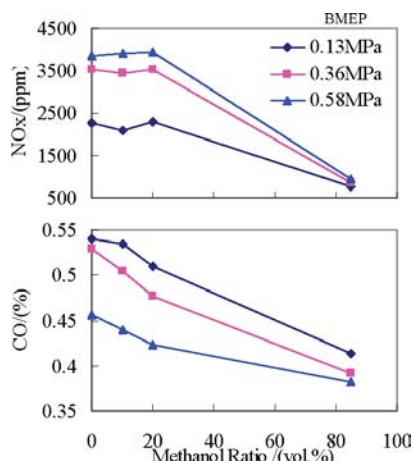


Figure 6. Effects of methanol ratio on CO and NO<sub>x</sub> emissions.

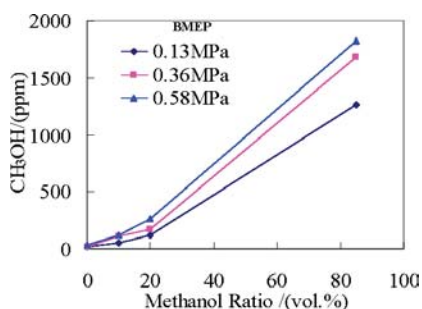


Figure 7. Effect of methanol ratio on CH<sub>3</sub>OH emission.

factors, the NO<sub>x</sub> emissions of the low fraction blends M10 and M20 are approximately equal to those of gasoline,<sup>2,4</sup> but when fueled with M85, NO<sub>x</sub> emission is reduced by 60–80% under overall operating conditions. The latter two factors take the dominant role.

**3.4. CH<sub>3</sub>OH Emission Characteristics.** When the SI engine runs on gasoline, THC emissions contain hundreds of different types of organic matter, such as paraffin, olefin, aromatics, phenol, alcohol, aldehydes, ketene, acid, ester, and so on. While operated on methanol/gasoline blends, lots of methanol will be emitted.<sup>10,16,17</sup> Because methanol is usually less evaluated by an FID, it is necessary to separate methanol from other HCs. In this study, unburnt methanol in exhaust is detected by GC2010 with an FID. It is calibrated by standard methanol gas.<sup>18</sup>

As can be seen in Figure 7, methanol emission increases with increasing methanol in the blends. For methanol blend operations, the exhaust methanol is produced in two ways. One is the intermediate product (MIP,  $M_{IP}$ ) from the gasoline combustion, and the other is from the unburnt methanol (MUB,  $M_{UB}$ ). For pure gasoline operation, the emitted methanol is only the intermediate product of combustion, so it is no more than 45 ppm. However, it is much higher for the methanol/gasoline blends. The methanol emissions for M10 and M20 are about 4 and 8.5 times higher, respectively, than that for pure gasoline. So  $M_{UB}$  takes the dominant role in the methanol emission. For M85, methanol emission is around 80 to 90 times that of pure gasoline operation.

Figure 8 shows the relationship between the mass of the cyclic methanol injected ( $M_F$ ,  $M_F$ ) and the concentration of the emitted

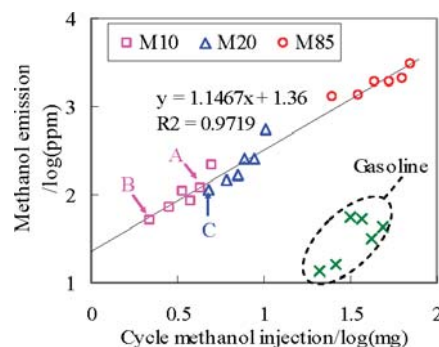


Figure 8. Effect of cyclic injected methanol on CH<sub>3</sub>OH emission.

methanol ( $M_E$ ,  $M_E$ ) in the form of logarithms. Although at points B and C both 21.0 mg of M10 and M20 were injected, 2.18 mg and 4.73 mg of methanol were also injected, which resulted in 50.7 ppm and 115.5 ppm of  $M_E$ , respectively. But at point A, although 41.5 mg, nearly twice the amount of M10, was injected, 4.27 mg of methanol was provided; similarly with M20 at point C, 119.3 ppm of methanol was emitted. This phenomenon indicates that  $M_E$  depends on  $M_F$  rather than on the methanol ratio in blends. When the SI engine is under  $\lambda$  closed-loop control, the equivalent air/gasoline ratio is controlled at around 1.02; the methanol emission is approximately linear to the amount of  $M_F$ . They follow the relation

$$\log(C_E) = 1.1467 \log(M_F) + 1.36 \quad (3)$$

$$R^2 = 0.9719$$

where  $C_E$  is the concentration of the emitted methanol (ppm) and  $M_F$  is the mass of the methanol injected per cycle (mg).

On the other hand, with the same amount of  $M_F$  and gasoline injection,  $M_E$  of the methanol blends operation is nearly 100 times higher than that for gasoline operation. This proves that methanol emission is mainly caused by the addition of methanol into fuel blends.

Figure 9 shows the effect of a three-way catalyst (TWC) on methanol emission. For gasoline, M10, and M20 operations, the exhaust methanol can be oxidized effectively by TWC under normal operating conditions.<sup>17</sup> But as to M85, although the conversion efficiency is high, there is still about 50 ppm of methanol in the exhaust.

**3.5. Effects of Methanol Ratio on THC Emission.** THC emission is commonly measured by an FID.<sup>19</sup> An FID analyzer generally shows the response in proportion to the carbon numbers and provides excellent features including linearity across a broad range of concentrations, high sensitivity, and fast response. Figure 10 shows the THC emission measured by a HORIBA 7100 DEGR gas analyzer. It seems that THC first increases with the augmentation of methanol and then decreases to be around 80%. The most accepted explanation should be, when fueled with methanol/gasoline blends, that the combustion process is advanced and thus exhaust temperature decreases, which weakens the post oxidation of THC. As a result, THC emission increases. However, as to M85, most fuel is methanol. THC emission is greatly reduced because methanol unlike gasoline does not have heavy HCs.<sup>14</sup> However, the FID responsibility will differ depending on the kind of HC, especially if the HC coexists with oxygen. The response of CH<sub>3</sub>OH is 0.4 times that of CH<sub>4</sub>.<sup>20</sup> That is the reason why there is a conflict

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(17) Lv, S. C.; Li, H.; Cuty Clemente, E. R.; Qi, D. H.; Liu, S. H. Measurement of non-regulated pollutants from SI engine fuelled with methanol/gasoline blends. *Transactions of the Chinese Society for Internal Combustion Engines (CSICE)* **2006**, *24*, 57–61.

(18) Handbook, Shimadzu GC solution, V2.0.

(19) Handbook, Horiba MEXA-7100DEGR, THC analyzer FIA-715A.

(20) Li, H. C. *Analytical Chemistry Handbook*, 2nd ed.; China Chemistry Industry Press: Beijing, 1999; Vol. 5 (Gas Chromatography Analysis), Table 9-5.

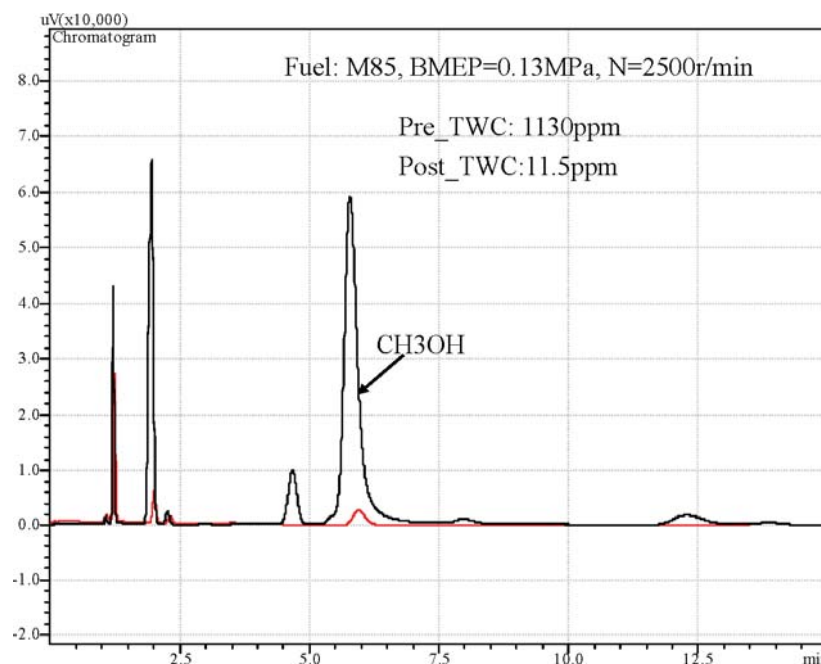


Figure 9. Chromatogram of CH<sub>3</sub>OH emission before and after TWC.

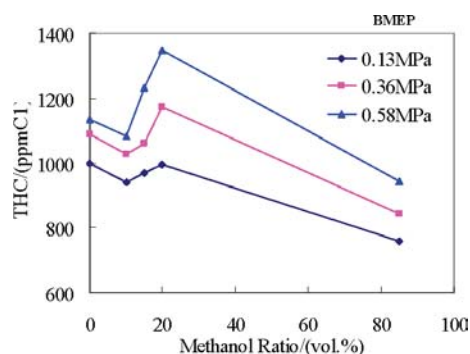


Figure 10. Effects of methanol ratio on THC emission (unrevised).

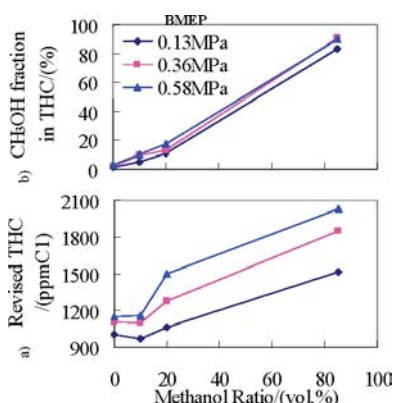


Figure 11. Revised THC emissions.

in that the CH<sub>3</sub>OH emission can be as high as 2000 ppm for M85 while the THC emission is not more than 1000 ppm. For methanol/gasoline blends, the emitted methanol takes a large percentage in THC emission, so the real value of THC emission must be revised by the data measured by both the Horiba device and the GC device. THC emission should be

$$\text{THC}_{\text{real}} = \text{THC}_{\text{Horiba}} + 0.6C_{\text{CH}_3\text{OH}} \quad (4)$$

The corrected THC emission is shown in Figure 11a; it increases with increasing methanol ratio. Given the same volume of fuel, the number of carbon atoms in methanol is about half

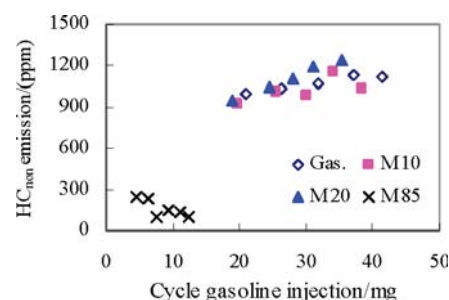


Figure 12. Effect of cyclic injected gasoline on HC<sub>non</sub> emission.

of that in gasoline. Mixing methanol into gasoline actually deteriorates the THC emission. The fraction CH<sub>3</sub>OH in THC increases with methanol ratio in blends too, as shown in Figure 11b; it is approximately equal to the methanol/gasoline ratio. That indicates that the methanol emission of fuel blends is dominantly produced by the mixed fuel methanol.

The nonmethanol HC (HC<sub>non</sub>) emissions are mainly from gasoline. They can be calculated by the following equation,

$$\text{HC}_{\text{non}} = \text{THC}_{\text{Horiba}} - 0.4C_{\text{CH}_3\text{OH}} \quad (5)$$

Figure 12 shows the relationship between HC<sub>non</sub> and cyclic injected gasoline, so it is a function of the air/gasoline ratio and less affected by the gasoline quantity. CH<sub>3</sub>OH and non-CH<sub>3</sub>OH emissions result from the fuel of CH<sub>3</sub>OH and gasoline independently.

#### 4. Conclusions

The conclusions from this study can be drawn as follows:

(1) The engine power varies with the cyclic injected energy, and the addition of methanol improved the brake thermal efficiency; however, the improvement depended slightly on the methanol ratio.

(2) With the increasing methanol ratio, the ignition delay and the combustion duration are shortened and the peak combustion pressure becomes higher around the TDC.

(3) With the increase of the methanol fraction in gasoline, the CO emission decreases and the reduction is 25% for M85,

and the low methanol ratio fuel blends have no significant effect on reducing the  $\text{NO}_x$  emission while M85 gives an 80% reduction.

(4) The addition of methanol increases the unregulated  $\text{CH}_3\text{OH}$  emission, and the value is likely to be logarithmically proportional to the mass of the cyclic injected fuel methanol. Its fraction in THC emission is proportional to the methanol ratio in the fuel blends.

(5) Nonmethanol emission varies little with the quantity of gasoline injection. The air/gasoline ratio is the major factor.

#### Nomenclature

ATDC = after top dead center

BTDC = before top dead center

BMEP = brake mean effective pressure

$^\circ\text{CA}$  = degree of crank angle

FID = flame ionization detector

GC = gas chromatography

Gas. = gasoline

$\text{HC}_{\text{non}}$  = nonmethanol hydrocarbon emissions

LHV = lower heating value,  $\text{MJ/m}^3$

MIP,  $M_{\text{IP}}$  = intermediate product methanol

ME,  $M_{\text{E}}$  = emitted methanol

MF,  $M_{\text{F}}$  = fuel methanol

MUB,  $M_{\text{UB}}$  = unburnt methanol

$N$  = engine speed, rpm

$p_{\text{max}}$  = maximum cylinder pressure, MPa

SI = spark ignition

THC = total hydrocarbon

TWC = three-way catalytic converter

WOT = wide open throttle

$\lambda$  = air/gasoline ratio

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