

Carbonyls emission from ethanol-blended gasoline and biodiesel-ethanol-diesel used in engines

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Abstract

Detailed carbonyls emissions from ethanol-blended gasoline (containing 10% v/v, ethanol, E-10) and biodiesel-ethanol-diesel (BE-diesel) were carefully investigated on an EQ491i gasoline engine equipped with a three-way-catalyst (TWC) and a Commins-4B diesel engine. In engine-out emissions for the gasoline engine, total carbonyls from E-10 varied in the range of 66.7–99.4 mg kW⁻¹ h⁻¹, which was 3.1–8.2% less than those from fossil gasoline (E-0). In tailpipe emissions, total carbonyls from E-10 varied in the range of 9.2–20.7 mg kW⁻¹ h⁻¹, which were 3.0–61.7% higher than those from E-0. The total carbonyls emissions from BE-diesel were 1–22% higher than those from diesel at different engine operating conditions. Compared with fossil fuels, E-10 can slightly reduce CO emission, and BE-diesel can substantially decrease PM emission, while both alternative fuels increased slightly NO_x emission.

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1. Introduction

Carbonyl compounds are an important class of vehicular total hydrocarbons (TCH) emission. In urban, atmospheric carbonyls are mainly emitted from vehicular exhaust (Grosjean et al., 2001). They play a critical role on the tropospheric chemistry and are important precursors to free radicals, ozone, and peroxyacylnitrates (Carter, 1995; Gaffney et al., 1997). Some carbonyls are toxic, mutagenic, and even carcinogenic to human body (Carlier et al.,

1986). Therefore, carbonyls emission from vehicular exhaust is of special importance to study, especially from the vehicles fueled by oxygenated fuels (Cardone et al., 2002; Magnusson et al., 2002; Pouloupoulos et al., 2001; Sharp et al., 2000).

Two oxygenated biofuels (biodiesel and ethanol) have received intensive attention as potential alternative fuels for vehicle engines due to their renewable property and reduction of fossil CO₂ discharge which most probably contributes to the global climate changes. In recent years, both biodiesel and ethanol-blended gasoline (E-gasoline) are being used in fleet vehicles in China. In nine provinces of China, all gasoline was sold with an addition of 10% (v/v) ethanol. The primary motive for this effort is to

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minimize the dependence on imported petroleum sources. Another reason is that biofuels can substantially reduce CO and particulate matter (PM) emissions (Hansen et al., 2005). Ethanol-blended gasoline (E-gasoline) was widely used as alternative fuel in some countries such as Brazil, USA, European Union, Canada and Thailand (Magnusson et al., 2002; Leonga et al., 2002). Biodiesel-ethanol-diesel (BE-diesel) is a new form of biofuel blend from renewable material that has energy values comparable to those of fossil fuels and has superior lubricity and environmentally friendly characteristics (McCormick and Parish, 2001). In recent years, the influence of biofuels on exhaust emissions has attracted many researchers' interest. For E-gasoline, there are several studies concerning about the regulated emissions and some unregulated emissions including carbonyls (Pouloupoulos et al., 2001; Song et al., 2006). However, those studies concerning carbonyls are only limited to formaldehyde and acetaldehyde. More detailed carbonyls emission studies have been rarely conducted (Gaffney et al., 1997; Magnusson et al., 2002; Zervas et al., 2002; Caplain et al., 2006). For BE-diesel, a few studies used different blends of biodiesel, ethanol and diesel, respectively in a diesel engine to investigate the emissions of regulated pollutants (Ali et al., 1995; Shi et al., 2005). It was found that THC, PM and CO were substantially reduced from BE-diesel in comparison with fossil diesel. In our previous study (Pang et al., 2006), the carbonyls emissions from BE-diesel were studied but only mass concentrations were reported. Investigating specific emission factors (the mass emission per kW hour, $\text{g kW}^{-1} \text{h}^{-1}$) of carbonyls are of importance to scientifically evaluate the environmental influence of the oxygenated fuels used in China and also can provide basic data for those model calculations which realize to the contribution of carbonyls from oxygenated fuels to atmospheric pollution on a large scale.

The target of this study is to investigate the specific emission factors of carbonyls from a gasoline engine and a diesel engine fueled by E-gasoline, BE-diesel and fossil fuels under different engine operating conditions.

2. Experimental

2.1. Test fuels, engine and experimental procedure

Four test fuels were used in this study. The first was commercial Chinese in-use gasoline fuel (RON: 93), and is marked as E-0 hereinafter, which was

used as a reference fuel and a base fuel for the preparation of ethanol-blended gasoline. The second was ethanol-blended gasoline containing ethanol 10% (v/v), and is marked as E-10 hereinafter. The third was commercial Chinese in-use diesel fuel, which was used as a reference fuel and a base fuel for preparation of BE-diesel blends. The fourth was BE-diesel mixture containing 5% ethanol, 20% biodiesel, and 75% diesel (v/v), respectively. The properties of the four fuels are presented in Table 1.

All tests were performed on four-cylinder electronic fuel injection gasoline engine (EQ491i) and a Commins-4B diesel engine, respectively. The parameters of the two engines are listed in Table 2. The gasoline engine was equipped with a three-way-catalyst (TWC, Delphi35222), while the diesel engine had no oxidation catalyst. Two types of engine operating conditions were conducted in this study: constant load/varying speed tests (1200, 1600, 2000, 2400 and 2800 rpm at 100% load, respectively, for diesel engine) and constant speed/varying load tests (3, 30, 50, 90, 130, and 161 Nm at 2800 rpm, respectively, for gasoline engine, 60, 110, 160, 180, and 220 Nm at 1800 rpm, respectively, for diesel engine). Prior to running each experiment, the engine was fully warmed.

Table 1
Properties of E-10 gasoline, E-0 gasoline, diesel and BE-diesel

| Properties | E-10 | E-0 | Diesel | BE-diesel |
|--|------|------|--------|-----------|
| Density (g ml^{-1}) at 20 °C | 0.74 | 0.73 | 0.84 | 0.845 |
| Oxygen (wt%) | 3.5 | n/a | n/a | 3.9 |
| Carbonate (wt%) | 83.4 | 86.4 | 87 | 83 |
| Hydrogen (wt%) | 13.1 | 13.6 | 13 | 12.8 |
| Cetane number | 95 | 93 | – | – |
| Octane number | – | – | 46 | 45 |
| Gross heat content (MJ kg^{-1}) | 42.2 | 46 | 42.5 | 40.9 |

Table 2
Engine specifications of tested engines

| Parameter | Gasoline engine | Diesel engine |
|---|-----------------|---------------|
| Cylinder number | 4 | 4 |
| Bore (mm) × stroke (mm) | 91 × 77 | 102 × 120 |
| Displacement (L) | 1.993 | 3.92 |
| Compression ratio | 9.5:1 | 17.5:1 |
| Rated power (kW)/speed (r min^{-1}) | 76/5200 | 76/2800 |
| Maximum torque (Nm)/speed (r min^{-1}) | 155/4000 | 245/1600 |

2.2. Sampling and analysis of regulated emissions and carbonyls

The measurements of regulated pollutants including NO_x, CO, CO₂ and THC, were achieved at an AVL CEB-11 exhaust gas analyzer on-line by means of usual analytical techniques (nondispersived infrared instrument for CO and CO₂, chemiluminescence for NO_x, and flame ionization detection for TCH, respectively) (Shi et al., 2005). At each operating condition, the sampling duration was 10 min. Total PM emission was only measured from diesel engine by an AVL PM analyzer and collected on PTFE coated glass filter (AVL, USA). The filter was conditioned at 25 °C and 50% humidity, and it was weighed before and after the sampling procedure.

For gasoline engine, carbonyls emitted from engine-out and tailpipe were collected upstream and downstream the TWC through two 1 m long Teflon tubes (i.d. 6 mm) by two 2,4-dinitrophenylhydrazine (DNPH)-coated silica gel cartridges (Waters, USA) in series, respectively. For diesel engine, the sampling site was about 1 m away from the outlet of exhaust emission of the engine. The exhaust gas temperatures at the sampling sites were usually <90 °C, which were lower than the melting points of DNPH and DNPH hydrozones (>199 °C). The plastic material of the cartridge was found to be nearly melted when sampling time was set to >4 min. However, if sampling time was <3 min, the cartridges can be stable enough for collecting the hot gases samples. The collection efficiencies (no breakthrough) of the cartridges and the repeatability (the relative standard deviation) for the parallel samples as mentioned below imply the cartridges used in this study are stable for collecting the air samples under the case of hot gases. Condensed water was observed in the Teflon tube during sampling, which could result in somewhat loss of the carbonyls due to adsorption, thus, our results could be considered as the lower limit. The gas flow rate was regulated at 0.81 min⁻¹ and sampling time was set to be 3 min. After sampling, the cartridges were transported to the analysis laboratory in a temperature controlled container at 0 °C and were stored at -4 °C before analysis.

Carbonyls were analyzed as their DNPH derivatives by a high-performance liquid chromatography (HPLC) system (Waters 2659 Separations Module) with a photodiode array detector at

360 nm. A standard solution (Supelco, USA) containing 15 aldehydes was used for the chromatograph calibration and for the identification of each aldehyde. In addition, Alliance 2695 HPLC/quatrope-time of flight mass spectrometer (Q-TOF MS) (Waters) with atmospheric pressure chemical ionization (APCI) in negative model was used to qualify the different carbonyl-DNPHs by their quasi-molecular ions. The parameters of MS were as the following: current of corona, 5.0 μA; voltage of sample cone, 20.0 V; voltage of extraction cone, 3.0 V; APCI probe temperature, 400 °C; source temperature, 105 °C; range of *m/z*, 100.0–500.0.

2.3. Repeatability

During experiments, five parallel samples from each engine (under the same operating condition: 30 Nm/2800 rpm for gasoline engine and 60 Nm/1800 rpm for diesel engine) were collected, respectively. The relative standard deviations of the concentration of the investigated carbonyl compounds were found to be <14% for E-0 and E-10 and below 8% for diesel and BE-diesel (Table 3). No breakthrough was found under our experimental condition for all samples collection.

Table 3

Relative standard deviations (%) of the carbonyl compounds in five parallel samples, which were sampled under the same operating conditions^a of the engines with fossil and oxygenated fuels

| Fuels | E-0 | E-10 | Diesel | BE-diesel |
|------------------------|------|------|--------|-----------|
| Formaldehyde | 11.2 | 10.6 | 4.5 | 4.1 |
| Acetaldehyde | 8.5 | 6.8 | 5.6 | 4.8 |
| Acrolein | 10.5 | 11.3 | 4.2 | 4.7 |
| Acetone | 7.6 | 5.8 | 4.8 | 5.3 |
| Propionaldehyde | 12.3 | 11.3 | 4.1 | 5.4 |
| Crotonaldehyde | 11.1 | 10.5 | 5.7 | 5.1 |
| Methylacrolein | 13.5 | 11.5 | 5.4 | 5.2 |
| Butyraldehyde | 8.9 | 9.6 | 5.8 | 5.5 |
| Benzaldehyde | 11.6 | 12.5 | 4.6 | 5.7 |
| <i>o</i> -Tolualdehyde | 12.3 | 11.5 | 6.8 | 5.2 |
| <i>m</i> -Tolualdehyde | 11.7 | 12.5 | 6.4 | 5.6 |
| Valeraldehyde | 12.3 | 10.5 | 6.3 | 6.2 |
| Hexaldehyde | 11.3 | 9.8 | 7.2 | 6.7 |
| Dimethylbenzaldehyde | 12.5 | 13.2 | 7.3 | 6.5 |

^a30 Nm/2800 rpm for gasoline engine and 60 Nm/1800 rpm for diesel engine.

3. Results and discussion

3.1. Regulated emissions and technique parameters of gasoline engine

The regulated emissions in engine-out and tailpipe emissions and some technique parameters of the engines are shown in Figs. 1 and 2, respectively. It was found that CO emissions were slightly reduced (1.5–6%) from E-10 in comparison with E-0 gasoline in engine-out emission. The oxygenated agents (ethanol) blended with gasoline can effectively deliver oxygen to the pyrolysis zone of the burning gasoline spray resulting in less CO generation (McCormick and Parish, 2001; Wang et al., 2000). In engine-out exhaust, THC emissions from E-10 were lower than that of E-0 at the torque of 3 Nm, but higher than those from E-0 by increments of 2–17% under other operating conditions.

Meanwhile, the specific fuel consumption (SFC; $\text{g kW}^{-1} \text{h}^{-1}$) of E-10 was lower than E-0 by decrease of 2.5% at torque of 3 Nm, but were higher than E-0 by the increment of 1.8–5.0% (Fig. 2). It could be concluded that the different SFC of E-10 and E-0 may be responsible for the difference of THC emissions between E-10 and E-0. Some studies show that the use of ethanol can reduce THC emissions (Hsieh et al., 2002; Al-Hasan, 2003), but the increase of THC emissions by using ethanol have also been reported (Poulopoulos et al., 2001; Magnusson et al., 2002). The reason for the inconsistent results was considered as the effects of oxygenates which vary a lot depending on both fuel and engine type (Magnusson et al., 2002). In engine-out exhaust, THC and CO emissions at different load levels showed similar tendency with their maxima at low load (3 Nm) and minima at torque of 130 Nm for both E-0 and E-10. The THC and CO

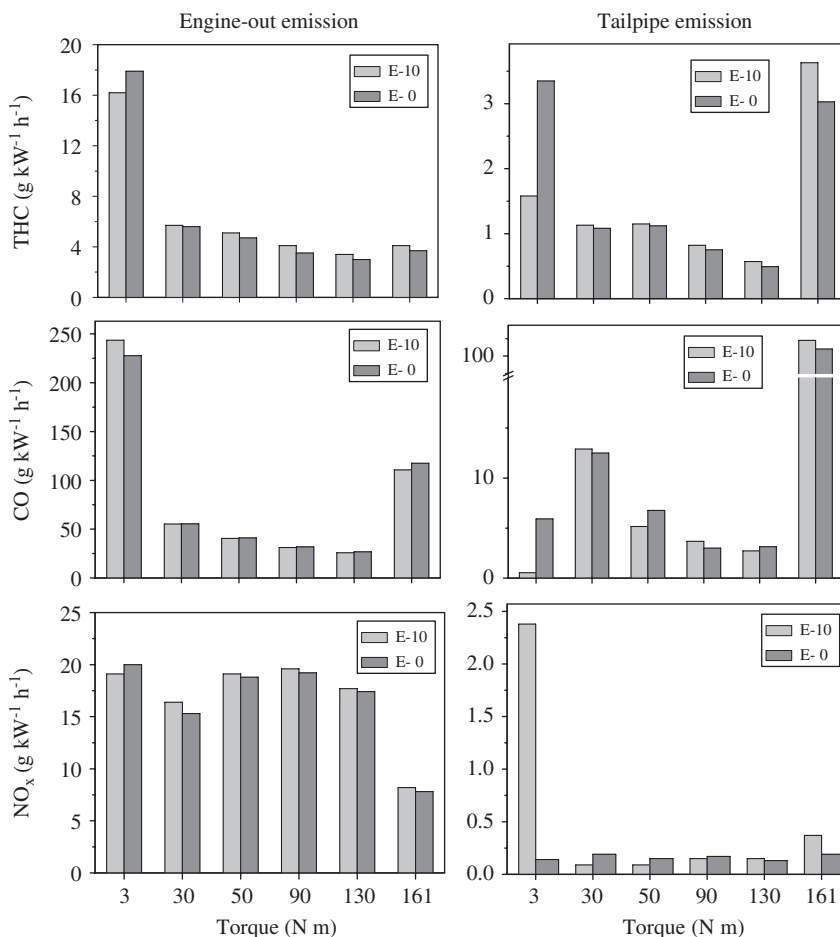


Fig. 1. Regulated emissions from engine-out emission and tailpipe emission of gasoline engine at different torques (load levels) under stable speed (2800 rpm).

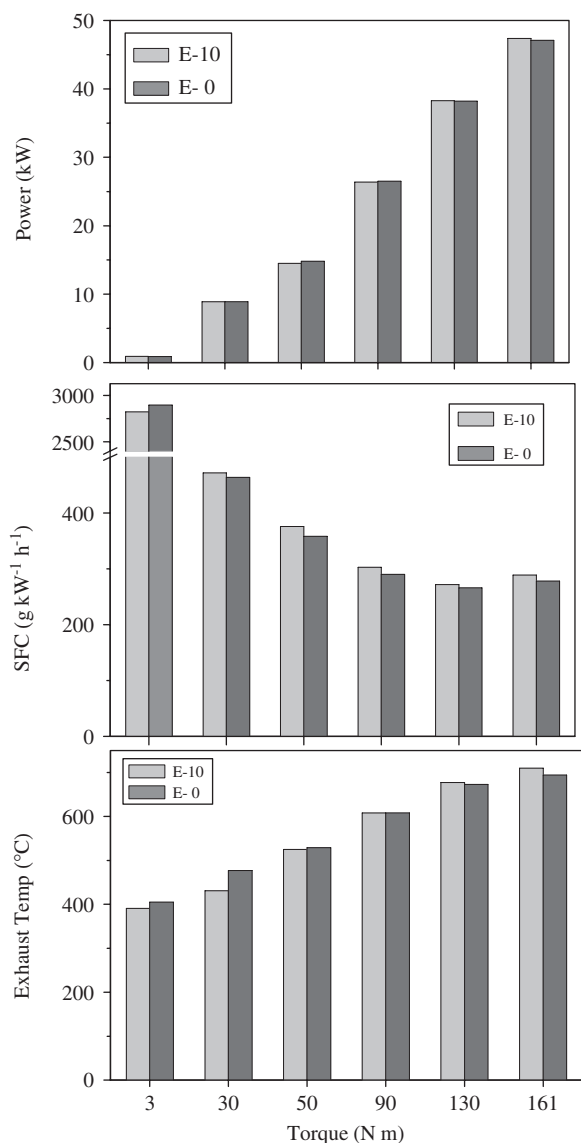


Fig. 2. Technique parameters of gasoline engine at different torques (load levels) under stable speed (2800 rpm).

emissions were found to be strongly correlated with fuel consumption (Magnusson et al., 2002). As for NO_x and CO_2 emissions, there were no obviously difference between E-0 and E-10. Compared with fossil gasoline, lower engine power, lower engine-out exhaust temperature and higher SFC for E-10 were due to its lower heating value (Cardone et al., 2002).

The detailed regulated emissions from diesel engine were carefully discussed in our previous study (Pang et al., 2006). In short, the PM and THC emissions were significantly reduced by 22–40% and

8.8–10.3% for BE-diesel in comparison with diesel. Slightly higher NO_x emission was also observed from BE-diesel than the fossil diesel. There were no substantial differences between BE-diesel and diesel for CO and CO_2 emissions.

3.2. Carbonyls emissions from ethanol-gasoline in engine-out and tailpipe exhausts

The identified carbonyl compounds and their concentrations in the engine-out and tailpipe exhausts at different load levels were shown in Figs. 3 and 4, respectively. Fourteen carbonyls were identified in engine-out exhaust while only 11 species were found in tailpipe emission due to high efficient catalytic conversion of acrolein, hexaldehyde and dimethylbenzaldehyde by the TWC.

In engine-out emission, total carbonyls emission from E-10 and E-0 varied in the range of 66.7–512.5 and 71.3–530.3 $\text{mg kW}^{-1} \text{h}^{-1}$, respectively (Figs. 3 and 4). The emission level of carbonyls except for acetaldehyde (no data of acetaldehyde are available in the study of Caplain et al., 2006) in this study was comparable with that of European gasoline cars (Caplain et al., 2006), but was substantially lower than that of a two-stroke engine (Magnusson et al., 2002), which had lower combusting efficiency compared with four-stroke engine used in this study. The phenomena of formaldehyde dominated for E-0 gasoline and acetaldehyde dominated for ethanol-blended gasoline obtained by this study agree with above two studies. The total carbonyls obtained by this study accounted for 1.7–3.2% and 1.8–2.95% of the THC for E-10 and E-0 gasoline, respectively, which are in accordant with the reported values by Zervas et al. (2002). Formaldehyde, acetaldehyde, acrolein, aromatic aldehydes (benzaldehyde and tolualdehyde) were found to be the dominant components which accounted for 72.2–82.2% and 75.9–85.1% of total carbonyls emission for E-10 and E-0 gasoline (Figs. 5 and 6), respectively. This result was in agreement with other gasoline engine studies (Magnusson et al., 2002; McGinty and Dent, 1995). As for formaldehyde, acrolein, acetone, butyraldehyde and aromatic aldehydes, the emissions from E-10 gasoline decreased about 5.1–26%, 2–22%, 10–100%, 4.5–28.5%, 6.9–11.2%, respectively compared with those from E-0. Only with the exception for aromatic aldehydes, the decreases of other aldehydes from E-10 gasoline largely exceeded the repeatability (<14%, Table 3) under our experimental condition. It was reported that the

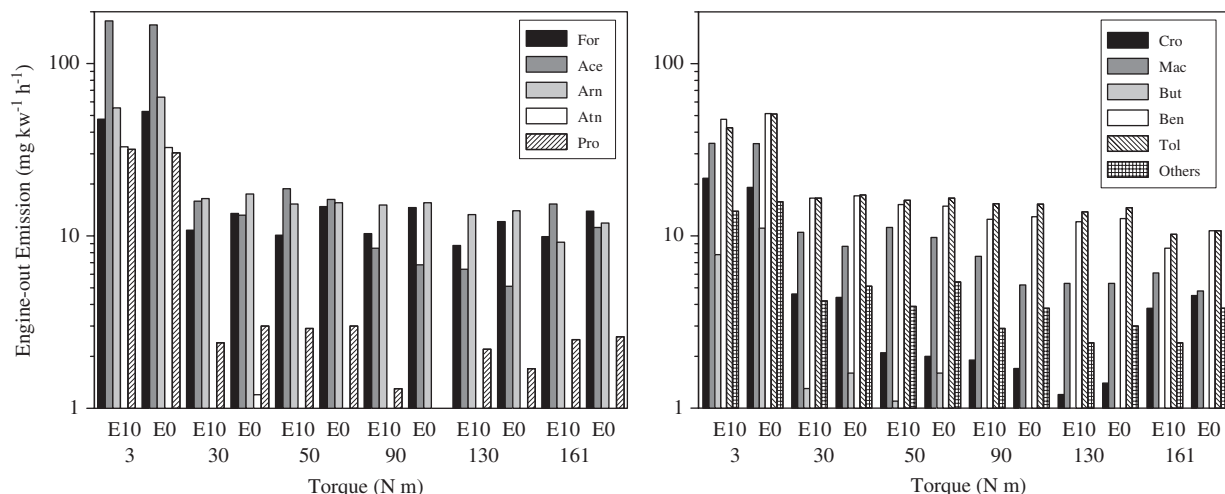


Fig. 3. Carbonyl compounds from engine-out emission at six torques (load levels) under stable speed (2800 rpm) from E-10 and E-0 gasoline. For (formaldehyde), Ace (acetaldehyde), Arn (acrolein), Atn (acetone), Pro (propionaldehyde), Cro (crotonaldehyde), Mac (methylacrolein), But (butyraldehyde), Ben (benzaldehyde), Tol (*m*-tolualdehyde, *p*-tolualdehyde), others include valdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde).

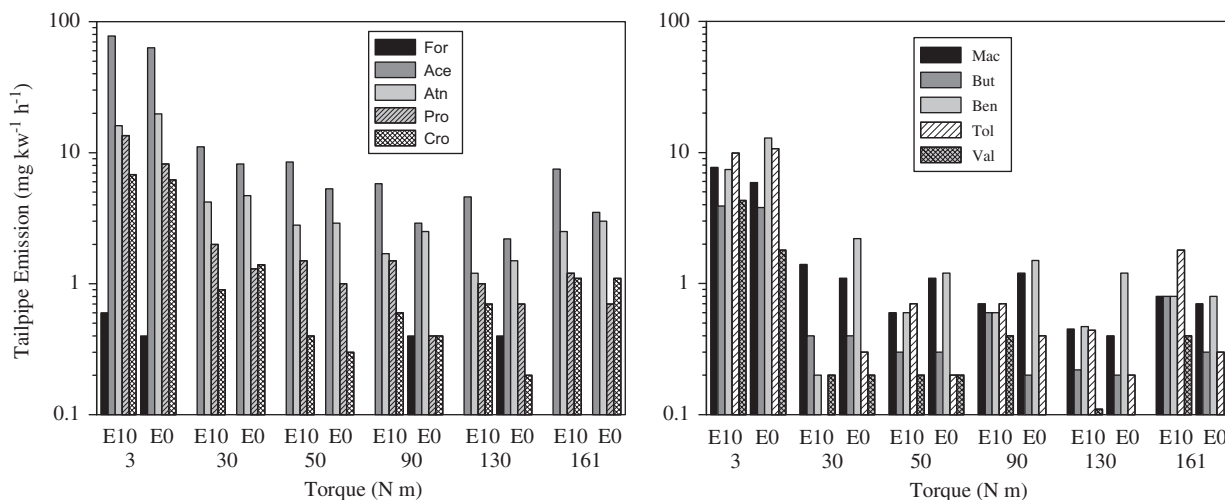


Fig. 4. Carbonyl compounds from tailpipe emission at six load levels under stable speed (2800 rpm) from E-10 and E-0 gasoline.

fuel composition can significantly influence the emissions of carbonyl compounds (Kaiser et al., 1991; Zervas et al., 2002). The decreases of aldehydes except for acetaldehyde from E-10 gasoline compared with E-0 might be due to the different fuel composition. For example, formaldehyde in vehicle exhaust mainly comes from the incomplete combustion of saturated aliphatic hydrocarbons which account for larger percentage in E-0 than E-10 (Magnusson et al., 2002). In addition, the ethanol blending could slightly restrain the oxidation of acrolein, acetone, butyraldehyde precursors (Zervas et al., 2002). The acetaldehyde emissions

from E-10 were significantly higher than those from E-0 gasoline with increments of 5.4–36% (Figs. 3 and 4). Ethanol added into gasoline is an important precursor of acetaldehyde and results in higher acetaldehyde emission (Pouloupoulos et al., 2001; Magnusson et al., 2002).

Compared with those in the engine-out emissions, the total carbonyls emissions were in the ranges of 9.2–147.2 and 7.1–133 mg kW⁻¹ h⁻¹, with decreases of 71–86% and 73–89% for E-10 and E-0, respectively. The emissions of formaldehyde, acrolein, hexaldehyde and dimethylbenzaldehyde in the tailpipe exhaust from both E-10 and E-0 were

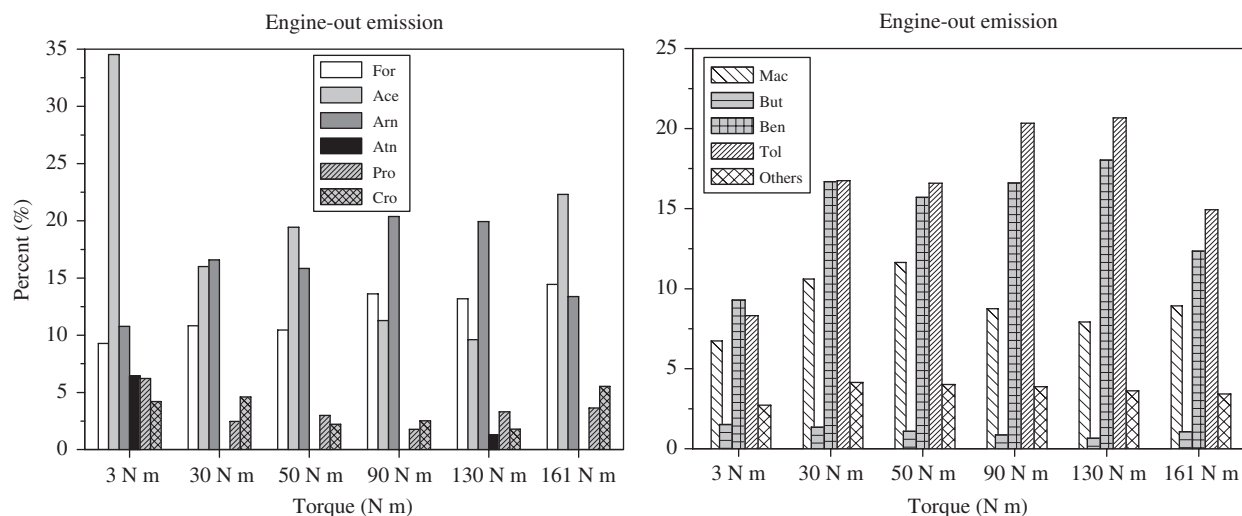


Fig. 5. Percentage of carbonyl compounds in engine-out emission from E-10 gasoline at six load levels under stable speed (2800 rpm). Others include valdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde.

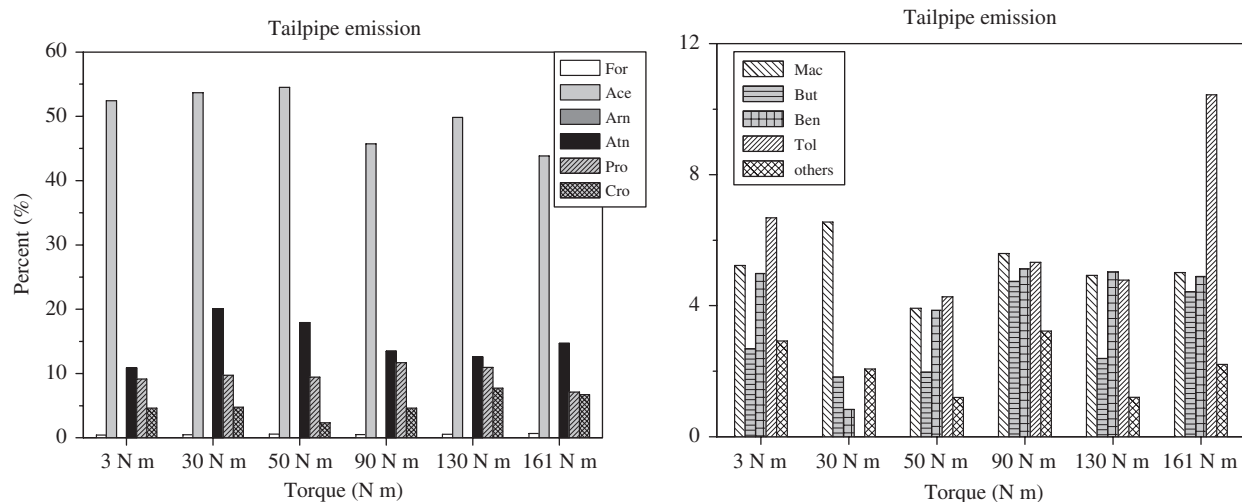


Fig. 6. Percentage of carbonyl compounds in tailpipe emissions from E-10 gasoline at six load levels under stable speed (2800 rpm). Others include valdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde.

extremely low (their concentrations were lower than the detection limits of our system) with decreases of $\sim 100\%$, while those of acetaldehyde, propionaldehyde only decreased 30–56% and 15–57% for E-10, and 37–61% and 56–73% for E-0, respectively. The reason for this phenomenon may be that the precursors of the two carbonyls in engine-out emission can be further oxidized to acetaldehyde and propionaldehyde by the TWC (Poulopoulos et al., 2001; Zervas et al., 2002). It should be noticed that acetone emission in tailpipe exhaust did not decrease but increase to 1.2–4.8 and 1.5–4.7 mg

$\text{kW}^{-1} \text{h}^{-1}$ from 0–0.8 to 0–1.2 $\text{mg kW}^{-1} \text{h}^{-1}$ with increases of more than 10% for E-10 and E-0 under torques other than 3 Nm torque, indicating that TWC can enhance the oxidation of acetone precursors under those operating conditions. Since each carbonyl emission varied at different extent after passing through TWC, the proportion of each component to the total carbonyls varied correspondingly in tailpipe exhaust. As Figs. 5 and 6 show, the proportions of acetaldehyde and acetone to the total carbonyls increased to 43.8–54.5% and 10.8–20.1% in tailpipe emission from 9.6–34.5% to

0–1.2% in engine-out emission for E-10. The similar phenomenon also occurred in tailpipe emission for E-0 gasoline.

3.3. Influence of load level on carbonyls emission from E-gasoline

As shown in Figs. 3 and 4, total carbonyls from the engine-out emissions for the two fuels both exhibited their maxima (512 and 531 $\text{mg kW}^{-1} \text{h}^{-1}$ for E-10 and E-0, respectively) at the low load (3 Nm), which were extremely higher (nearly five times higher) than those of other loads. At 3 Nm load, the operating condition of the engine is almost identical to the idle (no-load) condition, high excess fuel incompletely combustion will happen under this condition with low cylinder temperature (Fig. 2). The less efficient combustion of fuel resulted in significantly high carbonyls and other pollutants emissions. At other loads, the carbonyls emissions varied in the range of 70–110 $\text{mg kW}^{-1} \text{h}^{-1}$ and displayed their minima at the middle load (130 Nm), indicating that the fuel combust completely and exhaust emission was reduced extremely at 130 Nm load level. It was reported that the load level (air/fuel ratio) of engine could significantly influence carbonyls emission (Magnusson et al., 2002). The air/fuel ratio at middle load (130 Nm) may be the optimal ratio for the fuel combustion. At high load (161 Nm), incomplete combustion would still happen due to deficient air at high air/fuel ratio despite high cylinder temperature, which led to high carbonyls emissions. The same tendency of total

carbonyls emission and load level was also found in tailpipe emission. Compared with those in engine-out exhaust, the carbonyls emissions in tailpipe exhaust were much lower due to the conversion of TWC.

It was also found that the conversion efficiency (TWC) of total carbonyls had a positive correlation with load level. The conversion efficiency of total carbonyls increased from 71% to 86% for E-10 and from 74% to 90% for E-0 when load level increased from 3 to 160 Nm. This phenomenon may be caused by the higher engine-out exhaust temperature with higher load level (Fig. 2), which is in favor of conversion efficiency of TWC.

3.4. Comparison of carbonyls emissions between BE-diesel and diesel

Thirteen carbonyls were identified and quantified in diesel exhaust. The emissions of those carbonyls in the exhaust at different engine speeds and load levels were shown in Figs. 7 and 8. The total carbonyls emissions from BE-diesel (245–837 $\text{mg kW}^{-1} \text{h}^{-1}$) were higher than those from diesel (223–642 $\text{mg kW}^{-1} \text{h}^{-1}$) with increments varying from 1% to 22% depending on the engine operating conditions. The higher emission of carbonyls from BE-diesel may be attributed to the ethanol and oxygenated ester group present in the BE-diesel. This result is in agreement with those of the previous studies (Cardone et al., 2002; Gorse et al., 1991; Reuter et al., 1992).

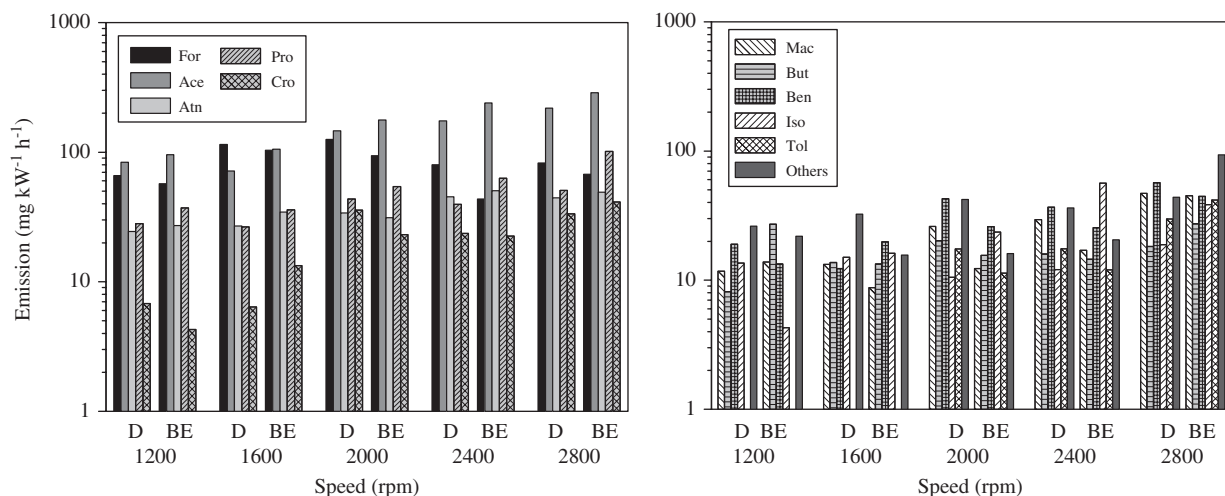


Fig. 7. Carbonyl compounds emission under different speeds at full load from diesel and BE-diesel; D: diesel and BE: BE-diesel. Others include valdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde.

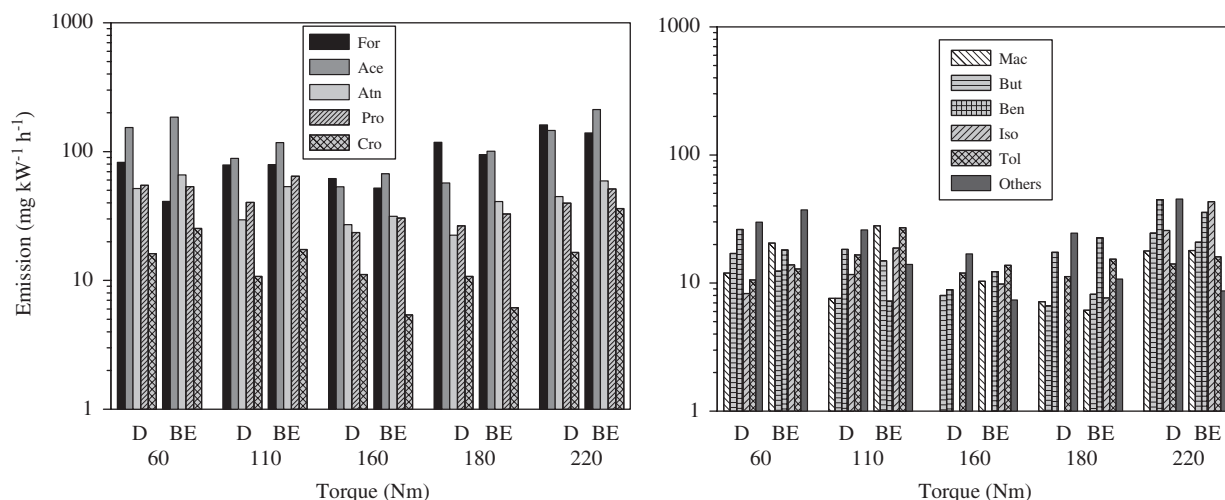


Fig. 8. Carbonyl compounds emission under different loads at stable speed from diesel and BE-diesel; D: diesel and BE: BE-diesel. Others include valdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde.

Acetaldehyde was found to be the most abundant component in total carbonyls from BE-diesel with the emissions of $67.3\text{--}287\text{ mg kW}^{-1}\text{ h}^{-1}$ and accounted for 28–38% of total carbonyls emissions, while formaldehyde was the dominant component from diesel with the emissions of $62\text{--}161\text{ mg kW}^{-1}\text{ h}^{-1}$ and accounted for 13–39% of total carbonyls emissions. Compared with the carbonyls from diesel, acetaldehyde, acetone, and propionaldehyde emissions from BE-diesel were significantly higher by increments of 12–69, 3–34, and 7–24 $\text{mg kW}^{-1}\text{ h}^{-1}$ in emission factor and 20–78%, 5–85% and 13–88% in percentage, respectively. Ethanol and mono alkyl ester from biodiesel in BE-diesel may be the precursors of those carbonyls and increase their emissions. As for formaldehyde, benzaldehyde, 2,5-dimethylbenzaldehyde, *m*-, *p*-tolualdehyde, their emissions from BE-diesel were less than those from diesel. Formaldehyde and aromatic aldehydes in vehicle exhaust mainly comes from the incomplete combustion of saturated aliphatic hydrocarbons and aromatic hydrocarbons (Magnusson et al., 2002). Lower percent of saturated aliphatic and aromatic hydrocarbons in BE-diesel (no aromatic hydrocarbons in biodiesel) may be responsible for their lower emissions. For other carbonyls, there were no obvious differences in their emissions from BE-diesel and fossil diesel.

3.5. Effects of engine speed and load level on carbonyls emission from BE-diesel

As Fig. 8 shows, a positive correlation was found between total carbonyls emission and engine speed.

The increment of total carbonyls emission may be ascribed to the higher SFC with the higher engine speed (Pang et al., 2006).

The total carbonyls emissions from BE-diesel decreased from $487\text{ mg kW}^{-1}\text{ h}^{-1}$ at the low load (60 Nm) to its minimum of $245\text{ mg kW}^{-1}\text{ h}^{-1}$ at the middle load level (160 Nm) and then increased to $640\text{ mg kW}^{-1}\text{ h}^{-1}$ at the full load (220 Nm). The same trend was also found in carbonyls emissions at different load levels for diesel. As mentioned above, low efficient combustion at low load would happen due to the high excess fuel and low cylinder temperature. On the other hand, at high load, incomplete combustion would also happen due to low cylinder temperature (Cardone et al., 2002). High carbonyls emission would happen under these low efficient combustion conditions.

4. Conclusions

Detailed emissions factors of carbonyls from ethanol-blended gasoline, biodiesel-ethanol-diesel and fossil fuels were carefully investigated in present study. Although substantial reduction of PM for BE-diesel and CO for E-gasoline were achieved, the significant increment of carbonyls emission (3.0–61.7% and 1–22% for E-gasoline and BE-diesel, respectively) should arouse public attention because of their potential healthy and environmental effect.

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