Carbonyl compound emissions from passenger cars fueled with methanol/gasoline blends

Hong Zhao a,b, Yunshan Ge a,⁎, Chunxiao Hao a, Xiukun Han a, Mingliang Fu a, Linxiao Yu a, Asad Naeem Shah a

a National Lab of Auto Performance & Emission Test, Beijing Institute of Technology, Beijing 100081, China
b College of Mechanical & Electronic Engineering, Qingdao University, Qingdao 266071, China

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ABSTRACT

Carbonyl compound emissions from two passenger cars fueled with different methanol/gasoline blends (M15 and M100) and operated with three-way catalytic converters (TWC) were investigated. The tests were performed on a chassis dynamometer with constant volume sampling over the New European Driving Cycle (NEDC). Carbonyls were trapped on dinitrophenylhydrazine (DNPH) cartridges. The hydrazones formed on the cartridge were analyzed by means of high-performance liquid chromatography (HPLC) and detected with a variable wavelength detector. The results show that when cars were fueled with methanol/gasoline blends, carbon monoxide (CO) and total hydrocarbon (THC) emissions decreased by 9–21% and 1–55% respectively, while nitrogen oxides (NOx) emissions increased by 175–233%. Compared with gasoline vehicles, formaldehyde emissions with M15 and M100 were two and four times higher respectively, and total carbonyls with M15 and M100 increased by 3% and 104% respectively. With the use of the new TWC, both regulated gas pollutants and formaldehyde decreased. The new TWC caused a decrease of 5% and 31% in formaldehyde concentration for M15 and M100, respectively. Specific reactivity (SR) with the new TWC was reduced from 5.92 to 5.72 for M15 and from 7.00 to 6.93 for M100, indicating that M15 and M100 with the new TWC were friendlier to the environment.

1. Introduction

The global energy crisis and growing environmental concerns have prompted many countries to search for alternative energy sources (Agarwal, 2007; He et al., 2009). Methanol (CH3OH) has many advantages which make it a favorable non-petroleum-based environmentally friendly alternative fuel. Methanol can be produced from natural gas, gasification of coal, wood, straw, plant stalks, and even combustible trash, which are all available in abundance (Wei et al., 2008). Moreover, methanol has a high flammability limit and burning speed and low carbon/hydrogen ratio. It has a high latent heat of vaporization, which cools the air entering the engine and increases the volumetric efficiency and power output (Bilgin and Sezer, 2008; Yao et al., 2008; Brusstar et al., 2002).

The excellent combustion properties of methanol have made it an attractive alternative fuel for the automotive industry. Therefore, it has been used as a fuel for automotive engines in many countries (Abu-zaid et al., 2004; Zhang et al., 2009; Zervas et al., 2002). A comparison of various properties of methanol with gasoline is shown in Table 1. Methanol has a low boiling point and high octane number, which is more suitable for spark ignition engines. When a gasoline engine is fueled with methanol/gasoline blends, few modifications to the engine are needed. Methanol is oxygenated, so when it is added into gasoline, the fuel blend contains more oxygen, which leads to lower carbon monoxide (CO) emissions (Liu et al., 2007). Moreover, the lower boiling point makes it evaporate more easily, which is beneficial for combustion, resulting in lower hydrocarbon (HC) emissions (Hu et al., 2007). Methanol does not contain sulfur or complex organic compounds. The organic emissions (ozone precursors) from methanol combustion have lower reactivity, and hence lower ozone-forming potential compared with gasoline. Its lower emissions, and higher engine power and thermal efficiency have aroused wide interest in its use as an environmentally friendly alternative to gasoline.

However, methanol can produce more toxic unregulated pollutants such as formaldehyde and unburned methanol (Wei et al., 2008). Methanol is toxic, has corrosive characteristics, and emits formaldehyde, which can also lead to the formation of ozone. Formaldehyde is carcinogenic and has great adverse effects on human health. Other carbonyl compounds, such as acetaldehyde and acetone, are also toxic to humans and play a major role in photochemical reactions.

Some studies on emissions and performance of engines fueled with methanol/gasoline or methanol/diesel blends have been reported (Li et al., 2009; Liao et al., 2006; Chao et al., 2000; Cheng et al., 2008; Chao et al., 2001). However, these studies are all about engines and limited to formaldehyde and unburned methanol emissions. Few investigated vehicles with primary focus on carbonyl compounds aside from
formaldehyde. In this study, two passenger cars fueled with different methanol/gasoline blends (M15 and M100) were investigated. Thirteen carbonyl compound emissions were identified and quantified. This paper is focused on the effects of variation of methanol/gasoline ratio and three-way catalytic converter (TWC) on regulated and carbonyl compound emissions.

2. Experimental setup and measurement

The experiments were performed using two passenger cars (Vehicle A: Odometer 62,253 km, Vehicle B: Odometer 30,970 km). They both have displacement of 1.8 L and are fitted with TWC. Commercial 93 gasoline was used as the base fuel. Industrial grade methanol was mixed in fractions of 15% and 100% by volume, and the commercial standard mixtures (Supelco, USA). The carbonyls were trapped by reacting with DNPH inside the cartridges to form the stable corresponding hydrazones derivatives. Then, the cartridges were diluted with 3 mL of HPLC grade acetonitrile on a solid phase extractor (SPE), and the extracts were filtered through 0.45 μm of EconoFilter (Agilent, USA). The final volume was adjusted to 5 mL with acetonitrile. The final solution was analyzed by high-performance liquid chromatography (HPLC, Agilent 1200, USA) using ultraviolet detection at 360 nm. A 4.6×150 mm Eclipse XDB C18 column (Agilent, USA) was used. A mixture of 60% acetonitrile and 40% water was used as mobile phases. The carbonyls of ambient air were sampled and analyzed in the same way. The effects of ambient air were all subtracted from the final results.

Identification was made by matching retention time with those of commercial standard mixtures (Supelco, USA). The five-point external standard methods were used to obtain linear calibration curves for quantification; the correlation coefficient was more than 99.9%. The standard mixture contains 14 components: formaldehyde (FOR), acetaldehyde (ACE), acrolein (ACR), acetone (ATE), propionaldehyde (PRO), crotonaldehyde (CRO), methyl ethyl ketone (MEK), methacrolein (MET), butyraldehyde (BUT), benzaldehyde (BEN), valeraldehyde (VAL), tolualdehyde (TOL), cyclohexanone (Cyc), and hexanaldehyde (HEX). Because the column used cannot separate ACR and ATE, acrolein and acetone were quantified together.

3. Results and discussion

3.1. Emissions of regulated gas pollutants

The regulated gas pollutant emissions for the two vehicles with original TWC are listed in Table 2. In general, when cars were fueled with methanol/gasoline blends, CO and THC emissions decreased by

![Fig. 1. Schematic diagram of the measurement system for vehicle exhaust emissions.](image-url)
9–21% and 1–55% respectively, while NO\textsubscript{x} emission increased by 175–233%. The higher the methanol fraction in the fuel blend, the lesser the THC and CO emissions and the greater the NO\textsubscript{x} pollution.

Methanol contains only about 37.5% carbon, as opposed to gasoline, which contains 85.82%. This carbon converts directly to CO during combustion, so the CO formation and emission is quantitatively reduced when using methanol. Moreover, when methanol is added into gasoline, the fuel blend contains more oxygen; the “pre-mixed oxygen effect” makes the reaction go to a more complete state, thus reducing CO and THC emissions (Liu et al., 2007). In the case of M100, THC emissions are

<table>
<thead>
<tr>
<th>Vehicle A</th>
<th>Vehicle B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>M15</td>
</tr>
<tr>
<td>CO 0.820</td>
<td>0.747</td>
</tr>
<tr>
<td>THC 0.090</td>
<td>0.089</td>
</tr>
<tr>
<td>NO\textsubscript{x} 0.028</td>
<td>0.077</td>
</tr>
</tbody>
</table>

Table 2
Regulated gas pollutant emissions for the two passenger cars (ppm).

Fig. 2. Time-resolved emissions of regulated gas pollutants.
greatly reduced because methanol – unlike gasoline – does not have heavy HCs. The methanol/gasoline blends have two effects on NOx emissions. First, the fast flame propagation speed and the enhanced combustion temperature tend to increase NOx emissions. Second, the high latent heat and the large gas heat capacity of the triatomic molecules reduce the peak combustion temperature, and thus tend to reduce NOx emissions (Wei et al., 2008). In these tests, the first factor played a dominant role.

During the test cycle, the emissions of regulated gas pollutants and the vehicle speed changed with time, as well as air fuel ratios. The time-resolved emissions of regulated gas pollutants are shown in Fig. 2, in which it can be seen that the emission trends of CO and THC are similar. For M15 and gasoline vehicles, the trends of CO emissions are similar. Most of the CO was produced in the first ECE cycle. In this phase, rich mixture for acceleration resulted in more engine out CO. At the same time, the TWC had not reached the light-off temperature and was not able to function effectively. Therefore, the emission reduction was diminished. Generally speaking, catalysts in methanol fueled engines have longer light-off times caused by the lower exhaust temperature compared to gasoline (Wagner and Wyszynski, 1996).
After the first ECE cycle, the TWC had fully warmed up and its conversion efficiency increased quickly. Therefore, CO emissions decreased greatly and remained very low. THC emissions had a similar trend with CO emissions.

On the other hand, the gasoline vehicle emitted low NO\textsubscript{x} in the first two ECE cycles because the temperature of the engine cylinder was not high enough to produce NO\textsubscript{x}. NO\textsubscript{x} emissions reached their maximum value in the third ECE cycle. Afterward, the TWC reached its operating temperature and caused NO\textsubscript{x} concentrations to decline.

However, for the M15 vehicle, every acceleration in each cycle caused a NO\textsubscript{x} emission peak, which was related to the deviation from stoichiometric air fuel ratio during acceleration and deceleration. For the M100 fueled vehicle, more fuel must be injected into the engine to start the vehicle easily. This rich mixture condition lasted for a long time in the first ECE cycle, thus emitting more CO. The time-resolved NO\textsubscript{x} emissions for M100 were similar to those for M15.

Table 3

<table>
<thead>
<tr>
<th>Carbonyls</th>
<th>Vehicle A</th>
<th></th>
<th>Vehicle B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gasoline</td>
<td>M15</td>
<td>Gasoline</td>
<td>M100</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.632</td>
<td>1.111</td>
<td>1.278</td>
<td>4.824</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.308</td>
<td>0.249</td>
<td>0.526</td>
<td>0.107</td>
</tr>
<tr>
<td>Acrolein + Acetone</td>
<td>0.207</td>
<td>0.090</td>
<td>0.236</td>
<td>0.054</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.047</td>
<td>0.024</td>
<td>0.068</td>
<td>0.010</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>0</td>
<td>0.016</td>
<td>0.052</td>
<td>0</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>0.144</td>
<td>0.187</td>
<td>0.123</td>
<td>0</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>0</td>
<td>0</td>
<td>0.087</td>
<td>0</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>0.074</td>
<td>0.082</td>
<td>0.227</td>
<td>0.045</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tolualdehyde</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.303</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hexanaldehyde</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total Carbonyls</td>
<td>1.715</td>
<td>1.759</td>
<td>2.510</td>
<td>5.127</td>
</tr>
</tbody>
</table>

3.2. Carbonyl emissions

Carbonyl compound emission factors of gasoline and methanol/gasoline blend fueled vehicles are presented in Table 3. Formaldehyde is the most abundant carbonyl in the exhaust, followed by acetaldehyde, acrolein + acetone, benzaldehyde, and propionaldehyde. Formaldehyde can be produced from alcohols and paraffin, but the generation of formaldehyde from methanol oxidation is easier than from HCs, which results in higher formaldehyde for a methanol/gasoline blend fueled engine. Formaldehyde emissions from the M100 fueled vehicle are four times higher than those from the gasoline fueled one, while the emissions from the M15 are two times higher than those from its counterpart. With the increase in methanol content, the formaldehyde concentration is increased.

In the case of acetaldehyde emissions, compared with gasoline fueled vehicles, the emission factors of M15 and M100 decreased by 19% and 80%, respectively. Total carbonyls of M15 and M100 increased by 3% and 104%, respectively. From the results of formaldehyde and total carbonyls, it is evident that when the vehicle was fueled with methanol/gasoline blends, the TWC provided by the original equipment manufacturer did not reduce the unregulated emissions effectively.

3.3. Influence of new TWCs on regulated and unregulated emissions

CO, HC, and NO\textsubscript{x} are the main exhaust emissions of a gasoline vehicle. Through the retrofitting with a TWC, these exhaust pollutants can be reduced by up to 95%. The main target of the TWC is the oxidation of CO and HC, and the reduction of NO\textsubscript{x}. Carbonyl compounds are also affected by the TWC. Fig. 3 shows the regulated gaseous emissions with M15 and M100 in the case of both original and new TWC. With the use of the new TWC, CO, THC, and NO\textsubscript{x} were decreased by 24%, 27%, and 61% respectively for M15, and 14%, 33%, and 19% respectively for M100.

Fig. 4 shows individual carbonyl comparison between original TWC and new TWC for M15 and M100 respectively. With the use of
the new TWC, formaldehyde was decreased from 1.11 to 1.05 mg/km for M15, and from 4.82 to 3.34 mg/km for M100. As compared with the original TWC, the new TWC decreased formaldehyde concentration by 5.4% and 30.8% for M15 and M100, respectively. For M15, the new TWC decreased the emissions of formaldehyde and methyl ethyl ketone, while increasing higher carbonyls such as acetaldehyde, methacrolein, and butyraldehyde. M15 contains more gasoline, which tends to produce higher carbonyls than methanol. On the other hand, the new TWC decreased the emissions of formaldehyde, acetaldehyde, acetone, and methacrolein, while increasing butyraldehyde and benzaldehyde for M100.

The carbonyl compounds not only have direct effects on human health, but also affect the environment and have ozone-forming potential. The widely accepted method used to classify and compare the effect of an exhaust component on ozone-forming potential is measuring the maximum incremental reactivity (MIR) developed by Carter and Lowi (1990). In order to evaluate the ozone-forming potential of alternative fuels, the California Air Resources Board (CARB) has provided the MIR of carbonyl compounds and the method of determining the specific reactivity (SR) (CARB, 1999). Fig. 5 compares the SR caused by carbonyl compounds with original TWC and new TWC for M15 and M100. In case of new TWC, specific reactivity was reduced from 5.92 to 5.72 and from 7.00 to 6.93 for M15 and M100, respectively. The SR with the new TWC is lower than that with the original TWC because of its lower relative contribution of formaldehyde, which has the highest MIR among 14 carbonyls. This leads to the conclusion that the use of M15 and M100 with new TWC are friendlier to the environment.

![Fig. 4. Individual carbonyl comparison between original TWC and new TWC for M15 and M100.](image1.png)

![Fig. 5. Comparison of specific reactivity between original TWC and new TWC.](image2.png)
4. Conclusions

Carbonyl compound emissions from two passenger cars fueled with M15 and M100 and operated with the original as well as new TWC were investigated over the NEDC. Thirteen carbonyl compounds were identified and quantified. The influences of variation of methanol/gasoline fraction and TWC on regulated and carbonyl compounds emissions were studied. When cars were fueled with methanol/gasoline blends, CO and THC emissions were reduced by 9–21% and 1–55% respectively, while NOx emissions increased by 175–233%. The higher the methanol fraction in the fuel blend, the lesser the THC and CO emissions and the greater the NOx pollution. Compared with gasoline vehicles, formaldehyde emissions with M15 and M100 were two and four times higher respectively. With the increase in methanol content, the formaldehyde concentration decreased by 9% for M15 and 14%–21% for M100. The new TWC caused a decrease of 5% and 31% in formaldehyde concentration for M15 and M100, respectively. Specific reactivity of the new TWC was investigated over the NEDC. Thirteen carbonyl compounds were studied.

Acknowledgments

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