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Comparative effects of MTBE and ethanol additions into gasoline on exhaust emissions

Chong-Lin Song*, Wen-Mei Zhang, Yi-Qiang Pei, Guo-Liang Fan, Guan-Peng Xu

State Key Laboratory of Engines, Tianjin University, Tianjin 300072, China

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Abstract

The effects of the additives of ethanol (EA) and methyl *tert*-butyl ether (MTBE) in various blend ratios into the gasoline fuel on the exhaust emissions and the catalytic conversion efficiencies were investigated in an EFI gasoline engine. The regulated exhaust emissions (CO, THC and NO_X) and the unregulated exhaust emissions (benzene, formaldehyde, acetaldehyde, unburned EA and MTBE) before and after the three-way catalytic converter were measured.

The experimental results showed that EA brought about generally lower regulated engine-out emissions than MTBE did. But, the comparison of the unregulated engine-out emissions between both additives was different. Concretely, the effect of EA on benzene emission was worse than that of MTBE on the whole, which was a contrast with formaldehyde emission. The difference in the acetaldehyde comparison depended much on the engine operating conditions, especially the engine speed. Both EA and MTBE were identified in the engine exhaust gases only when they were added to the fuel, and their volume fraction increased with blend ratios. The catalytic conversion efficiencies of the regulated emissions for the EA blends were in general lower than those for MTBE blends, especially at the low and high engine speeds. There was little difference in the catalytic conversion efficiencies for both benzene and formaldehyde, while distinct difference for acetaldehyde.

Keywords: EFI gasoline engine; MTBE; Ethanol; Regulated emission; Unregulated emission; Catalytic conversion efficiency

1. Introduction

Methyl *tert*-butyl ether (MTBE) was authorized by USA for use as a gasoline additive in late 1979 (Braids, 2001). From then on, MTBE has been used worldwide for its compatibility with gasoline and functional benefit to the fuel's chemical and physical characteristics. MTBE, as an oxygenate additive in gasoline, not only can enhance the octane number but also reduce exhaust emissions (Kivi et al., 1992; Noorman, 1993; Li et al., 1995). Additionally, from the refinery perspective, MTBE has highly favorable properties, such as acceptable blending vapor pressure, high miscibility in gasoline, moderate boiling point and stability in storage (Zhang and Ajay, 2001). Statistically, over 85% of reformulated gasoline (RFG) contained MTBE to meet the Clean Air Act Amendments of 1990 and similar regulations. By 1998, MTBE was ranked fourth in bulk chemical production in United States (An et al., 2002; He et al., 2003).

*Corresponding author. Tel.: +86 22 27406840 8020; fax: +86 22 27403750.
E-mail address: songchonglin@tju.edu.cn (C.-L. Song).

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MTBE has been forbidden adding into gasoline since 31 December 2002 and 1 January 2004 in California and New York, respectively, since its presence in the exhaust gas when MTBE-containing gasoline is used (Warner-Selph and Harvey, 1990; Hamai et al., 1992; Poulopoulos and Philippopoulas, 2000). Furthermore, MTBE not only has high mobility in aquatic environment and drinking water system due to its solubility and lack of polarity, but also has resistance to decomposition for it is not significantly affected by microorganisms. This adds cost and longevity to gasoline cleanups (Braids, 2001), and moreover, inhalation of MTBE at high concentrations may have adverse health effects (Hartley et al., 1999). Therefore, it is necessary to find a substitute for MTBE.

Presently, ethanol (EA) as an oxygenous biomass fuel is considered as a predominant alternative to MTBE for its biodegradable, low toxicity, persistence and regenerative characteristic (Cassada et al., 2000). Researches indicated that addition of ethanol to gasoline not only increases reid vapor pressure (RVP) of the blended fuel (Pumphrey et al., 2000), but also alters fuel distillation curve and composition (Hsieh et al., 2002). Since oxygen mass content in an ethanol molecule is approximately twice that of MTBE, less ethanol is required to meet specified oxygen content in fuel.

It is considered that ethanol, as a substitute for MTBE in RFG, has some benefits in reducing water contamination and poses no significant adverse impacts on public health and environment (Nadim et al., 2001). However, the addition of ethanol into gasoline will decrease the heat value of the blended fuel (Hsieh et al., 2002).The main concern about contamination by ethanol-amended gasoline is focused on the complex physical, chemical and biological interactions between ethanol and gasoline constitutes, which may limit the selection of proper environmental restoration technologies (Henry and Fabio, 2001).

Numerous studies have been performed on the correlations between oxygenate additives into gasoline and pollutant concentrations in the engine exhaust gas. Many authors presented a decrease of exhaust emissions by the addition of oxygenates. Kisenyi et al. (1994) have studied the effect of MTBE addition (15% v/v) into unleaded gasoline on the regulated exhaust emissions, and the result showed that MTBE can reduce CO by 10–15%, NO_X by 1.0–1.7%, THC by 10–20%. Furey and King (1981) investigated the exhaust emissions from cars running on the unleaded gasoline and the blended fuel (10% v/v ethanol added into the gasoline), and they concluded that THC, CO and NO_X emissions were significantly lower with oxygenated fuels than with gasoline. But others presented no change, for example, the addition of MTBE did not change the emissions of CO (Lange and Muller, 1994), HC (Petris et al., 1993), or NO_X (Chou and Long, 1996), and an increase was even noticed in the case of NO_X after the addition of ethanol or MTBE (Neimark et al., 1994). These differences may be explained by the different methods used for the precise determination of λ, especially in the early works.

Some work has also been done related to the comparison of oxygenates' effect on regulated emissions. The study of Neimark et al. (1994) calculated that CO reduction activity was in the order: alcohols > ethers, the THC reduction activity was in the order: ethers > alcohols, and the NO_X increasing reactivity was in the order: ethers > alcohols. Zervas et al. (2003) have investigated the influence of fuel composition and air/fuel equivalence ratio on the exhaust emissions of regulated pollutants. They concluded that at stoichiometry, the addition of oxygenated compounds methanol, ethanol, 2-propanol, and MTBE into the pure gasoline (5% and 20% v/v) could decrease exhaust CO, HC and NO_X up to 30%, 50% and 60%, respectively. The addition of 5% of 2-propanol was the most effective for the reduction of CO, 20% of ethanol for the reduction of HC, 5% of MTBE for the NO_X.

The addition of oxygenated compounds affects the exhaust emission of some unregulated pollutants. For example, the addition of MTBE increased exhaust formaldehyde and ethanol addition increased exhaust acetaldehyde emissions (Reuter et al., 1992; Zervas et al., 2002). The oxygenated compounds also increased the exhaust emission of organic acids (Zervas et al., 2001). In contrast, benzene emission from engine was decreased with oxygenates into gasoline (Poulopoulos and Samaras, 2001; Zervas et al., 2004).

In this paper, specific emphasis is given to the comparison of the effects of these two gasoline additives, MTBE and EA, on the engine exhaust emissions from an EFI engine with a typical commercial three-way catalytic converter. Besides the regulated emissions, some important unregulated compounds as benzene, formaldehyde, acetaldehyde, unburned EA and MTBE were measured

before and after the catalytic treatment in order to determine the comparisons of the engine-out emissions and the conversion efficiencies.

2. Experimental section

2.1. Test fuels

Eight blended test fuels were used in this study. An unleaded gasoline (RON: 92.5) without any additive was used as a base fuel (BF) for the preparation of gasoline/EA blends and gasoline/MTBE blends. Gasoline/MTBE blends contained MTBE 5%, 10%, 15% and 20% (v/v), marked: M1, M2, M3 and M4, respectively. Then gasoline/EA blends were concocted according to the oxygen content of gasoline/MTBE blends named E1, E2, E3 and E4 which contained EA 2.45%, 4.90%, 7.34% and 9.79% (v/v), respectively. The properties of the fuels used are presented in Table 1.

2.2. Experimental equipment and procedure

The experiments were performed on a multi-point port injection four-cylinder electronic fuel injection (EFI) gasoline engine with a bore of 95 mm, a stroke of 100 mm and a compression ratio of 7.6. A typical commercial three-way catalytic converter (Pt/Pd: 8/1) with ceramic monolithic support was used in the test. The EFI system chose a close-loop control mode at part engine loads to keep the engine operating near stoichoimetric air/fuel ratio and then changed to an open-loop control mode at full engine loads to produce maximum power.

The engine was started and allowed to warm up for a period of 20–30 min. Engine tests were operated at the speed of 1600, 2600 and 3400 rpm on various loads. Before running the engine with a new blended fuel, it was allowed to use the new fuel to cleanout the remaining fuel from the pipeline of the engine to avoid the leftover interfering each other.

The measured variables included engine rotational speed, torque, air-fuel ratio, exhaust emissions concentrations of CO, NO_X, THC, benzene, formaldehyde, acetaldehyde, unburned EA and MTBE. For each experiment, all tests were repeated at least twice on the same operation to ensure the veracity and reliability of the results, and average values were used to reduce the experimental error.

Exhaust gases were sampled from the inlet and outlet of the catalytic converter at each operation condition and then the regulated emissions were measured on line by an HORIBA exhaust analyzer (MEXA-7100 DEGR) with a resolution of 0.001% for CO emission and 1 ppm for THC and NO_X emissions. Specifically, CO was analyzed by a non-dispersive infrared (NDIR) analyzer, NO_X by a chemiluminescent detector (CLD) and THC by a flame ionization detector (FID).

Samples collected from the exhaust gases before and after the catalytic converter at each operation condition were analyzed in a gas chromatograph (HP6890) equipped with a 25 m long, 0.25 mm inner diameter capillary column (CP-WAX58) for formaldehyde and acetaldehyde. The cold on-column injection method was applied in order to improve their detection limits to 0.01 ppm. Whereas other unregulated emissions such as benzene, unburned EA and MTBE were measured in a Varian GC-3800 gas chromatograph equipped with HP-5 type capillary column (30 m × 0.32 mm), and the detection limits for them were 0.01 ppm. All the unregulated emissions were analyzed by a FID. The signals from the chromatograph were processed by a personal computer.

The relative experimental error is less than 3% for the CO emission, 5% for the THC and NO_X

Table 1
Properties of different gasoline/oxygenant blended fuels

Property items	E1	E2	E3	E4	M1	M2	M3	M4	BF
RON	93.0	93.5	94.2	94.8	93.8	94.7	96.0	96.8	92.5
RVP (p kPa^{-1})	54.5	55.0	58.5	56.5	51.5	52.5	51.0	54.5	55.0
Distillation temperature (°C)									
10 vol%	52	52	53	54	58	54	57	54	58
50 vol%	97	93	90	83	93	91	86	80	97
90 vol%	162	163	158	158	160	162	161	156	161
End point	189	187	187	186	188	185	187	185	189

emissions, from 8% to 15% for the benzene emission, from 10% to 20% for the formaldehyde emission, and from 5% to 15% for the unburned EA and from 10% to 15% for the acetaldehyde and unburned MTBE emissions.

3. Experimental results and discussions

To investigate the effects of different blended fuels on regulated pollutant emissions, six torque points were selected at each engine speed while five torque points were selected for the unregulated ones. Attentively, at each operating condition, the engine should not be adjusted.

Parameters η_x and Δ_x are chosen to compare the effect of the MTBE/BF blended fuels and the EA/BF blended fuels on the regulated exhaust emissions. Particularly, η_x stands for the relative increase of the engine-out emissions of the EA/BF blended fuels compared with those of the MTBE/BF blended fuels with equivalent oxygen content; while Δ_x represents the difference of the emission conversion efficiency between EA/BF and MTBE/BF blended fuels, and the subscript "x" designates the species of the exhaust emission. The formulas for η_x and Δ_x can be written as

$$\eta_x = \frac{\delta_E - \delta_M}{\delta_M} \times 100\%, \quad \Delta_x = \varphi_E - \varphi_M,$$

where, δ_E and δ_M denote the engine-out regulated emission volume fractions for the EA/BF blends and MTBE/BF blends; φ_E and φ_M represent the catalytic conversion efficiency for the EA/BF blends and MTBE/BF blends.

Comparative effects of the blended fuels on exhaust emissions at different operating conditions are shown in the figures, in which the correlation between parameter η_x or Δ_x and brake mean effective pressure (BMEP) is presented.

3.1. Regulated emissions and conversion efficiencies

The ingredient of the exhaust emissions depended not only on the fuels composition but also on engine operating conditions. In this experiment, CO, THC and NO_X were chosen for regulated emissions analysis.

3.1.1. CO emission

Comparative effects of the blended fuels on CO emission at different operating conditions are shown in Figs. 1–3. At the engine speed of 1600 rpm, $\eta_{CO} < 0$ was tenable except for E2–M2 involved at the high engine loadings. Videlicet, compared with MTBE, equivalent EA blends resulted in less engine-out CO emission. The maximum absolute value of η_{CO} reached up to 22.6% (Fig. 1).

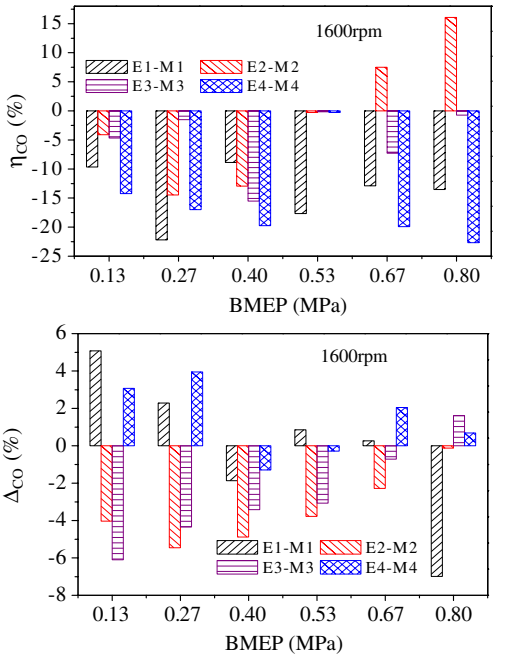

Fig. 1. Effects of the blended fuels on CO emission at 1600 rpm.

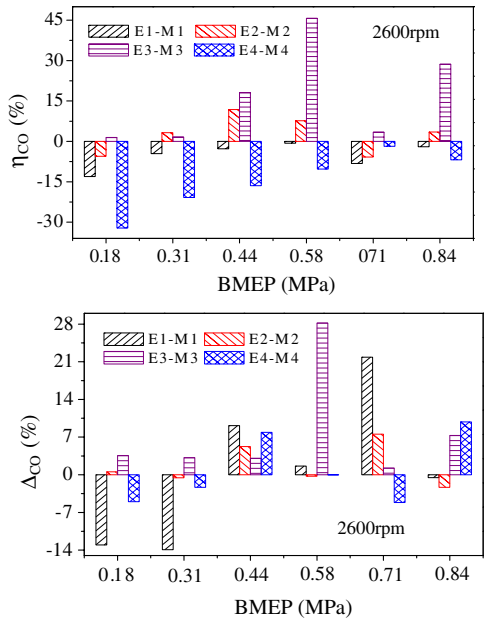

Fig. 2. Effects of the blended fuels on CO emission at 2600 rpm.

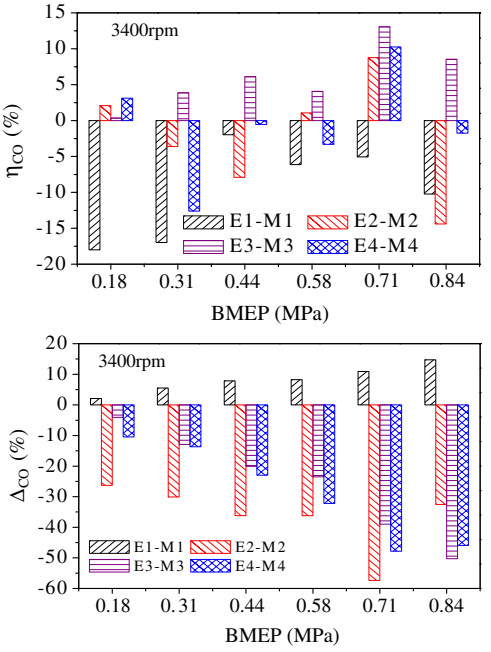

Fig. 3. Effects of the blended fuels on CO emission at 3400 rpm.

The comparison of CO catalyst conversion efficiencies can also be observed from Fig. 1. At the low loading, merely E1–M1 and E4–M4 engendered $\Delta_{CO}>0$, which indicated that the conversion efficiencies of E1and E4 were higher than those of M1 and M4; others resulted in $\Delta_{CO}<0$. At middle or high loading, Δ_{CO} was negative in general; that meant the conversion efficiencies of the EA/BF blends were lower than those of MTBE. Totally, the difference in the conversion efficiency between EA and MTBE was not very distinct for the range of Δ_{CO} was only −7% to 5%.

From Fig. 2, it can be observed that at middle speed of 2600 rpm, different adding proportion or operating conditions induced to different comparison results. E1–M1 and E4–M4 engendered $\eta_{CO}<0$, and the comparison of E3–M3 was a contrast to it. But there was no obvious trend of the result when E2 and M2 were compared.

The comparison of the catalyst conversion efficiencies demonstrated $\Delta_{CO}>0$ except at the low loading. In other words, the conversion efficiencies of CO for the EA/BF blends were higher than those for the MTBE/BF blends in most of the cases. The Δ_{CO} ranged from −13.9% to 28.2%.

At the high speed of 3400 rpm, comparison of the emission for E1–M1 showed $\eta_{CO}<0$, while for E3–M3 it was in the very opposition to that. And there was no obvious trend of η_{CO} for other blends, which related to the operating conditions very much.

The conversion efficiency comparison showed $\Delta_{CO}<0$, except the comparison for M1–E1 at the middle and high loading. The Δ_{CO} ranged from −57.3% to 12.9% (Fig. 3).

3.1.2. THC emission

Figs. 4–6 presents the results of the comparative effects of the blended fuels on THC emission under different operating conditions. At the speed of 1600 rpm, it was obvious that $\eta_{THC}<0$ was tenable when M4 and E4 used; namely, less engine-out THC was emitted by adding EA into the pure gasoline than that of MTBE. And the absolute value of η_{THC} was up to 60%. For other blends, it is difficult to obtain a conclusion to determine which additive was better for THC engine-out emission since the result depended on the operating conditions very much. It is clear that η_{THC} for E2–M2 and E3–M3 was degressive monotonously, which was a contrast with the result induced by E1–M1.

At 1600 rpm, the comparison of THC conversion efficiencies showed that Δ_{THC} was negative in the most cases, except when E1 and M1 were compared. But the difference was not very distinct as the range of Δ_{THC} was merely −8.6% to 4.7%.

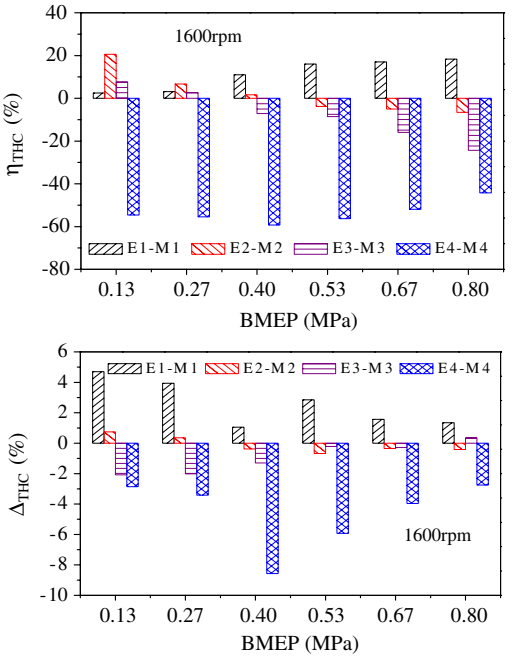

Fig. 4. Effects of the blended fuels on THC emission at 1600 rpm.

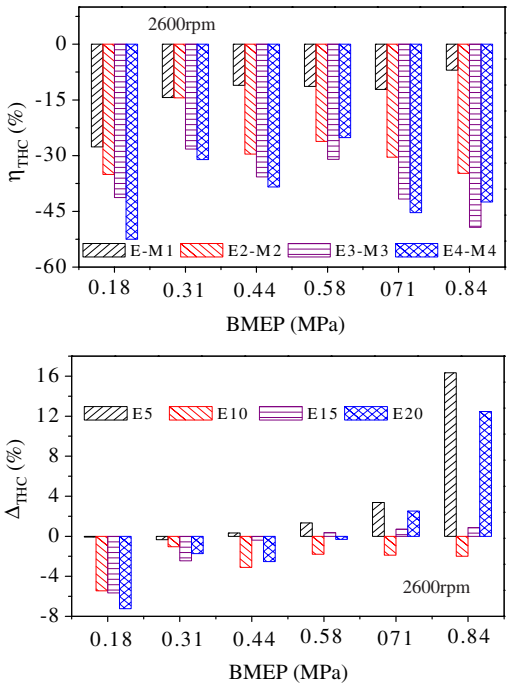

Fig. 5. Effects of the blended fuels on THC emission at 2600 rpm.

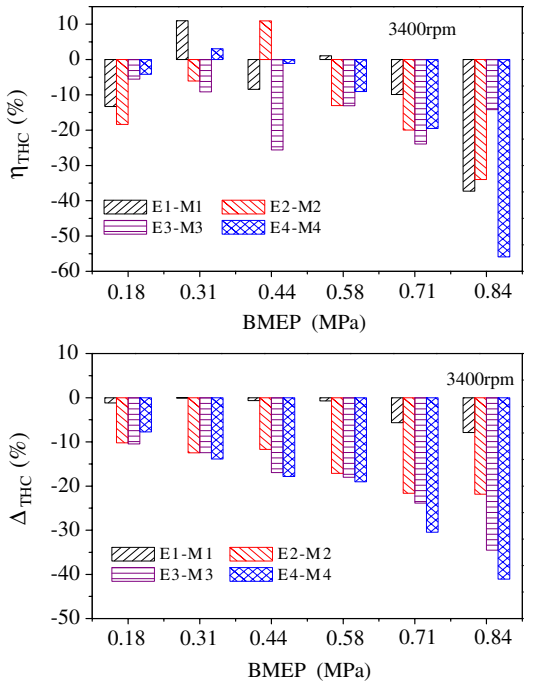

Fig. 6. Effects of the blended fuels on THC emission at 3400 rpm.

At the speed of 2600 rpm, it was obvious that less engine-out THC was emitted from EA blends than MTBE blends since η_{THC} was negative at all the operating conditions, and the absolute value of η_{THC} reached up to 50%.

The conversion efficiency difference, Δ_{THC}, increased with the engine loading at 2600 rpm. Because the conversion efficiency of EA was below that of MTBE at the lowest loading while the result is on the very reverse at the highest loading. And the range of Δ_{THC} was −7.2% to 16.3%.

At the speed of 3400 rpm, η_{THC} had the same trend as that at 2600 rpm, i.e. adding EA led to less THC engine-out emission than the MTBE blends with the same oxygen content; especially, the emission decrease was more obvious at the higher loading, and the difference η_{THC} could be up to 60%.

It was impressive that at all the operating conditions Δ_{THC} was negative at 3400 rpm. Moreover, the absolute value of Δ_{THC} increased as the oxygen content and the engine loading increased, and it could be up to 41.1%.

3.1.3. NO_X emission

The comparative effects of the blended fuels on NO_X emission at different conditions were shown in Figs. 7–9. At the engine speed of 1600 rpm, $\eta_{NO_X} < 0$ was tenable in most of the cases. Namely, additive of EA resulted in less engine-out NO_X emission compared with MTBE. The absolute value of $\eta_{NO_X} < 0$ was up to 27.7%.

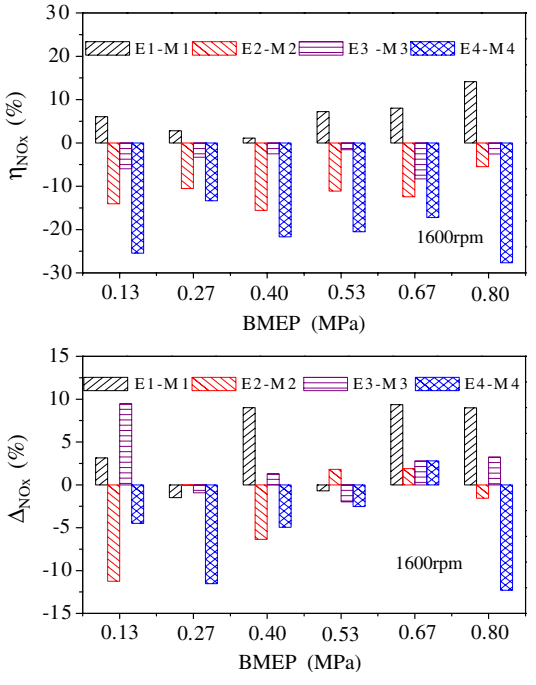

Fig. 7. Effects of the blended fuels on NO_X emission at 1600 rpm.

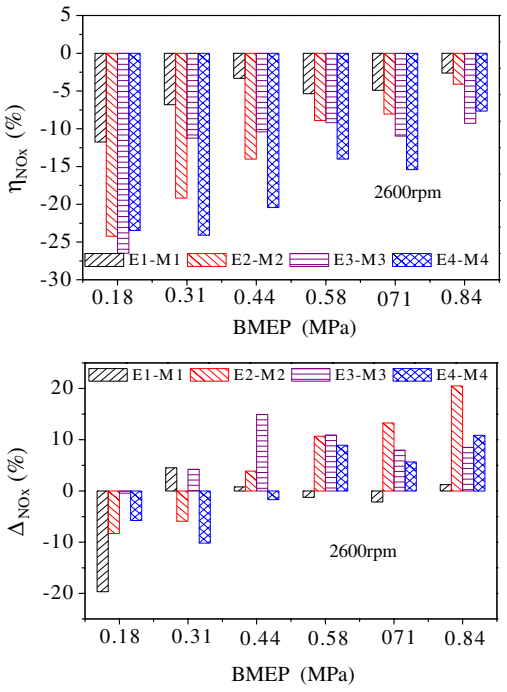

Fig. 8. Effects of the blended fuels on NO_X emission at 2600 rpm.

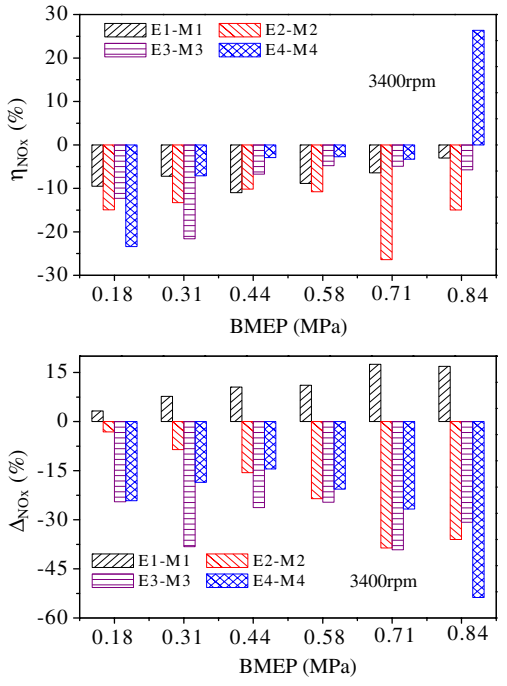

Fig. 9. Effects of the blended fuels on NO_X emission at 3400 rpm.

There is no clear correlation between Δ_{NO_X} and the blended fuels, because the conversion efficiency had much to do with the ingredients of the exhaust emissions, the temperature of the catalyzer, and so on. But the difference in the NO_X conversion efficiencies of the two additions was not very distinct since the range of Δ_{NO_X} was −12.3% to 9.5%.

At the middle speed (2600 rpm), it was obvious that at all the operating conditions $\eta_{NO_X} < 0$ was negative (Fig. 8). Namely, lower engine-out NO_X emission could be reached by adding EA into the gasoline rather than MTBE, and the maximal absolute value of $\eta_{NO_X} < 0$ was 26.5%.

Generally speaking, Δ_{NO_X} increased with the engine loading, and it was negative at the lowest loading while it was positive at the highest loading. The range of Δ_{NO_X} was −19.7% to 20.5%.

At the engine speed of 3400 rpm, $\eta_{NO_X} < 0$ was tenable except for the fuels E4–M4 at the highest engine loading (Fig. 9). Videlicet, compared with MTBE the equivalent EA resulted in less engine-out NO_X emission. And the absolute value of $\eta_{NO_X} < 0$ was up to 26.4%.

The conversion efficiency for EA blends was lower than that for MTBE since Δ_{NO_X} was negative except for the case of E1–M1. And the decrement can reach to 53.8%.

3.2. Unregulated emissions and conversion efficiency

Among the various compounds in exhaust emissions, the following unregulated emissions were measured: benzene, formaldehyde, acetaldehyde, unburned EA and MTBE.

Benzene was selected because it belonged to aromatics which were accused of cancerogenic substances. Formaldehyde and acetaldehyde were involved in the photochemical smog generation cycle while acetaldehyde was also a toxic compound. Furthermore, a possible increased acetaldehyde emission was the main complaint against the use of the ethanol fuels; while the increase of formaldehyde concentrations in exhaust gases was a large problem for MTBE addition into fuel. Consequently, the measurements of acetaldehyde and formaldehyde emissions were essential. Finally, unburned EA and MTBE emissions related to the presence of EA and MTBE in fuel were also examined.

In this part, the emissions of benzene, formaldehyde and acetaldehyde for the base fuel were also detected, because just the comparison between the emissions of the BF/EA blended fuels and those of BF/MTBE blended fuels is inadequate to estimate the effects of oxygenates on those emissions.

Additionally, the parameters v_x and μ_x are chosen for the comparison of benzene and acetaldehyde engine-out emissions. Concretely, v_x and μ_x represent the relative increasing percent of the engine-out emissions of the EA/BF blends and MTBE/BF blends compared with those of the BF. The comparative effects of EA and MTBE into gasoline on benzene and acetaldehyde emissions can be obtained on the basis of the correlation between v_x and μ_x indirectly. The formulas for v_x and μ_x are as follows:

$$v_x = \frac{\delta_E - \delta_{BF}}{\delta_{BF}} \times 100\%, \quad \mu_x = \frac{\delta_M - \delta_{BF}}{\delta_{BF}} \times 100\%,$$

where δ_E, δ_M and δ_{BF} are the engine-out emission volume fractions for the EA/BF blends, MTBE/BF blends and the base fuel, respectively. And the subscript "x" designates benzene or acetaldehyde emission. The definition of Δ_x for benzene and acetaldehyde was in accordance with that for the regulated ones.

3.2.1. Benzene emission

The effect of the blended fuels on benzene emission under different conditions were shown in Figs. 10–12. It was clear that the parameters v_{Ben} and μ_{Ben} were negative in all operating conditions, which meant that both EA/BF blends and MTBE/BF blends induced lower benzene emission concentration than the base fuel, which was mainly because adding oxygenates into the fuels made the engine tend to operate under leaner conditions.

From the comparison of v_{Ben} and μ_{Ben}, it can be obtained that at the engine speed of 1600 rpm, E1, E2 and E3 had less activity in the reduction of benzene than M1, M2 and M3 in the most cases, respectively. On the contrary, benzene reduction activity of E4 was higher than that of M4 (Fig. 10).

Generally, the conversion efficiency for EA blends was lower than that for MTBE blends, because Δ_{Ben} was negative in the most cases. And the range of Δ_{Ben} was about −19.4% to 11.6%.

At the speed of 2600 rpm, the reduction activity of engine-out benzene emission is in the order: MTBE > EA, since the absolute value of v_{Ben} was smaller than that of μ_{Ben} except at the lowest loading (Fig. 11). The trend of the results at 3400 rpm was almost identical with that at 2600 rpm (Fig. 12).

At 2600 rpm, Δ_{Ben} was naught because the conversion efficiencies of benzene from oxygenated

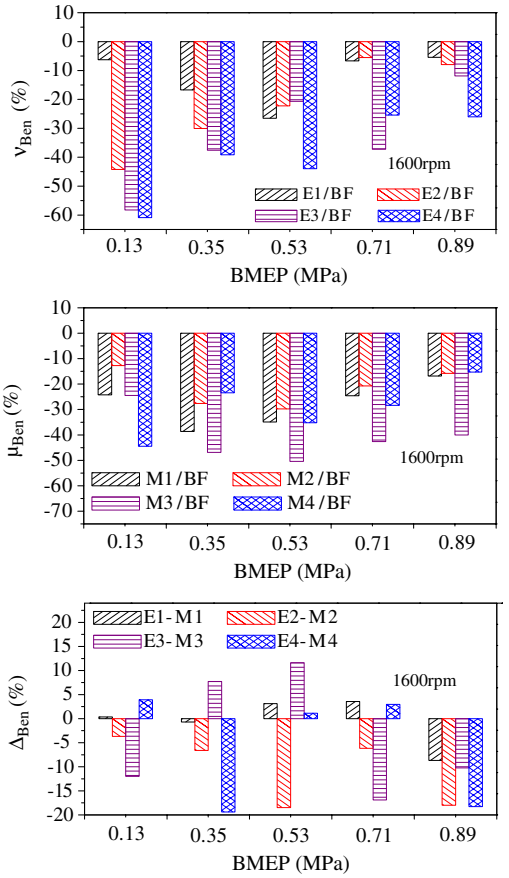

Fig. 10. Effects of the blended fuels on Benzene emission at 1600 rpm.

fuels were almost 100%; therefore, the catalyst had perfect oxidation effect on benzene. That was also true at the middle loading of 3400 rpm.

At, Δ_{Ben} was naught, while it gave priority to be positive at other operating conditions, and the maximum of Δ_{Ben} was up to 26.5%.

3.2.2. Formaldehyde emission

Engine-out formaldehyde emission was shown in Table 2. It is clear that lower formaldehyde emission can be obtained by adding EA into gasoline in the most cases, even under many operating conditions formaldehyde emission was not detected in the exhaust gases. However, MTBE increased the formaldehyde emission evidently. Therefore, the addition of EA had much better effect on formaldehyde engine-out emission than MTBE.

No tailpipe emission was found except few engine operating conditions, such as at the highest engine loading of each speed. In other words, the catalytic

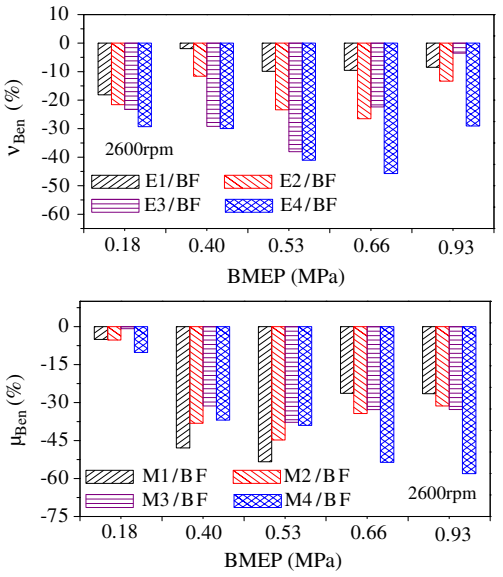

Fig. 11. Effects of the blended fuels on Benzene emission at 2600 rpm.

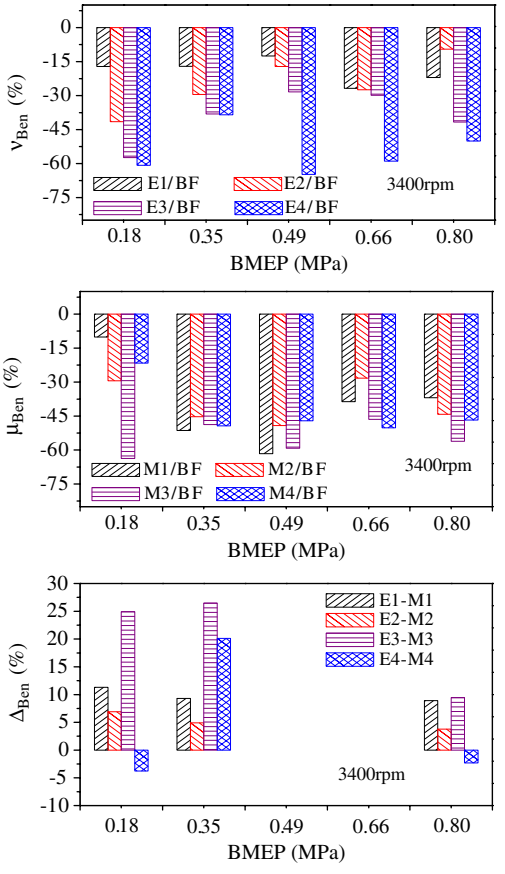

Fig. 12. Effects of the blended fuels on Benzene emission at 3400 rpm.

conversion of formaldehyde was almost complete for both EA and MTBE.

3.2.3. Acetaldehyde emission

The effects of the blended fuels on acetaldehyde emission at different conditions were shown in Figs. 13–15. At 1600 rpm, the parameters $v_{aldehyde}$ and $\mu_{aldehyde}$ were positive in all the operating conditions, which meant that compared with the emission of the base fuel, both the emissions of EA/BF blends and that of MTBE/BF blends increased (Fig. 13). It was obvious that $v_{aldehyde}$ increased with the EA content increasing, while for the group of MTBE blends, the maximum $\mu_{aldehyde}$ was gained when M3 was used. On the basis of the comparison between $v_{aldehyde}$ and $\mu_{aldehyde}$, it also can be observed that each additive had its strong point, and EA's effect on acetaldehyde emission was equal to MTBE's in total.

The conversion efficiency difference $-\Delta_{aldehyde}$ ranged from −45.4% to 40.7%, but there was no distinct correlation between the $\Delta_{aldehyde}$ and the composition of the fuels.

The result of 2600 rpm showed that the relationship, $v_{aldehyde} > \mu_{aldehyde} > 0$, was true in any operating condition, from which it can be observed that both EA and MTBE led to more acetaldehyde in the exhaust gas than the base fuel, and the increasing activity was in the order EA > MTBE. The result at high speed (3400 rpm) was in accordance with that at 2600 rpm (Fig. 15).

The conversion efficiency for acetaldehyde from the fuel containing EA was lower than that from the fuel containing MTBE as the $\Delta_{aldehyde}$ was negative in the most cases. Especially, $\Delta_{aldehyde}$ could reach to −77.5% when E1–M1 was compared (Fig. 14).

At 3400 rpm, the difference in the conversion efficiency $\Delta_{aldehyde}$ ranged from −80.6% to 37.2%. The conversion efficiency for the fuels contained EA was lower than that for the fuels contained MTBE because $\Delta_{aldehyde} < 0$ was tenable except for individual operating modes.

Some previous literatures reported that fuel ethanol increases acetaldehyde and MTBE has no effect, which are not in accordance with current results. There is no clear interpretation for the difference; the probable one is that for different test engines, the differences in controlling strategy, air/fuel equivalence ratio, combustion chamber's geometry, intake swirl ratio and chemical composition of the base fuel may affect the combustion reaction process and cause the different experimental results.

Table 2
The volume fraction of formaldehyde emission

Speed (rpm)	T (Nm)	Engine-out formaldehyde emission (ppm)								
		BF	M1	E1	M2	E2	M3	E3	M4	E4
1600	200	7.76	10.54	12.18	11.15	12.69	12.59	9.10	17.31	0
	160	2.25	1.81	2.01	3.76	1.50	9.10	0	12.69	0
	120	0.91	1.30	1.19	5.71	2.01	7.05	1.09	9.10	0
	80	1.79	2.53	2.63	3.97	4.58	8.07	3.45	11.87	2.76
	30	3.92	7.56	10.74	10.13	12.28	13.21	9.10	16.90	5.63
2600	210	4.65	3.35	0	5.61	0	7.25	0	9.00	1.19
	150	3.49	4.38	0	6.53	0	3.45	0	6.94	0.89
	120	0.65	2.12	0	5.09	0	5.92	0	7.87	0
	90	3.35	3.97	0.17	5.51	0	6.02	0	7.97	4.17
	40	6.16	4.58	0	7.97	0.06	10.95	0	11.67	0
3400	180	0.06	3.45	0	2.22	5.71	4.48	0	4.07	0
	150	0.99	1.19	0	2.94	0	3.55	0	5.20	0
	110	0.47	1.19	0.37	1.91	0	2.84	0	3.45	0
	80	1.67	1.40	0	2.73	0	3.14	0	3.86	0
	40	0.58	0.68	0	1.81	0	3.97	1.71	4.99	1.60

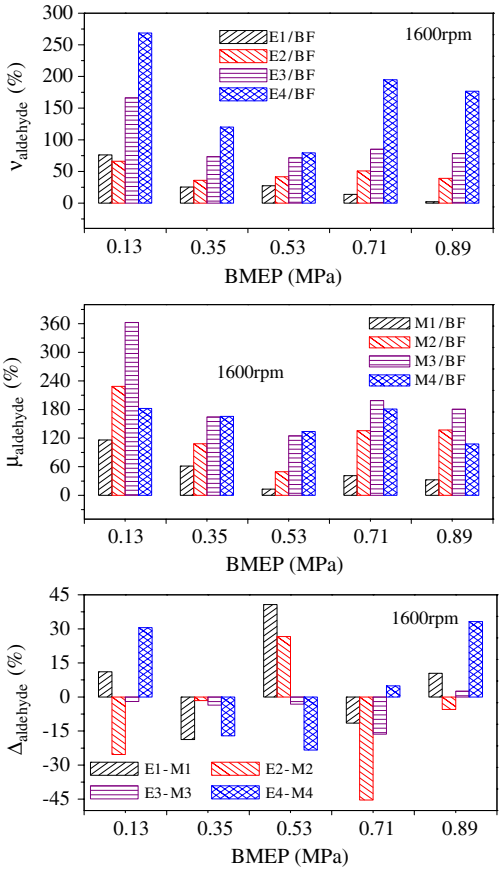

Fig. 13. Effects of the blended fuels on acetaldehyde emission at 1600 rpm.

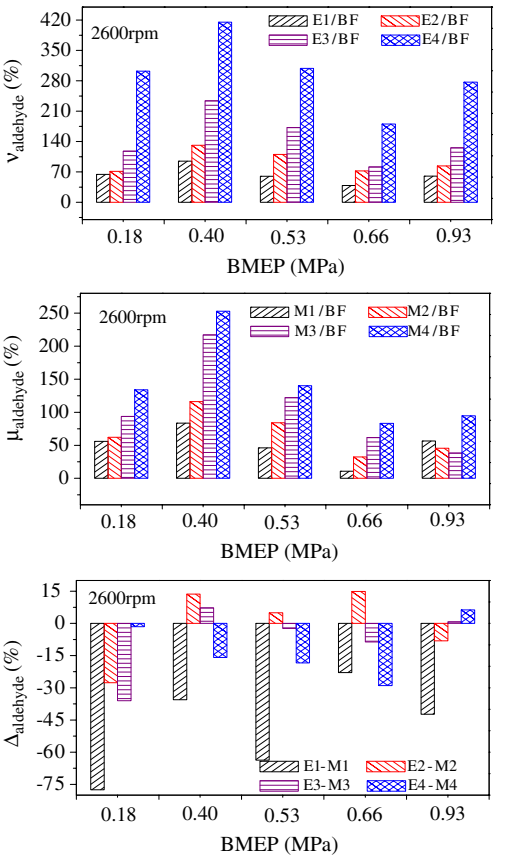

Fig. 14. Effects of the blended fuels on acetaldehyde emission at 2600 rpm.

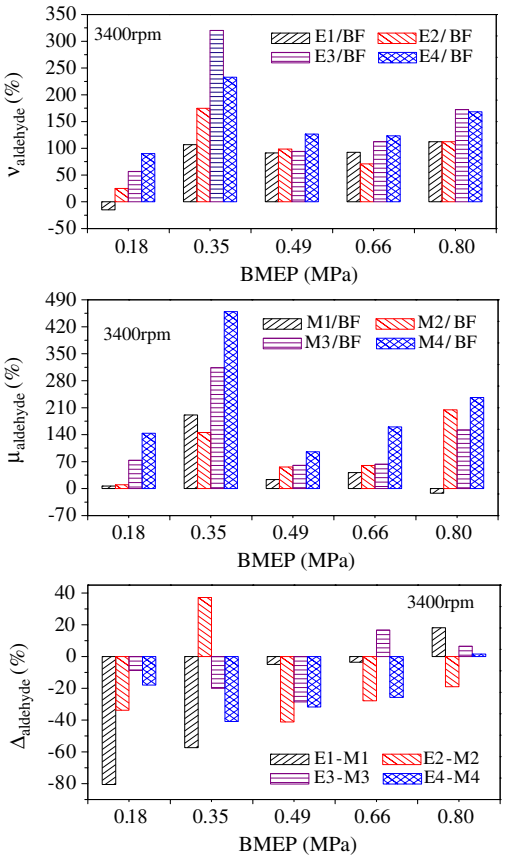

Fig. 15. Effects of the blended fuels on acetaldehyde emission at 3400 rpm.

3.2.4. EA and MTBE emissions

Both EA and MTBE were identified in the engine exhaust gases only when they were present in the fuel, respectively. As shown in Fig. 16, at the engine speed of 1600 rpm, it was noteworthy that engine-out EA emission at low or high loading was much more than the emission at the middle loading. At 2600 rpm, the EA emission was almost in accordance with the results at 1600 rpm, except for the emission from E4 (Fig. 17). At 3400 rpm, the most EA was emitted from the engine at the highest loading, and the lowest emission still obtained at the middle loadings (Fig. 18). Generally speaking, the unburned EA emission was increasing with the EA proportion in the blended fuels, which was induced by the incomplete combustion. The range of the engine-out EA emission was 1.92–29.52 ppm.

As shown in Figs. 19–21, at each speed, engine-out MTBE emission at low or high loading was much higher than that at the middle loading. The range of engine-out MTBE emission was 3.84–18.67 ppm.

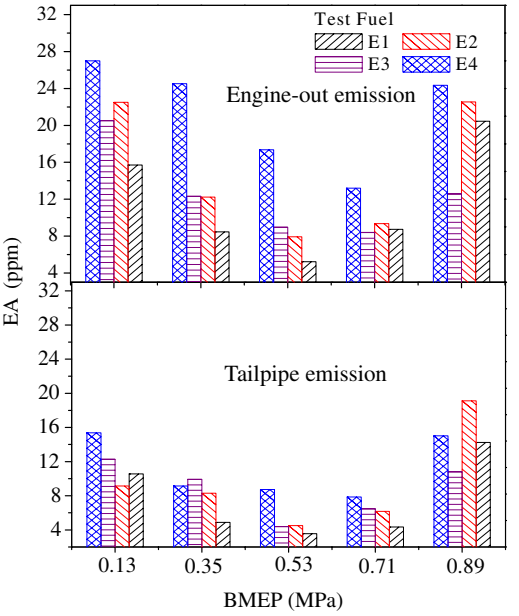

Fig. 16. EA emission at 1600 rpm.

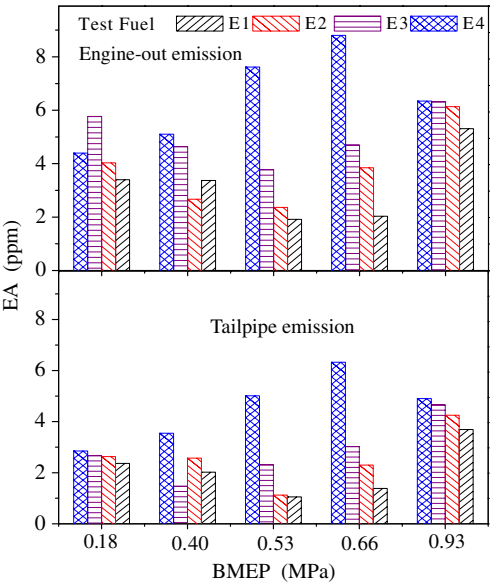

Fig. 17. EA emission at 2600 rpm.

The engine-out MTBE emission was lower than EA, since the average volume fractions of EA and MTBE were about 12.47 and 9.05 ppm, respectively.

It's observed that the catalytic conversion efficiencies of EA and MTBE were not very great by comparing the engine-out emissions with the tailpipe emissions. EA was more resistant to oxidation over the catalytic converter than MTBE

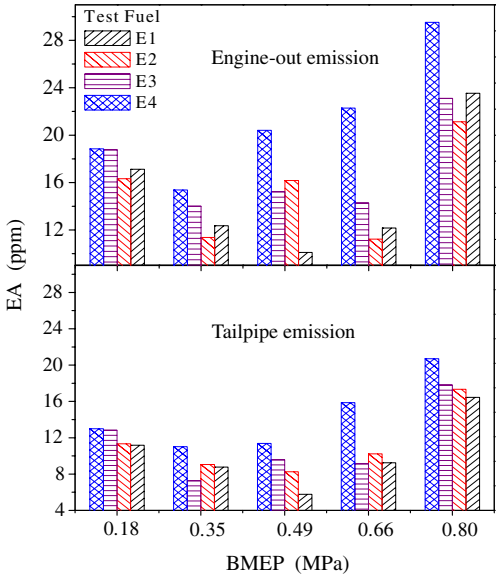

Fig. 18. EA emission at 3400 rpm.

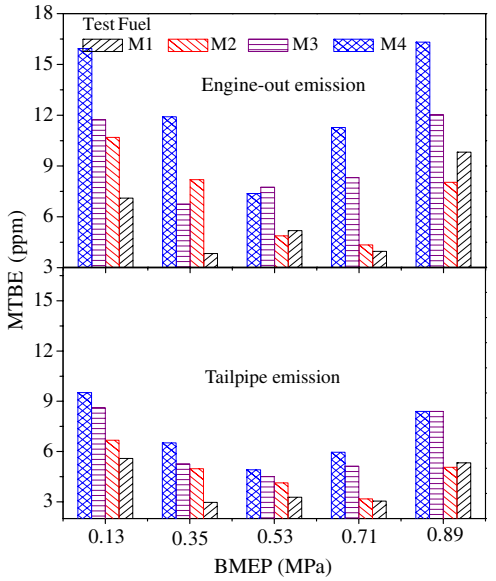

Fig. 19. MTBE emission at 1600 rpm.

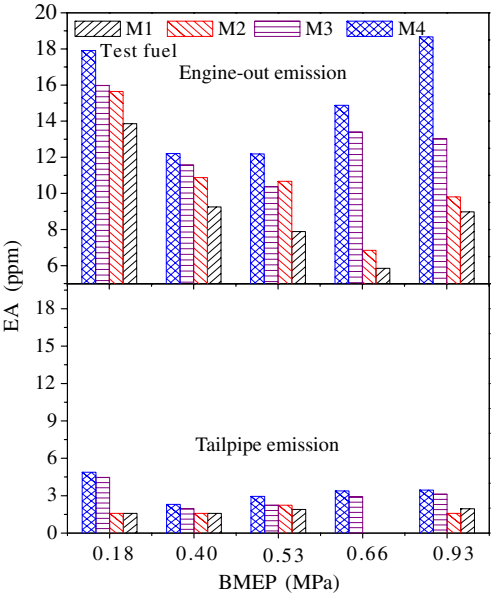

Fig. 20. MTBE emission at 2600 rpm.

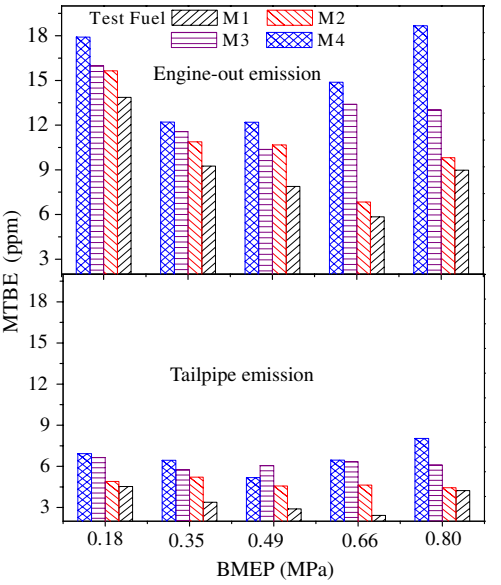

Fig. 21. MTBE emission at 3400 rpm.

as their average efficiencies were 34.79% and 49.53%, respectively.

4. Conclusions

From the discussions above, the main conclusions obtained are:

(a) EA has a better performance than MTBE on the regulated engine-out emissions as η_x for the regulated emissions is negative in the most cases, and it can be up to −59.3%.

(b) Comparison of the unregulated engine-out emissions shows that the effect of EA on benzene emission reduction is worse than that of MTBE because the absolute value of v_{Ben} was smaller than that of μ_{Ben} in the most cases. The engine-out formaldehyde emission concentration is in the order MTBE > BF > EA on

the whole. But the trend of the comparison of engine-out acetaldehyde emission depends much on the operating conditions especially the engine speed. Concretely, at low speed, EA has the same effect on engine-out acetaldehyde emission as MTBE, while at other speeds, EA blends give higher acetaldehyde emission concentrations than MTBE blends. However, both of the additives increase the engine-out acetaldehyde emission distinctly compared with that of the BF.

(c) Both EA and MTBE are identified in the engine exhaust gases only when they are present in the fuel respectively, and the content increases with added proportion.

(d) The additives of EA and MTBE have different effects on the catalytic conversion efficiency of the emissions.
The catalytic conversion efficiencies of the regulated emissions for the EA blends are lower than those for MTBE blends in general, and it is more obvious at the low and high engine speeds. The range of the difference in the regulated emissions is -57.3% to 45.7%.
There is little difference in formaldehyde's conversion efficiency due to the catalyst's full conversion activity, which is also true for benzene under several operating modes. However, the difference in acetaldehyde conversion efficiency is very distinct since Δ_{aldehyde} ranges from -80.6% to 40.7%, and $\Delta_{\text{aldehyde}}<0$ is tenable in general.

(e) The catalytic conversion efficiencies of EA and MTBE are not very great, and EA is more resistant to oxidation over the catalytic converter than MTBE.

On all aforementioned accounts, although EA and MTBE have both advantages and disadvantages in the unregulated emissions, the additive of EA has better effect than MTBE on the regulated emissions. Furthermore, considering the pollution of MTBE to aquatic environment and drinking water, EA is better than MTBE for using as a gasoline oxygenate additive.

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