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Effects of different mixing ratios on emissions from passenger cars fueled with methanol/gasoline blends

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Abstract

Regulated and unregulated emissions from four passenger cars fueled with methanol/gasoline blends at different mixing ratios (M15, M20, M30, M50, M85 and M100) were tested over the New European Driving Cycle (NEDC). Volatile organic compounds (VOCs) were sampled by Tenax TA and analyzed by thermal desorption-gas chromatograph/mass spectrometer (TD-GC/MS). Carbonyls were trapped on dinitrophenylhydrazine (DNPH) cartridges and analyzed by high performance liquid chromatography (HPLC). The results showed that total emissions of VOCs and BTEX (benzene, toluene, ethylbenzene, *p*, *m*, *o*-xylene) from all vehicles fueled with methanol/gasoline blends were lower than those from vehicles fueled with only gasoline. Compared to the baseline, the use of M85 decreased BTEX emissions by 97.4%, while the use of M15 decreased it by 19.7%. At low-to-middle mixing ratios (M15, M20, M30 and M50), formaldehyde emissions showed a slight increase while those of high mixing ratios (M85 and M100) were three times compared with the baseline gasoline only. When the vehicles were retrofitted with new three-way catalytic converters (TWC), emissions of carbon monoxide (CO), total hydrocarbon (THC), and nitrogen oxides (NO*x*) were decreased by 24%–50%, 10%–35%, and 24%–58% respectively, compared with the cars using the original equipment manufacture (OEM) TWC. Using the new TWC, emissions of formaldehyde and BTEX were decreased, while those of other carbonyl increased. It is necessary that vehicles fueled with methanol/gasoline blends be retrofitted with a new TWC. In addition, the specific reactivity of emissions of vehicles fueled with M15 and retrofitted with the new TWC was reduced from 4.51 to 4.08 compared to the baseline vehicle. This indicates that the use of methanol/gasoline blend at a low mixing ratio may have lower effect on environment than gasoline.

Key words: mixing ratio; methanol/gasoline blend; BTEX; carbonyl compounds; new three-way catalytic converter

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Introduction

In recent years, the dual worldwide crises of fossil fuel depletion and environmental degradation have posed increasingly enormous threats to humans. To mitigate these threats from vehicles, many countries have made various efforts such as fuel quality improvement and introduction of exhaust aftertreatment technologies (Biswas et al., 2009; Zhao et al., 2010; Jiang et al., 2010). The development of alternative fuels to reduce automotive emissions and provide energy independence is becoming more important, especially following the increased public attention on energy security and environmental pollution (Tang et al., 2007). Compressed natural gas, alcohols (ethanol and methanol), biodiesel and other fuels have been used as alternative fuels (Kado et al., 2005; Agarwal, 2007; Zhang et al., 2009a; Lapuerta et al., 2008; He et al., 2010). Among these alternative fuels, methanol is one of the most widely investigated fuels. Methanol (CH_3OH) has many advantages, which has made it an attractive non-petroleum-based alternative fuel for the automotive industry in many countries (Abu-zaid et al., 2004; Zervas et al., 2002).

Methanol can be easily synthesized from natural gas or from gasification of coal or biomass (Kumabe et al., 2008). It has excellent combustion properties, low emission characteristics and improved engine power and thermal efficiency. Methanol is more suitable for spark ignition engines because it has a low boiling point and high octane number (da Silva et al., 2005). The high octane number allows methanol engines to have much higher compression ratios, thereby increasing thermal efficiency. In methanol/gasoline fuel blends, as the amount of methanol increases, the octane number increases. Compared with gasoline, the fuel economy and thermal efficiency are improved. When a gasoline engine is fueled with a methanol/gasoline blend, few modifications to the

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engine are needed. However, cold start and formaldehyde emissions are two main problems for vehicles fueled with methanol. If these two problems were resolved, methanol may be used in more applications.

The use of methanol can reduce regulated emissions, such as carbon monoxide (CO) and hydrocarbons (HC), even though it might produce more toxic unregulated pollutants such as formaldehyde and unburned methanol (Liu et al., 2007; Hu et al., 2007; Li et al., 2009; Wei et al., 2009). Burning methanol can also produce other volatile organic compounds (VOCs), such as benzene, toluene, ethylbenzene and xylene. These VOCs can act as primary toxic and carcinogenic pollutants and play a precursor role in the formation of photochemical species (Nelson et al., 2008; You et al., 2007).

Previous studies have focused on emissions and performance of the engine fueled with methanol/gasoline or methanol/diesel blends (Li et al., 2010; Liao et al., 2006; Zhang et al., 2009b). However, these studies are entirely about engine-out emissions and limited to some carbonyl compounds (Chao et al., 2000; Wei et al., 2008). Few studies have investigated on tailpipe emissions with primary focus on the effects of different mixing ratios and emissions of VOCs. In this study, four passenger cars fueled with methanol/gasoline blends at different mixing ratios were investigated. Emissions of eight VOCs and thirteen carbonyl compound were identified and quantified. This article is focused on the effects of different mixing ratios of methanol/gasoline blends and new three-way catalytic converters (TWC) on regulated and unregulated emissions, especially VOC and carbonyl compound emissions.

1 Materials and methods

1.1 Vehicles, fuels and driving conditions

Four passenger cars were tested in thirteen configurations. Commercial 93# gasoline was used as the base fuel. Industrial grade methanol was mixed in fractions of 15%, 20%, 30%, 50%, 85% and 100% by volume, and the fuel blends were named M15, M20, M30, M50, M85 and M100. Vehicle 1 (mileage: 1000 km), vehicle 3 (mileage: 1000 km) and vehicle 4 (mileage: 22,751 km) were each powered by 1.8 L gasoline engines and were tested in three configurations: (1) fueled with baseline gasoline and using the original equipment manufacturer (OEM)-installed TWC; (2) fueled respectively with M15, M85 and M100 and using the OEM-installed TWC; (3) fueled respectively with M15, M85 and M100 and retrofitted with a new TWC which was designed specifically only for each vehicle with a main aim to reduce formaldehyde emissions. Vehicle 2 (mileage: 105,000 km) was powered by a 1.6-L gasoline engine and was only tested with different fuels namely, gasoline, M20, M30 and M50 with the OEM-installed TWC.

The emission testing was performed on a chassis dynamometer. The drive cycle used was the New European Driving Cycle (NEDC), which includes four ECE (urban cycle) and one EUDC (extra-urban cycle). The whole test cycle lasts for 1180 sec. Before testing, all cars were conditioned at a temperature of (25 ± 2)°C over 16 hr. The measurements were carried out twice at the same conditions, and all results were averaged over the two measurements.

1.2 Sampling and analysis

Figure 1 shows a schematic diagram of the measurement system for vehicle exhaust emissions. The vehicle exhaust was diluted using a constant volume sampler (CVS). A Horiba META-7200H motor exhaust gas analyzer (Horiba Ltd., Japan) was used to detect carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx) and total hydrocarbon (THC) emissions by means of usual analytical techniques (non-dispersive infrared for CO and CO_2, chemiluminescence for NOx and flame ionization detection for THC).

VOCs from the CVS-diluted exhaust were collected through a battery-operated air pump at a flow rate of 750

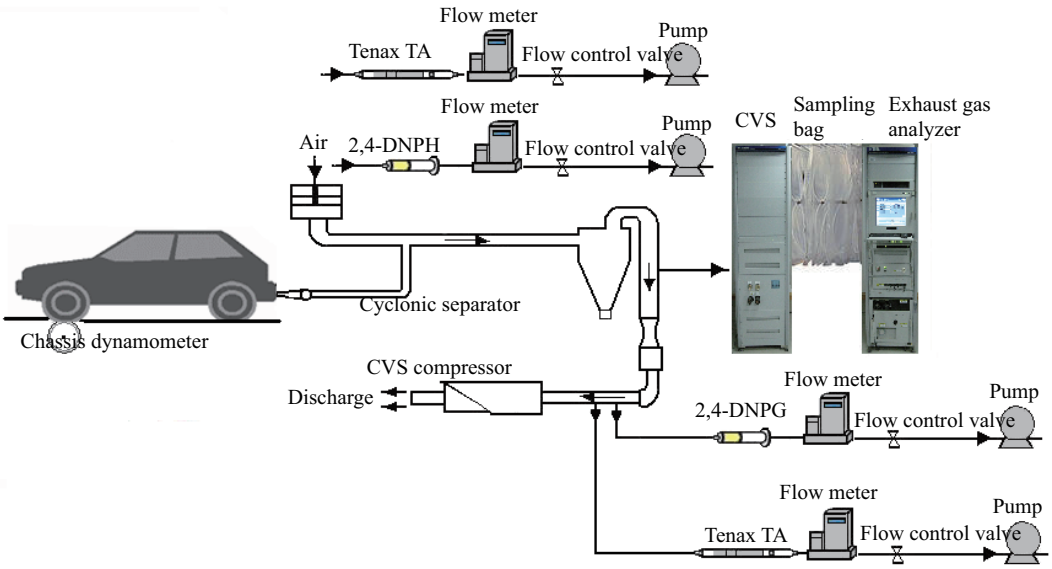

Fig. 1 Schematic diagram of measurement system for vehicle exhaust emissions.

mL/min using a Tenax TA sorbent tube. Tenax samples were analyzed by the thermal desorption preconcentration method, followed by identification by high resolution gas chromatography with a mass spectrometer detector (GC/MS). The thermal desorption system (Marks, UK) has two stages of desorption. At the first stage the analytes were desorbed with nitrogen flow from a sample tube then refocused onto a cold trap kept at –10°C. The second stage was a trap heated at 280°C to release materials into the gas chromatograph capillary column (HP-5MS; 30 m × 0.25 mm ID, film thickness: 0.25 μm). The column was kept isothermal at 35°C for 5 min and then heated up to 280°C at a rate of 5°C/min. Subsequently, the column temperature was kept at 280°C for 10 min. The MS was run in SCAN mode with mass of 35–550 amu. VOCs were identified by comparing mass spectra with those contained in the NIST library and quantified by comparing area response with those of standard compounds using the external standard technique. The standard mixture of VOCs (SEPA, China) contains benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene, styrene, *n*-butylacetate and *n*-undecane. Due to difficulties in resolving the chromatography peaks, the results for *m*-xylene and *p*-xylene are represented as a sum.

Carbonyl compounds in the dilution tunnel were sampled through a battery-operated air pump at a flow rate of 1200 mL/min using a 2,4-dinitrophenylhydrazine (DNPH)-coated silica cartridge (Supelco, USA). The carbonyls reacted with DNPH to form corresponding hydrazones derivatives and were trapped. After elution and pretreatment, 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. Carbonyls were identified and quantified by comparison of their retention time and area response to those of the standard compounds using the external standard technique. The standard mixture (Supelco, USA) contains 14 components, namely, formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methyl ethyl ketone, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, tolualdehyde, cyclohexanone and hexanaldehyde. Because the column used cannot separate acrolein and acetone, they were quantified together.

The five-point external standard methods were used to make linear calibration curve for quantification of VOCs and carbonyl compounds. The correlation coefficients were more than 99.9%. VOCs and carbonyls of ambient air were sampled and analyzed in the same way as those from the vehicle emissions. The effects of ambient air were all subtracted from the final results.

2 Results and discussion

2.1 Regulated emissions

Figure 2 presents the regulated emissions results as well as relative emissions contributions from each stage of the entire test cycle. Compared to the baseline cars fueled only with gasoline, CO and THC emissions from cars fueled with methanol/gasoline blends were decreased by 11%–34% and 10%–49%, respectively, while NO*x* emissions were increased by 53%–474%. The decreases in THC and CO emissions from vehicles fueled with methanol/gasoline blends are consistent with results reported by Liu et al. (2007) and Liao et al. (2006). The reduction in CO is due to the fact that methanol contains only about 37.5% carbon, while gasoline contains 85.8% carbon. This carbon converts directly to CO during combustion, so the CO formation and emissions are quantitatively reduced when using methanol. Moreover, methanol has a high oxygen content (50 wt.%). When methanol is added into gasoline, the methanol/gasoline blend contains more oxygen. This "pre-mixed oxygen effect" enables the reaction go to a more complete state, thus reducing CO and THC emissions (Hu et al., 2007). The increase in NO*x* emissions is due to the fast flame propagation speed and the enhanced combustion temperature.

For all the cars, most of the CO was produced during the first ECE cycle. In this stage, rich mixtures during acceleration resulted in more engine-out CO. Simultaneously, the TWC had not reached the light-off temperature and was not able to function effectively. Therefore, the emission reductions were diminished. Generally speaking, for CO emissions, the contribution to total emissions from the first ECE cycle in methanol/gasoline-fueled cars was greater than that in gasoline-fueled cars, which always were over 90%. Furthermore, the catalysts used with the methanol/gasoline-fueled engines have longer light-off times because of the lower exhaust temperatures as compared to gasoline-fueled engines. However, beginning with the second ECE and through the EUDC cycle, the TWC had fully warmed, thus the CO emissions decreased greatly. The THC emissions showed a similar trend, but were not as prominent as CO emissions.

In addition, cars that were fueled with low-to-middle mixing ratio blends of methanol/gasoline were easy to start. However, for M85 and M100-fueled vehicles, more fuel had to be injected into the engine to start the vehicle. This rich mixture condition lasted for a long time in the first ECE cycle, thus emitting more CO and THC. Therefore, when the cars were fueled with low-to-middle mixing ratio blends of methanol/gasoline (M15, M20, M30 and M50), the higher the mixing ratio, the lower the THC and CO emissions. When the cars were fueled with high mixing ratio blends (M85 and M100), the THC and CO emissions were higher than those fueled with low-to-middle mixing ratio blends.

Vehicles fueled with methanol/gasoline blends emitted low NO*x* in the ECE cycles because the temperature of the engine cylinder was not high enough to produce NO*x*. NO*x* emissions reached a maximum value in the EUDC cycle, during which 60%–70% of total NO*x* were emitted from M15, M85 and M100-fueled vehicles. For the whole NEDC cycle, higher fractions of methanol blended into gasoline resulted in higher NO*x* emissions.

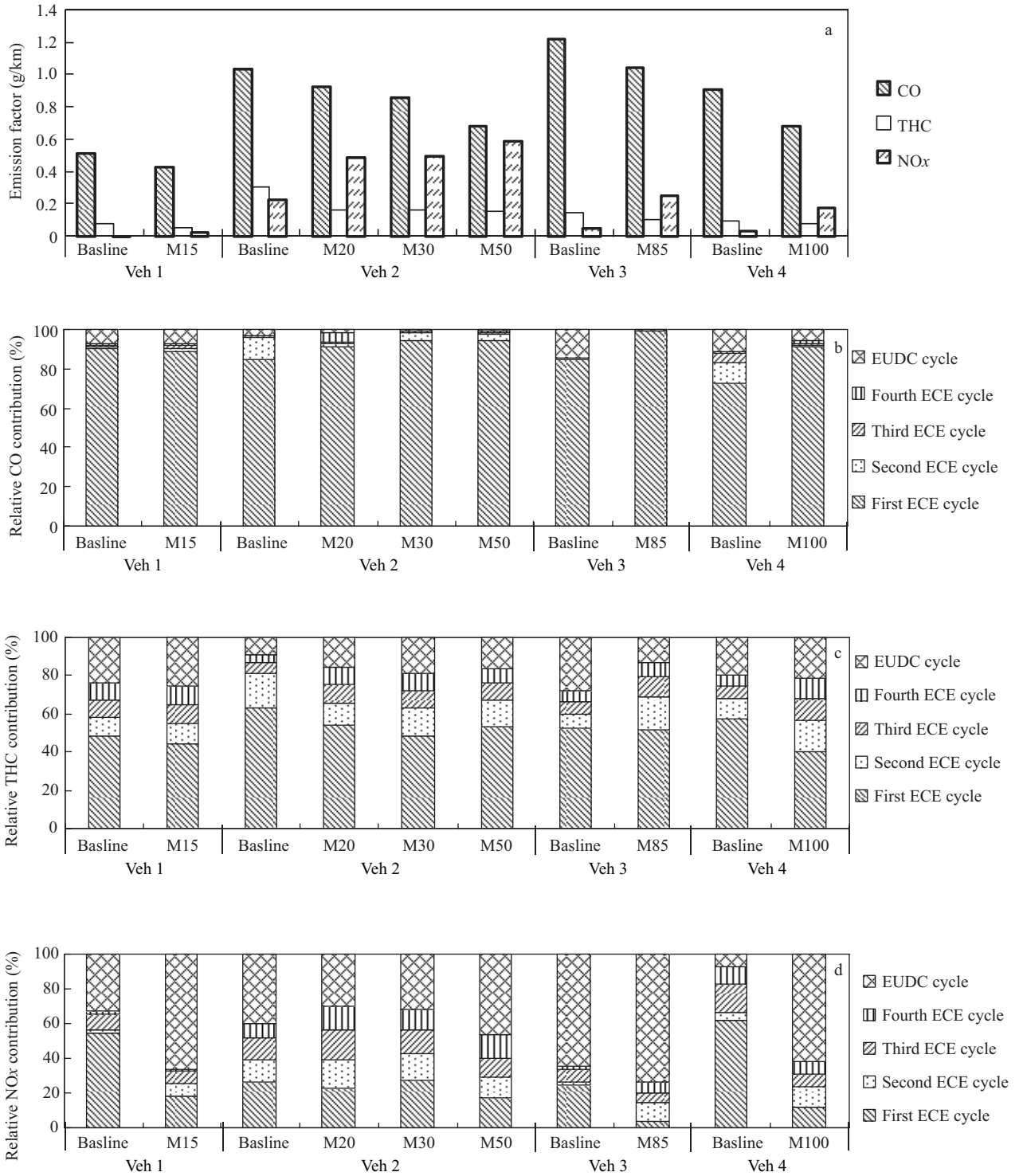

Fig. 2 Regulated emissions and relative contributions from each stage of the test cycle. (a) regulated emissions; (b) relative CO contribution; (c) relative THC contribution; (d) relative NO*x* contribution.

2.2 VOC emissions

Table 1 shows the average VOC emission factors for vehicles fueled with methanol/gasoline blends at different mixing ratios. BTEX (benzene, toluene, ethylbenzene, *p*, *m*, *o*-xylene) account for about 95% of total VOCs. For all methanol/gasoline blends, total VOCs and BTEX emissions were decreased as compared with baseline vehicle fueled only with gasoline. For BTEX emissions, M85 showed the highest decrease (97.4%) while M15 showed the lowest decrease (19.7%) compared with the baseline. Toluene dominated BTEX and total VOC emissions for all methanol/gasoline blends, accounting for approximately 40%–50% of all VOCs. Unsaturated hydrocarbons in the fuel are precursors responsible for the formation of aromatic species. Since methanol is free of unsaturated hydrocarbons, it has the effect of reducing the aromatic precursors, leading to a reduction of aromatics. Xylene emissions are related to the aromatic content of the fuel. Aromatics are not present in methanol, hence xylene

Table 1 VOC emission factors for different mixing ratios of methanol/gasoline fueled vehicles (unit: mg/km)

	Vehicle 1		Vehicle 2				Vehicle 3		Vehicle 4	
	Gasoline	M15	Gasoline	M20	M30	M50	Gasoline	M85	Gasoline	M100
Benzene	0.434	0.497	1.658	1.030	1.208	1.060	2.415	0.032	0.848	0.202
Toluene	1.559	1.231	7.594	4.338	4.963	2.375	4.957	0.152	1.875	0.588
n-Butylacetate	0.021	0.018	0.010	0.010	0.037	0.034	0.034	0.014	0.021	0.015
Ethylbenzene	0.335	0.217	2.396	0.943	0.803	0.319	1.313	0.026	0.402	0.110
p,m-Xylene	0.481	0.342	2.429	1.088	0.952	0.448	1.755	0.059	0.577	0.160
Sturene	0.089	0.037	0.352	0.271	0.130	0.099	0.401	0.013	0.116	0.020
o-Xylene	0.380	0.274	1.951	0.866	0.755	0.394	1.621	0.044	0.439	0.129
n-Undecane	0.028	0.015	0.099	0.047	0.035	0.010	0.016	0.008	0.037	0.009
Total VOCs	3.327	2.631	16.489	8.593	8.883	4.739	12.512	0.348	4.315	1.233

emissions are reduced when the cars are fueled with methanol/gasoline blends.

2.3 Carbonyl compound emissions

Carbonyl compound emission factors from vehicles fueled with methanol/gasoline blends at different mixing ratios are presented in Table 2. Formaldehyde emissions were the most abundant carbonyl for all methanol/gasoline blends 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 hydrocarbons, which results in higher formaldehyde emissions from engines fueled with methanol/gasoline blends as compared with baseline gasline-fueled engines. With the increase in methanol content, the formaldehyde concentrations also increased. Similar results were also obtained by Zervas et al. (2002) and Wei et al. (2009). Moreover, Wei et al. (2009) found that formaldehyde emission characteristics are approximately linear to the amount of cyclic-supplied fuel methanol. In our study, with low-to-middle ratio methanol/gasoline blends (M15, M20, M30 and M50), formaldehyde emissions had a slight increase compared with the baseline, while that of high ratio blends (M85 and M100) were three times higher than the baseline.

However, there was a decrease in acetaldehyde emissions of 13%–65% with different ratios of methanol/gasoline blends. In the case of other carbonyls, there was an increase or decrease more or less. The sharp increase in formaldehyde emissions eventually resulted in the increase of total carbonyls with the exception of M20, which showed no obvious change from the baseline. Although M20, M30 and M50 were all tested on Vehicle 2, the category and quantity of additives of the three fuels were different, which resulted in the total carbonyls emitted from M50 being slightly higher than that from M20 but significantly lower than that from M30.

2.4 Effects of new TWC on emissions

Formaldehyde emissions are always a barrier to the development of methanol/gasoline blend vehicles. New TWCs were designed respectively for M15, M85 and M100-fueled vehicles with the main aim of reducing formaldehyde emissions. Figure 3 shows comparisons between emissions of regulated emissions, BTEX and carbonyls between vehicles fitted with the OEM TWC and the new TWC for M15, M85 and M100-fueled vehicles, respectively. Retrofitted with the new TWCs, CO, THC, and NOx were decreased by 24%–50%, 10%–35%, and 24%–58% respectively as compared with vehicles fitted with OEM TWC for methanol/gasoline blends.

Although the main aim of the new TWCs was to reduce formaldehyde emissions, they also affected other regulated and unregulated emissions. With the use of the new TWC, formaldehyde emissions were decreased from 1.89 to 0.60 mg/km for M15, from 5.96 to 4.97 mg/km for M85 and from 5.73 to 3.79 mg/km for M100. All BTEX also decreased to some extent, though other carbonyls such as acetaldehyde and acrolein+acetone showed an increase.

VOCs and cabonyls are also important precursors of photochemically-formed secondary pollutants, such as

Table 2 Carbonyl compound emission factors for different mixing ratios of methanol/gasoline fueled vehicles (unit: mg/km)

	Vehicle 1		Vehicle 2				Vehicle 3		Vehicle 4	
	Gasoline	M15	Gasoline	M20	M30	M50	Gasoline	M85	Gasoline	M100
Formaldehyde	1.496	1.878	2.918	3.270	5.045	5.182	2.140	5.956	1.784	5.348
Acetaldehyde	0.386	0.317	2.628	2.148	2.291	1.504	1.319	0.954	0.761	0.268
Acrolein + Acetone	0.241	0.263	0.821	0.614	0.684	0.541	0.696	0.460	0.474	0.181
Propionaldehyde	0.076	0.076	0.399	0.266	0.247	0.210	0.212	0.207	0.141	0.076
Crotonaldehyde	0	0.016	0.049	0	0	0	0.085	0.075	0.052	0
Methyl ethyl ketone	0.216	0	0	0	0.507	0	0.347	0.264	0.123	0.068
Methacrolein	0	0.159	0.303	0.281	0.150	0.439	0	0	0.039	0
Butyraldehyde	0	0	0.498	0.480	0	0	0.074	0.032	0	0.020
Benzaldehyde	0.133	0.138	0.181	0	0.105	0.080	0.565	0.332	0.258	0.121
Valeraldehyde	0.015	0.020	0.103	0.053	0	0	0.044	0	0	0
Tolualdehyde	0	0	0	0	0	0	0	0	0	0
Cyclohexanone	0	0	0	0	0	0	0	0	0	0
Hexanaldehyde	0	0.080	0	0	0	0	0	0	0	0.080
Total carbonyls	2.563	2.948	7.900	7.112	9.029	7.956	5.482	8.281	3.630	6.162

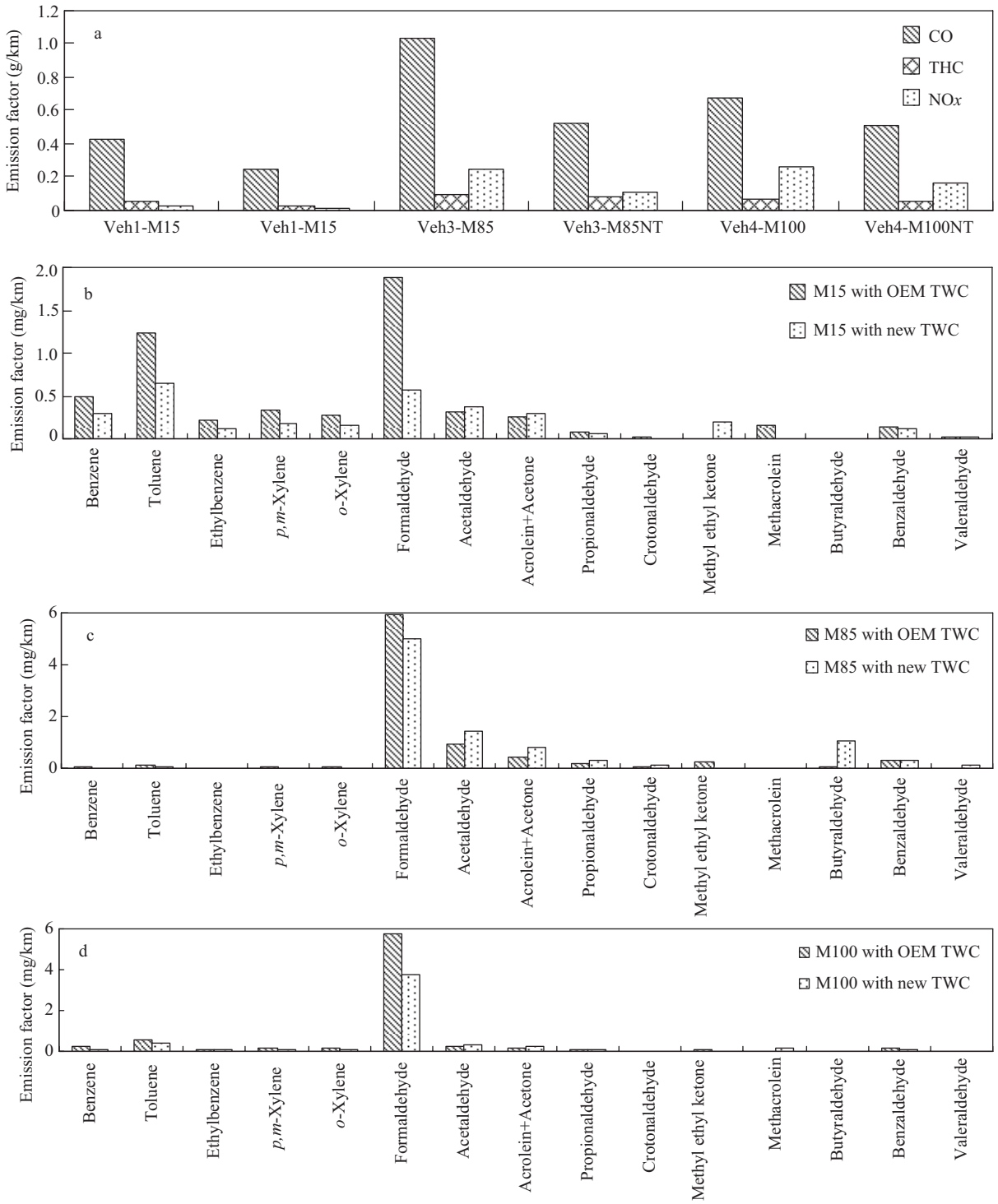

Fig. 3 Regulated emissions, BTEX and carbonyls comparison between OEM TWC and new TWC for M15, M85 and M100 respectively. (a) regulated emissions; (b) M15; (c) M85; (d) M100.

ozone, which poses a serious air pollution problem under specific summertime conditions. Since the individual VOCs and carbonyls react with different rates and different mechanisms, they also differ in their contribution to photochemical ozone formation (Schmitz et al., 2000).

In the case of the use of new TWC, the specific reactivity was reduced from 4.84 to 4.08, from 6.14 to 5.98, and from 6.22 to 6.14 for M15, M85 and M100, respectively. Formaldehyde and *p,m*-xylene also have the highest maximum incremental reactivity (MIR) (7.15 and 7.64 respectively). With the new TWC, emissions of formaldehyde and *p,m*-xylene decreased sharply and their relative contributions to ozone forming potential were lowered. This leads to the conclusion that the use of methanol/gasoline blends with the new TWC is friendlier to the environment. When a gasoline vehicle is modified into methanol/gasoline blend vehicle, it is necessary to be retrofitted with a new TWC. Moreover, when an M15-fueled vehicle is retrofitted with the new TWC, its SR is lowered (from 4.51 to 4.08) compared

with its gasoline counterpart with OEM TWC. For low mixing ratio methanol/gasoline blends, it is possible that methanol/gasoline blends have lower effect on environment than gasoline.

3 Conclusions

Regulated and unregulated emissions from four passenger cars fueled with different methanol/gasoline blends (M15, M20, M30, M50, M85 and M100) were investigated over the NEDC cycle. Emissions of eight VOCs and thirteen carbonyl compounds were identified and quantified. The effects of different mixing ratios and new TWCs on emissions of regulated and unregulated VOC and carbonyl compounds were studied.

Compared with baseline cars fueled only with gasoline, when cars were fueled with methanol/gasoline blends, CO and THC emissions decreased by 11%–34% and 10%–49% respectively, while NOx emission increased by 53%–474%. For all methanol/gasoline blends, total VOCs and BTEX decreased relative to the baseline. For BTEX emissions, as compared with the baseline, M85 had the highest decrease (97.4%) while M15 had the lowest decrease (19.7%). With low-to-middle ratio methanol/gasoline blends (M15, M20, M30 and M50), formaldehyde emissions had a slight increase, while that of high ratio blends (M85 and M100) were three times compared with gasoline counterparts.

Retrofitted with the new TWC, CO, THC, and NOx were decreased by 24%–50%, 10%–35%, and 24%–58% respectively for methanol/gasoline blends as compared with vehicles fitted with OEM TWC. Formaldehyde and BTEX were decreased while other carbonyls were increased. It is necessary for vehicles using methanol/gasoline blends to be retrofitted with a new TWC. Moreover, when a vehicle fueled with M15 is retrofitted with the new TWC, its SR was lower than its gasoline counterpart with OEM TWC, reducing from 4.51 to 4.08. This indicated that, for low mixing ratio methanol/gasoline blends, it is possible that vehicles fueled with methanol/gasoline blends have lower effect on the environment than vehicles fueled with gasoline only.

Acknowledgments

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