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Key words: air toxics; organic analysis; emissions; characterization.

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Abstract

The effect of ethanol-gasoline blends on organic air toxic emissions was investigated in a four-stroke carburetor motorcycle without a catalytic converter. An inhalation toxicity-based emission ranking for the toxics from each test fuel was also conducted. Four blends, containing 3, 10, 15, and 20 % (vol) ethanol in gasoline were tested. The commercial unleaded gasoline with methyl tert-butyl ether as the oxygenated additive was also tested as a reference case. The experimental data indicated that addition of ethanol may reduce emissions of selected air toxics, except those of acetaldehyde. The fuel with 15 % (vol) ethanol content performed the greatest reduction in emissions of organic air toxics. However, acetaldehyde emissions significantly increased by almost 10-fold, by using ethanol fuels. In addition, the results of the emission ranking of air toxics showed that the gasoline blend with 15 % (vol) ethanol had the lowest total mass-based emissions of air toxics, and ranked high in toxicity-weighted emissions due to associations with cancer and acute health effects.

Key words: air toxics; organic analysis; emissions; characterization.

Introduction

In the last decade, the application of alternative fuels has received more attention because of shortages of petroleum as well as concern about green house gases emissions. Biofuels have been promoted by many countries around the world, including the United State, Brazil, European Union member states, and Australia (Charles *et al.*, 2007). Ethanol is the most widely employed biofuel and many countries have established or have planned to promote ethanol gasoline (Niven, 2005), but the potential air pollution issues caused by such fuels still need to be considered seriously.

Many researchers have focused on the correlation between ethanol-gasoline blended fuels (3-85 % by volume) and air pollutant emissions of spark ignition engines with most of the studies being carried out on passenger cars. In general, total hydrocarbon and carbon monoxide exhaust emissions are lower with ethanol-blend fuels (Leong *et al.*, 2002; He *et al.*, 2003; Yüksel and Yüksel, 2004; U.S. EPA, 2010a). With regard to air toxics, addition of ethanol to gasoline has been observed to reduce benzene, 1,3-butadiene, toluene, and xylene emissions, but may significantly increase acetaldehyde emissions (Stump *et al.*, 1994; Poulopoulos *et al.*, 2001; Leong *et al.*, 2002; Niven, 2005). In addition, tests on ethanol gasoline have been observed to increase formaldehyde emissions (Stump *et al.*, 1994; CSIRO *et al.*, 2003), reduce emissions (Leong *et al.*, 2002; Schifter *et al.*, 2005) and give mixed results (Knapp *et al.*, 1998). The addition of ethanol into gasoline also has some adverse effects, e.g., increased fuel consumption (Al-Hasan, 2003), as well as the presence of unburned ethanol and increased aldehyde emissions

47 (Poulopoulos *et al.*, 2001; He *et al.*, 2003).

48 The quantification of pollutant emissions has mostly been done with passenger cars, and
49 studies related to the effects of ethanol-blended gasoline on the emission of air pollutants for
50 small engine capacity (less than 150 cm^3) motorcycles are rather limited (Magnusson *et al.*, 2002;
51 Jia *et al.*, 2005). The air toxics emissions from motorcycles are a critical issue in several
52 countries and metropolitan areas especially in Asian counties (e.g. China, India, Indonesia,
53 Taiwan, and Thailand) and South American. With different engine and fuel supply systems, the
54 emissions from cars and motorcycles are also different. Hsu *et al.* (2001) reported that volatile
55 organic compound (VOC) emissions from motorcycles are four times higher than those from
56 passenger cars due to the former is being used primarily for short distance travel and having a
57 relatively low average speed. VOCs are a concern because they are precursors of ambient ozone
58 formation via a photochemical reaction, and have many adverse health effects. Several VOCs are
59 classified as known or probable human carcinogens, such as benzene, 1,3-butadiene,
60 formaldehyde, and acetaldehyde. These are included in a list of 21 mobile source air toxics
61 published by the U.S. Environmental Protection Agency (U.S. EPA, 1994; Payne-Sturges *et al.*,
62 2004), and are likely to present the highest risks to public health and welfare. A thorough
63 analysis of air pollutant emissions from motorcycles is thus necessary. In addition, the effects of
64 using ethanol-blended gasoline on motorcycle emissions are currently not fully known,
65 especially with regard to the organic compounds, and this also deserves further study.

66 Four-stroke engine motorcycles are now the dominant type. A new motorcycles sold in Taiwan
67 have been four-stroke ones since 2004 (Yao *et al.*, 2009), and an estimated 85 % of new
68 motorcycle sales were four stroke engines in 2002 in Thailand (UNDP/ESMAP, 2003). In this
69 study, emissions of organic air toxics from a four-stroke motorcycle were evaluated by

conducting a chassis dynamometer experiment. Four test fuels of ethanol-blended gasoline (ethanol content from 3 to 20 % by volume) were used, and a commercial gasoline was also used as the reference to evaluate the effects on emission. In particular, an inhalation toxicity-based emission ranking for selected air toxics was calculated, which may provide useful information related to the potential health impact of different ethanol-blended gasoline.

Experimental Methods

Test fuels and motorcycle

The level of ethanol content in the gasoline was adjusted with reference to the practical engine conditions. The target levels established for the ethanol-blended gasoline were 3% (E3), 10% (E10), 15% (E15), and 20% ethanol (E20) by volume. A constant research octane number (RON) of 95 was controlled to accurately represent commercial gasoline. The four ethanol blends were prepared by the largest petroleum refinery in Taiwan (China Petroleum Corporation, CPC). A commercial unleaded gasoline was used as the reference fuel (RF). RF has an octane rating of 95 and has methyl tert-butyl ether (MTBE) as the oxygenated additive. It was purchased from a gasoline station operated by CPC. The composition analysis of the fuels was performed by CPC following the American Society for Testing Materials procedure. The properties of ethanol-blended gasoline and RF, measured by CPC, are presented in Table 1.

The weight of the test motorcycle was 101 kg. A carburetor was used for the fuel supply system, and the engine was air-cooled and used a capacitive discharge ignition with a single cylinder arrangement. The compressor ratio of the engine was 8.6 at the maximum power and the detailed specifications of the test motorcycle are shown in Table 2. The motorcycle was a non-catalyst model without any engine adjustment in order to accentuate the effects of the

ethanol-gasoline blends during testing.

Test procedures

A legislative test procedure, CNS 11386, was used for the motorcycle emission test (TEPA, 2001), and this is the same as that of the Economic Commission for Europe test cycle (ECE). One complete test cycle (780 s) includes idle (240 s), acceleration (168 s), cruising (228 s), and deceleration (144 s) stages. The total distance of the test was 4 km with average and maximum speeds of 19 and 50 km/h, respectively.

Emission tests were performed on a chassis dynamometer in a certified laboratory of a local motorcycle manufacturer. The main system was comprised of a chassis dynamometer (MEIDEN, 20KW), a dilution tunnel, a constant volume sampler unit (HORIBA, CVS-51S), and an exhaust gas analyzer (HORIBA MEXA-7200). Vehicle details (registration number, maker, category, and test weight) were entered into the dynamometer control computer for identification and calculation of the inertia loading applicable for the vehicle. The information was then saved to a dedicated file from which the test cycle was referenced to set the correct speed and loads during testing. The test room temperature ranged from 20-30 ^{o}C.

The sampling equipment for organic air pollutants is similar to that used in a previous work (Tsai *et al.*, 2003). A vacuum box containing a 10 L Tedlar bag was used to sample emissions over the entire ECE cycle. Exhaust gas was drawn in via a sampling pump with a controlled flow rate of 150 mL/min. Three-way control valves were used to direct samples into the sample bag. Due to the limitations of the sampling equipment, the sampling work was performed manually.

Prior to each emissions test, a fuel change protocol was followed to ensure minimal crossover between the test fuels and to ensure consistency between tests. To change fuel, the fuel tank was

drained, one liter of the new fuel was added, the engine was idled for five min to allow the new test fuel to flush through the fuel supply system thoroughly, and then the tank was drained again. Two liters of the new fuel were then added for the subsequent emissions test. The test motorcycle and fuel were then conditioned with 10 min of real road driving without emissions measurement. The motorcycle was left at room temperature for over 6 h prior to the start of the cold-start testing process. Six tests of various test fuels were conducted to detect organic compounds, including two tests each for E10, and E15, and one test each for commercial gasoline (RF), E3, and E20.

Analytical procedures

After sampling, the sample bags were immediately placed into a black container and taken to the laboratory for hydrocarbon species analysis within 24 h. Hydrocarbon species with a carbon number larger than 3 (> C3) were preconcentrated by a purge and trap system (Varian) and quantified using gas chromatography/mass spectrometry (Varian Star 3600 GC plus with a Varian Saturn 2000 MS). The temperature of the trap system was cooled to -160 ℃ by liquid nitrogen. The thermal desorber was then preheated to 200 ^{o}C for purging. The GC was equipped with a fused silica capillary column (DB-1, 60 m × 0.32 mm ID with 1.0 μm film thickness) and connected to the MS. Compounds with carbon numbers of 2 to 4 (C2 to C4), were analyzed using gas chromatography/flame ionization detection (Hewlett Packard 6890 GC/FID). The GC was equipped with a fused silica capillary column (HP-PLOT, 30 m × 0.32 mm ID) and connected to the FID.

Calibration standards were prepared by diluting the certified standard gas (56 Environ-Mat Ozone Precursor, Matheson, USA) with ultra high purity nitrogen (99.995%) in dilution bottles.

For GC/MS, the R-square (r^2) of the calibration curves of the 56 VOC species were generally higher than 0.995, the relative standard deviation (RSD) was < 10%, and the accuracy was in the range of 89 ± 6% to 107 ± 9%. The method detection limit ranged from 0.13 (cyclohexane) to 4.77 mg/m^3 (trans-2-butene). For GC/FID, the r^2 values of the calibration curves were higher than 0.999 for six C2 to C4 compounds, the relative standard deviation was less than 0.5%, and the accuracy was in the range of 91 ± 1% to 100 ± 1%. The method detection limit ranged from 0.06 (ethane) to 0.34 mg/m^3 (3-methyl-1-butene).

Carbonyl components in the exhaust were collected in commercially available cartridges filled with 2,4-dinitrophenylhydrazine (Supelco). The cartridge was first extracted with an aliquot of 2 mL acetonitrile (Merck) in the laboratory. The extraction step was repeated with 5 mL acetonitrile. The extraction solution was injected into a high performance liquid chromatographer (Hewlett Packard 1100 series HPLC) equipped with an auto sampler (Hewlett Packard G1313A) and an ultraviolet-visible detector (Hewlett Packard). A total of 15 carbonyl compounds were analyzed. Each carbonyl compound was quantified by its liquid standard calibration curve (Supelco). The r^2 of the carbonyl calibration curves was higher than 0.9999, the relative standard deviation was less than 5%, the accuracy ranged from 100 ± 2% to 103 ± 1%, and the method detection limit ranged from 6.46 μg/m^3 (acetone) to 222 μg/m^3 (2,5-dimethylbenzenealdehyde).

Background samples (room air) were also collected in the dynamometer laboratory and deducted from the test results. The results indicated that the VOC concentration was <176 mg/m^3 (toluene), and the VOC concentration of the dynamometer laboratory was negligible or less than 10^{-3} times that of the motorcycle exhaust.

Toxicity analysis

Six major air toxics, benzene, toluene, ethylbenzene, xylene (BTEX), formaldehyde, and acetaldehyde, were selected as target pollutants for evaluating the toxicity of emissions of each test fuel. Common indicators of toxicological validation of air toxics, included the toxic equivalency factor, toxic equivalence, cancer unit risk, and hazard quotients. The first two indicators are estimates of the toxicity of dioxin and dioxin-like compounds, and the other two are used to assess the health risk of hazardous air pollutants. A method adapted from Wu and Pratt (2001) was applied in this study to account for the inhalation toxicity of air toxics in the emission ranking. The toxicity-based emission ranking was calculated by dividing the total mass of emissions of each air toxic by the related health benchmark. The total mass emission of each pollutant was calculated using an emission factor based on vehicle kilometers traveled (VKT), and the average VKT for motorcycles with 101-125 cm^3 displacement is 4,930 km per year in Taiwan (Hu *et al.*, 2006).

Three types of inhalation health benchmarks were used: for cancer, acute effects, and chronic effects. The health benchmarks for cancer represent the concentrations that are associated with an upper-bound excess lifetime cancer risk of 1 in 100,000. The health benchmarks for acute and chronic effects represent the exposure concentrations that do not cause significant risk of harmful effects for the specified length of exposure (i.e., 1 hr and more than 1 year, respectively) (Wu and Pratt, 2001). The toxicity values for six air toxics are shown in Table 3. The health benchmarks were obtained from the following sources:

(1) US EPA Integrated Risk Information System (IRIS) (U.S. EPA, 2010b); and

(2) California Environmental Protection Agency, California Air Resources Board and Office of Environmental Health Hazard Assessment (CARB/OEHHA, 2009)

The cancer risk values of the carcinogens (i.e. benzene, formaldehyde, and acetaldehyde) were

from the U.S. EPA IRIS, and the data for the acute and chronic inhalation of the air toxics was from CARB/OEHHA, because the U.S. EPA does not provide acute or chronic dose-response values.

Results and Discussion

Emissions of organic air pollutants

The total organic air pollutant emission factor, i.e., the sum of alkanes (27 species), alkenes (13 species), aromatics (16 species), and carbonyls (15 species), of the reference fuel was 360 mg/km (Table 4). Figures 1 and 2 illustrate the major VOC species and carbonyl species emission factors (mg/km) of a four-stroke motorcycle exhaust for various ethanol blends, respectively. For all test fuels, isopentane and toluene are the compounds with the highest emissions accounting for 23, 22, 21, 18, and 19% of total organic air pollutant emissions for RF, E3, E10, E15, and E20 fuels, respectively.

The E3 fuel has the highest emission factor, with a value of 394 mg/km, which is 9% higher than that of the RF. The oxygen content of E3 blend (1.0 % by weight) is lower than that of the RF (1.8 % by weight), because the RF fuel has MTBE as the oxygenated additive, and the oxygen content in turn certainly influences the combustion efficiency of the motorcycle. Moreover, the fuel specifications show that the olefin, naphthene, aromatic, and benzene content levels in E3 fuel were the highest among the test fuels. The high VOC emissions for E3 fuel may be attributed to its heavy carbon content. Figure 1 shows that most of the detected alkane compound detection levels for E3 were higher than those of RF, except isopentane and n-pentane. Similar results were obtained for aromatic compounds, with the emissions of toluene, benzene, and m,p-xylene also being higher for E3 fuel.

208 The E15 blend exhibited the lowest organic compound emissions (152 mg/km) among the test
209 fuels and the greatest organic compound emission reduction (near 60%) as compared to RF.
210 Oxygen content in E15 was higher than that in RF, whereas aromatic and naphthene content
211 levels were lower than those in RF. E10 (196 mg/km) also had an emission reduction of 45 % as
212 compared to that of RF and its oxygen content was lower than that of RF. For E15 and E10, most
213 detected organic compound emissions were lower than those of RF (Figure 1), while carbonyl
214 compound emissions were higher (Figure 2). The carbonyl compound emission factors were 11.2,
215 18.0, 24.4, 47.6, and 13.8 mg/km for E3, E10, E15, E20, and the RF, respectively. In general, the
216 emission factors of the RF were lower than those of the ethanol blends (expect E3 fuel). It is
217 noteworthy that acetaldehyde emissions were extremely high when ethanol-blend fuels were
218 combusted in the motorcycle engine. As shown in Figure 2, acetaldehyde emissions for
219 ethanol-gasoline blends were 1.8- to 9.5-fold higher than those of RF.
220 E20 had organic compound emissions (363 mg/km) similar to those of RF (360 mg/km). The
221 excess air ratio (λ) of E20 (λ = 1.15 to 1.21 for the driving pattern) was outside the typical range
222 for gasoline engines (0.9-1.1). At the same conditions, the λ values were 1.01 to 1.04 for RF.
223 This implies that the E20 blend results may not be relevant for motorcycles equipped with a
224 carburetor engine. Moreover, since the test motorcycle could not adjust the intake rate of air into
225 the engine, the high oxygen level in E20 fuel caused the engine to operate over a certain lean
226 limit ($\lambda > 1.1$), and incomplete combustion thus occurred in the combustion chamber, leading to
227 increased hydrocarbon emissions (Hochgreb, 1998; Al-Farayedhi *et al.*, 2000).
228 In addition, according to the properties of the test fuels shown in Table 1, the carbon,
229 hydrogen, and oxygen content of the test fuels were all different. Under the assumption of carbon
230 balance, we calculated the proportion of CO_2 mass (as C) to the total carbon mass (g-C/g-fuel) of

each test fuel. The results show that the E15 blend had the highest proportion of CO_2 (93%) in comparison with the other test fuels, and the value was 89 % for E3, 92 % for E10, and 91 % for E20. This result implies that combustion with E15 blend was more complete than with the other test fuels. This may be one of the reasons for the low levels of organic compound emissions observed in E15 in the present study.

Emissions of four chemical groups of analyzed VOCs

The 71 species of analyzed VOCs were divided into four groups: alkanes, alkenes, aromatics, and carbonyls. Table 4 shows the VOC group emission factors (mg/km). Figure 3 shows the percentage of four chemical groups of the total organic compound emissions for various test fuels. For the RF, the order in mg/km was alkane (183) > aromatic (83) > alkene (80) > carbonyl (14). The contributions from the alkane, aromatic, alkene, and carbonyl groups were 51, 23, 22, and 4%, respectively. For the ethanol blends, the order was the same as that for RF. The contributions ranged from 47-57 %, 17–27 %, 13–17 %, and 3-16 %, respectively, for the alkane, aromatic, alkene, and carbonyl groups. Alkanes contributed the highest amount of emissions for all test fuels. The percentages of alkanes in E3 and E20 were higher than those in the RF. On the other hand, the percentages of alkenes and aromatics in the RF were higher than those of the ethanol blends. The percentage of carbonyl contribution was higher for ethanol-blend gasoline.

Compared to the RF, the alkane, alkene, and aromatic percentages decreased for E15 fuel, and the differences were -59, -68, and -68 %, respectively (see Figure 4). E10 fuel also exhibited reductions in these three chemical groups (by 37-57 %). In contrast, the emissions of the carbonyl group greatly increased for ethanol blends, and the emission factors rose by 30 % (E10), 76 % (E15), and 244 % (E20) as compared to those of the RF. As mentioned previously, high

acetaldehyde and acrolein emissions are the main cause of high carbonyl group emissions for ethanol blends.

For the four groups (alkane, alkene, aromatic, and carbonyl) the addition of oxygenated content (for E10, E15, and E20) decreased the exhaust alkene and aromatic emissions by 40-68 % and 19-68 %, respectively, in terms of emission factor per distance, and by 41-65 % and 20-65 %, respectively, in terms of emission factor by fuel consumption. The results also show that the ethanol blends emitted more carbonyl compounds than did the RF, expect the E3 fuel. Carbonyl emissions increased with increasing ethanol content, and high acetaldehyde emissions are the main cause of high carbonyl group emissions for ethanol blends.

Alkenes play a significant role in the formation of aldehydes (Altshuller 1991; Grosjean *et al.*, 1996), and a large decrease in alkene emissions (40-68 %) with increasing ethanol level was found in the present study. The reduction of alkene emissions may offset some of the increase in direct aldehyde emissions and secondary aldehyde formation from emissions of ethanol-gasoline blend, especially formaldehyde and acetaldehyde. Since the major air toxics emitted during ethanol gasoline combustion include benzene, toluene, ethylbenzene, xylene, formaldehyde, acetaldehyde, and 1,3-dutadiene, the net effect of ethanol-gasoline blends on air toxics levels in the ambient air needs further evaluation. Furthermore, the use of ethanol-gasoline blends in general results in a more than 45 % reduction in VOC emissions in our study, and this may positively influence ozone formation and air quality if there is a large-scale switch to ethanol blends, especially in highly motorized cities (USAID, 2009).

Emissions of air toxics

Six major air toxics, BTEX, formaldehyde, and acetaldehyde, were selected as target pollutant

277 according to the results of previous studies (Tsai *et al.*, 2003; Jia *et al.*, 2005). Figure 5 shows the
278 emission factors (mg/km) of air toxics for the ethanol-blended gasolines. An analysis of the
279 effects of ethanol-blend gasoline was carried out by calculating the emission variance of air
280 toxics for various ethanol fuels as compared to the reference fuel, and the results are shown in
281 Figure 6.

282 For the aromatic air toxics, BTEX, the results show significant reductions for E15 compared to
283 the reference fuel (Figure 6), and reductions of 64 % for benzene, 63 % for toluene, 77% for
284 ethylbenzene, and 69 % for xylene were obtained. E10 and E20 also showed emission reductions
285 in the range of 29-51 % and 14-34 %, respectively, for the four aromatic compounds as
286 compared to RF. However, the emissions increased by about 3, 34, 21, and 15 % for benzene,
287 toluene, ethylbenzene, and xylene, respectively, for E3 fuel.

288 Benzene emissions from the test motorcycle decreased with ethanol content in the gasoline.
289 These results are consistent with those reported in previous studies (Poulopoulos *et al.*, 2001;
290 Zervas *et al.*, 2004a). The lowest and highest benzene emissions were observed for E15 and E3,
291 respectively. The benzene content in gasoline provides the majority of exhaust benzene. Besides
292 being present in the fuel itself, benzene is also emitted from the tailpipe as a result of its
293 formation during the combustion process involving other fuel components, such as
294 alkylaromatics and cyclohexane (Zervas *et al.*, 1999). For fuel aromatics, the benzyl radical is
295 formed by dealkylation and then combines with hydrogen to produce benzene. This reaction is
296 more important at condition of lack of oxygen (Zervas *et al.*, 2004a), as in the case for E3. The
297 benzene, aromatic, and naphthene content levels in E3 were the highest among all of the test
298 fuels. In contrast, they were the lowest in E15.

299 Toluene emissions also decreased for ethanol-blended fuels. Compared to RF, toluene

emissions were reduced by 14 to 63 % for ethanol blends. The majority of exhaust toluene comes from unburned fuel. Some heavy aromatics may dealkylate into toluene (Goodfellow *et al.*, 1996; Zervas *et al.*, 2004b), increasing toluene exhaust emissions. Ethylbenzene emissions significantly decreased for the ethanol-blended fuels by 77 % (E15), 51 % (E10), and 27 % (E20). Exhaust ethylbenzene may come from unburned fuel. Fuel toluene and o-xylene may lose a hydrogen atom or methane molecule to form Φ-CH_2, which reacts with a methyl to produce ethylbenzene. Xylene emissions also showed a significant decrease (34 to 69 %) for ethanol-blended fuels, and this air toxic does not come from other fuel aromatics, but is only the product of unburned fuel (Zervas *et al.*, 2004a).

For aldehydes, the results show that ethanol-blended fuels produce less formaldehyde than RF does. In general, formaldehyde decreased with increasing ethanol content. A 30 to 63 % reduction in formaldehyde emissions was obtained from the test motorcycle without a catalytic converter for the ethanol-gasoline blends. The literature has reported that exhaust formaldehyde is produced from fuel methanol, ethanol, and MTBE (Reuter *et al.*, 1992; Stump *et al.*, 1994; Kirchstetter *et al.*, 1996), and some studies have shown that levels of formaldehyde may decrease or remain constant for ethanol-blended gasoline with an ethanol content of below 30 % (Warner-Selph and Harvey, 1990; Guerrieri *et al.*, 1995; Knapp *et al.*, 1998**;** Schifter *et al.*, 2005). Moreover, increasing fuel aromatic content may decrease formaldehyde emissions (Petit and Montagne, 1993). E15 and E20 have lower aromatic content than the RF, which may enhance formaldehyde reduction. E3 and E10 fuels also show large emission reductions as compared to the emissions of the RF and oxygen content may thus play an important role in carburetor motorcycle engines.

The exhaust acetaldehyde emissions for ethanol-gasoline blends were 1.8- to 9.5-fold those for

323 the RF. The emissions increased with ethanol content, and many studies have shown that fuel
324 ethanol increases acetaldehyde emissions and that MTBE has no effect (Zervas *et al.*, 1999;
325 Poulopoulos *et al.*, 2001; Jia *et al.*, 2005), which is consistent with our results. Acetaldehyde is
326 mainly produced from ethanol. The oxygen content of the fuel favors the oxidation of the
327 acetaldehyde produced during the combustion process. Acetaldehyde is produced through the
328 partial oxidation of ethanol (Poulopoulos *et al.*, 2001) and straight-chain hydrocarbons enhance
329 its formation (Zervas *et al.*, 2002).
330 In brief, the effects of using ethanol-gasoline blends on the air toxics emissions (i.e., BTEX,
331 formaldehyde, and acetaldehyde) from a carburetor motorcycle without a catalytic converter
332 were studied in this work. The results show that the addition of ethanol up to 15 % by volume
333 generally caused a decrease in the air toxics emissions. However, acetaldehyde emissions
334 significantly increased for ethanol fuels, and were almost 10-fold higher in some cases as
335 compared to the emissions for the RF.
336
337 ***Preliminary toxicity assessment***
338 The toxicity assessment was conducted using toxicity-based emission ranking. As mentioned
339 before, the ranking was calculated by dividing the total mass of emissions of each air toxic by the
340 related inhalation health benchmark (within the appropriate categories of cancer, acute, and
341 chronic effects, as shown in Table 3). Table 5 shows the air toxics mass-based and toxicity-based
342 emissions ranking for the five test fuels.
343 For carcinogenic toxics, i.e., benzene, formaldehyde, and acetaldehyde, the emission ranking
344 of the test fuels for each toxic was inconsistent based on the health benchmark of cancer. The
345 cancer-based emissions of the six air toxics were summed and the test fuels were ranked by total

emissions. The result shows that the fuel with the highest emissions in terms of carcinogenic effects was E20, and the high mass emission (185.2 g/year) and low cancer health benchmark (0.5 $\mu g/m^3$) of acetaldehyde were responsible for this. The acetaldehyde emissions of E20 were 2- to 11-fold higher than those for the other four test fuels (or 17.6-76.9 g/year). E15 also had a high ranking for the same reasons as E20, and was ranked second in terms of carcinogenic effects. In contrast, E3 had the lowest cancer effect among all the tested fuels. The cancer-based emissions of E20 were 1.8- to 2.7-fold higher than those of the other test fuels.

The emission rankings for acute effects were the same as those for the carcinogenic effects as E20 and E15 had the highest rankings, following by RF, E10, and E3. The acute-effects-based emissions of E20 were 1.6 to 2.4-fold higher than those of the other test fuels, which can be attributed to the high mass emission and low acute-effect value (470 $\mu g/m^3$) of acetaldehyde in E20. In addition, although E15 had the lowest mass emissions of BTEX, it ranked second based on acute-effects among all the tested fuels. The high emissions and low acute-effect values of formaldehyde and acetaldehyde may be responsible for the high acute effects of E15.

The RF had the highest total chronic-effect emissions of the six air toxics, following by E20, E3, E10, and E15. Formaldehyde and benzene have low chronic health benchmark values, at 9 and 60 $\mu g/m^3$, respectively. The high mass-based emissions and low chronic effect values of these two toxics are responsible for the high RF rank. E20 also ranked high because its acetaldehyde mass-based emissions were much higher than those of the other test fuels.

In brief, toxicity-based emission rankings for the six air toxics show that E20 and E15 have high emissions in terms of cancer and acute effects while the RF had the highest emissions in terms of the chronic effects. Moreover, the high mass-based emissions and low health benchmark values of acetaldehyde possibly contributed to the high toxicity-based emissions for E20 and E15.

The contributions of BTEX to the acute effects are small in comparison to these of acetaldehyde for ethanol-blended gasoline. For the chronic effects of the six air toxics, the RF and E20 had the highest emissions. Notably, E15 had the lowest total mass-based emissions of the air toxics, but it ranked high in the toxicity-weighted emissions based on the cancer and acute effects. In addition, for the six air toxics, the acute health benchmark values were generally higher than those of chronic and cancer health benchmarks by 1-2 orders of magnitude. Therefore, for the purpose of protecting against the most significant health effects, greater emphasis was focused on ranking by cancer and chronic effects.

It should be noted that the evaluation of the toxicity-weighed emission were limited to the inhalation route of pollution exposure, and other exposure routes in the environment, such as ingestion of food, intake of drinking water, or direct contact, were not considered. In addition, this ranking is not intended to replace risk assessment, because the emission factor does not equal an exposure estimate. Moreover, health benchmark values are highly conservative, as most of them are based on controlled exposures to laboratory animals at high levels while human exposure in the environment occurs at much lower levels, and thus they may tend to overstate pollutant toxicity (Wu and Pratt, 2001).

Limitations

Some limitations should be noted in this study. First, only one four-stroke carburetor motorcycle was tested in this study and was given small dataset, although it is representative. In order to assess statistical significance of results and provides better representative results, it is recommended that the large sample size is needed by considering the affordable cost. Moreover, in order to emphasize the effects of the ethanol levels in gasoline on organic compound

emissions, the test motorcycle was an uncontrolled one to avoid the interference from a catalyst. For application to ethanol blend fueled motorcycles, extensions of this study using catalytic converters for the control of air pollutants are recommended.

Finally, the toxicity-weighting emission only considered inhalation exposure, and not the other exposure routes in the environment. Therefore, toxicity-based emission ranking is not intended to replace risk assessment, because the emission factor does not equal an exposure estimate. However, this method does provide a simple way to evaluate emissions data within a context of toxicity.

Conclusions

The influence of ethanol-gasoline blends on organic air toxic emissions (VOCs and carbonyls) from a non-catalyst four-stroke motorcycle without any engine adjustment was investigated. Four types of ethanol blend (3, 10, 15, and 20 % by volume) were tested. The commercial unleaded gasoline (with MTBE) was also tested as reference case.

The results of emission factor per distance (mg/km) show that ethanol added into gasoline generally decreases total organic compound emissions, except carbonyl compound emissions. The 15% ethanol blend had the highest emission reductions compared to the RF. For the four organic chemical groups, i.e., alkanes, alkenes, aromatics, and carbonyl, the addition of oxygenated content (for E10, E15, and E20) decreased the exhaust alkene and aromatic emissions by 40-68 % and 19-68 %, respectively. The results also show that the ethanol blends emitted more carbonyl compounds than did the RF. High acetaldehyde emissions are the main reason for the high carbonyl group emissions for the ethanol blends.

The addition of ethanol to fuel up to 15 % (vol) generally resulted in a decrease in the selected

air toxics emissions. The presence of excess oxygen during combustion also had a significant effect on the emissions of the various oxygenated hydrocarbon species, including air toxics. BTEX and formaldehyde emissions decreased with increasing oxygenated content in gasoline. In addition, the acetaldehyde emission increased significantly for ethanol fuels due to acetaldehyde precursors being rapidly oxidized, which increased its formation in lean conditions. The results for the toxicity-based emissions of air toxics showed that E20 and E15 had the highest emissions in terms of cancer and acute effects while the RF and E20 had the highest emissions based on chronic effects. Notably, E15 had the lowest total mass-based emissions of air toxics, but it ranked highly in toxicity-weighted emissions based on the cancer and acute effects.

In conclusion, this research has shown a valid experimental approach to investigate the effects of ethanol-gasoline blends on exhaust emissions, although only one four-stroke carburetor motorcycle was tested. The chassis dynamometer test results showed that ethanol content in gasoline up to 15 vol% is appropriate for carburetor motorcycle without adjustment being made to the engine, with reduction in the emissions of most organic compounds. The toxicity-based emission ranking method thus provides a simple way to evaluate emissions data within a context of toxicity.

Nomenclature

BTEX: benzene, toluene, ethylbenzene, and xylene

CARB: California Air Resources Board

CSIRO: Commonwealth Scientific and Industrial Research Organisation

CPC: China Petroleum Corporation, the largest petroleum refinery in Taiwan

E3: Gasoline blend containing 3 % ethanol by volume

E10: Gasoline blend containing 10 % ethanol by volume

E15: Gasoline blend containing 15 % ethanol by volume

E20: Gasoline blend containing 20 % ethanol by volume

ECE cycle: Economic Commission for Europe test cycle

GC/FID: gas chromatography with flame ionization detection

GC/MS: gas chromatography with mass spectrometry

HPLC: high performance liquid chromatography

Lambda (λ): excess air ratio, the λ is defined as actual air-fuel ratio divided by stoichiometric air-fuel ratio

MTBE: methyl tert-butyl ether, used as the oxygenated additive in commercial unleaded gasoline

OEHHA: California Environmental Protection Agency, Office of Environmental Health Hazard Assessment

RF: reference fuel, i.e., commercial unleaded gasoline which does not contain ethanol

RON: research octane number

RSD: relative standard deviation

TEPA: Taiwan Environment Protection Administration

UNDP/ESMAP: United Nations Development Programme/World Bank Energy Sector Management Assistance Programme

USAID: United States Agency for International Development

U.S. EPA: U.S. Environmental Protection Agency

VKT: vehicle kilometers traveled

VOC: volatile organic compound

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Figure Captions

Figure 1. Top 15 VOC species emission factors in four-stroke motorcycle exhaust for various ethanol blends.

Figure 2. Top five carbonyl species emission factors in four-stroke motorcycle exhaust for various ethanol blends.

Figure 3. Percentage contribution of four chemical groups to the analyzed VOCs for various ethanol blends. (The percentage is calculated based on emission factor per distance)

Figure 4. Emission variance of four chemical groups to the analyzed VOCs for ethanol blends as compared to that of the RF. (The variance is calculated based on emission factor per distance)

Figure 5. Air toxics emission factors (mg/km) for the ethanol-blended gasoline.

Figure 6. Emission variance of the air toxics for ethanol blends as compared to that of the RF.

Table 1

Properties of test fuels.

Fuel property	RF[*1]	Ethanol-blended gasoline			
		E3	E10	E15	E20
Research octane number	95.0	94.9	95.1	95.2	95.1
Ethanol (vol%)	0	2.9	9.8	14.7	17.9
MTBE (vol%)	10.3	0	0	0	0
Oxygen content (wt%)	1.8	1.0	3.4	5.2	6.1
Aromatics (vol%)	29.9	37.0	31.6	22.9	20.2
Paraffins (vol%)	10.6	8.1	8.8	8.4	8.2
Olefins (vol%)	10.6	17.0	11.3	15.2	12.3
Naphthenes (vol%)	5.9	6.5	5.7	5.8	6.0
Benzene (vol%)	0.6	0.9	0.7	0.6	0.5
Heating value (J/g)	2577	2570	2526	2501	2446
Low heating value (J/g)	2450	2446	2397	2370	2308
Latent heat (J/g)	127	124	129	130	137

[*1]RF is a commercial unleaded gasoline manufactured by the largest petroleum refinery in Taiwan

Table 2

Specifications of the test motorcycle.

Item		Specification
Manufacturer		KYMCO
Model		GT 125
Displacement		125 cm^3
Odometer		0 km
Fuel supply system		Carburetor
Engine type		Four-stroke, single (horizontal)
Ignition system		Capacitor discharge ignition
Compression ratio		8.6:1
Maximum power		6.8 kW/7500 rpm
Cooling system		Air-Cooled
Air pollution prevention	Three-way catalyst	No
device	Air injection system	No

Table 3

Health benchmarks for cancer, acute, and chronic effects.

Air toxics	Cancer ($\mu g/m^3$)	Cancer data source	Acute ($\mu g/m^3$)	Acute data source	Chronic ($\mu g/m^3$)	Chronic data source
Benzene	1.3E+00	IRIS	1.3E+03	CARB/OEHHA	60	CARB/OEHHA
Toluene	---[*1]		3.7E+04	CARB/OEHHA	300	CARB/OEHHA
Ethylbenzene	---		---	CARB/OEHHA	2000	CARB/OEHHA
Xylene (mixed isomers)	---		2.2E+04	CARB/OEHHA	700	CARB/OEHHA
Formaldehyde	8.0E-02	IRIS	5.5E+01	CARB/OEHHA	9	CARB/OEHHA
Acetaldehyde	5.0E-01	IRIS	4.7E+02	CARB/OEHHA	140	CARB/OEHHA

[*1] "---" implies no value under the IRIS or CARB/OEHHA system

Table 4

Emissions (mg/km) of organic air pollutants from the four-stroke motorcycle for ethanol-blended gasolines.

Test fuel[*1]	Oxygen content (wt%)	Emission factor (mg/km)				
		VOCs[*1]	VOC Group			
			Alkanes	Alkenes	Aromatics	Carbonyls
RF	1.87	360	183	80	83	148
E3	1.04	394 (9%)[*2]	225	59	99	11
E10	3.51	196 (-46%)	92	34	52	18
E15	5.36	152 (-58)	75	26	27	24
E20	6.49	363 (1%)	199	48	68	48

[*1] EF of VOCs is the sum of alkanes (28 species), alkenes (12 species), aromatics (16 species), and carbonyls (15 species).

[*2] Values in parentheses ( ) show the emission variance of each ethanol blend as compared to the emissions for the RF.

Table 5

Ranking of air toxics emissions based on mass and toxicity for ethanol-blended gasolines.

	Test Fuel				
Mass emission (g/year)	RF	E3	E10	E15	E20
Benzene	86.5	89.0	57.5	30.7	57.8
Toluene	152.2	204.0	107.5	55.8	130.6
Ethylbenzene	18.6	22.6	9.2	4.3	13.6
Xylene	58.8	67.7	33.2	18.3	38.9
Formaldehyde	9.7	5.4	5.2	6.8	3.6
Acetaldehyde	17.6	18.0	49.2	76.9	185.2
Total	343.4	406.7	261.8	192.8	429.8
Ranking by emission					
Benzene	2	1	4	5	3
Toluene	2	1	4	5	3
Ethylbenzene	2	1	3	4	5
Xylene	2	1	4	5	3
Formaldehyde	1	3	5	4	2
Acetaldehyde	5	4	3	2	1
Total	3	2	4	5	1
Ranking by cancer effects					
Benzene	2	1	4	5	3
Toluene					
Ethylbenzene					
Xylene					
Formaldehyde	1	3	4	2	5
Acetaldehyde	5	4	3	2	1
Total	3	5	4	2	1
Ranking by acute effects					
Benzene	2	1	4	5	3
Toluene	2	1	4	5	3
Ethylbenzene					
Xylene	2	1	4	5	3
Formaldehyde	1	3	4	2	5
Acetaldehyde	5	4	3	2	1
Total	3	5	4	2	1
Ranking by chronic effects					
Benzene	2	1	4	5	3
Toluene	2	1	4	5	3
Ethylbenzene	2	1	4	5	3
Xylene	2	1	4	5	3
Formaldehyde	1	3	4	2	5
Acetaldehyde	5	4	3	2	1
Total	1	3	4	5	2

[*1] Total is the sum of six air toxics based on mass or toxicity

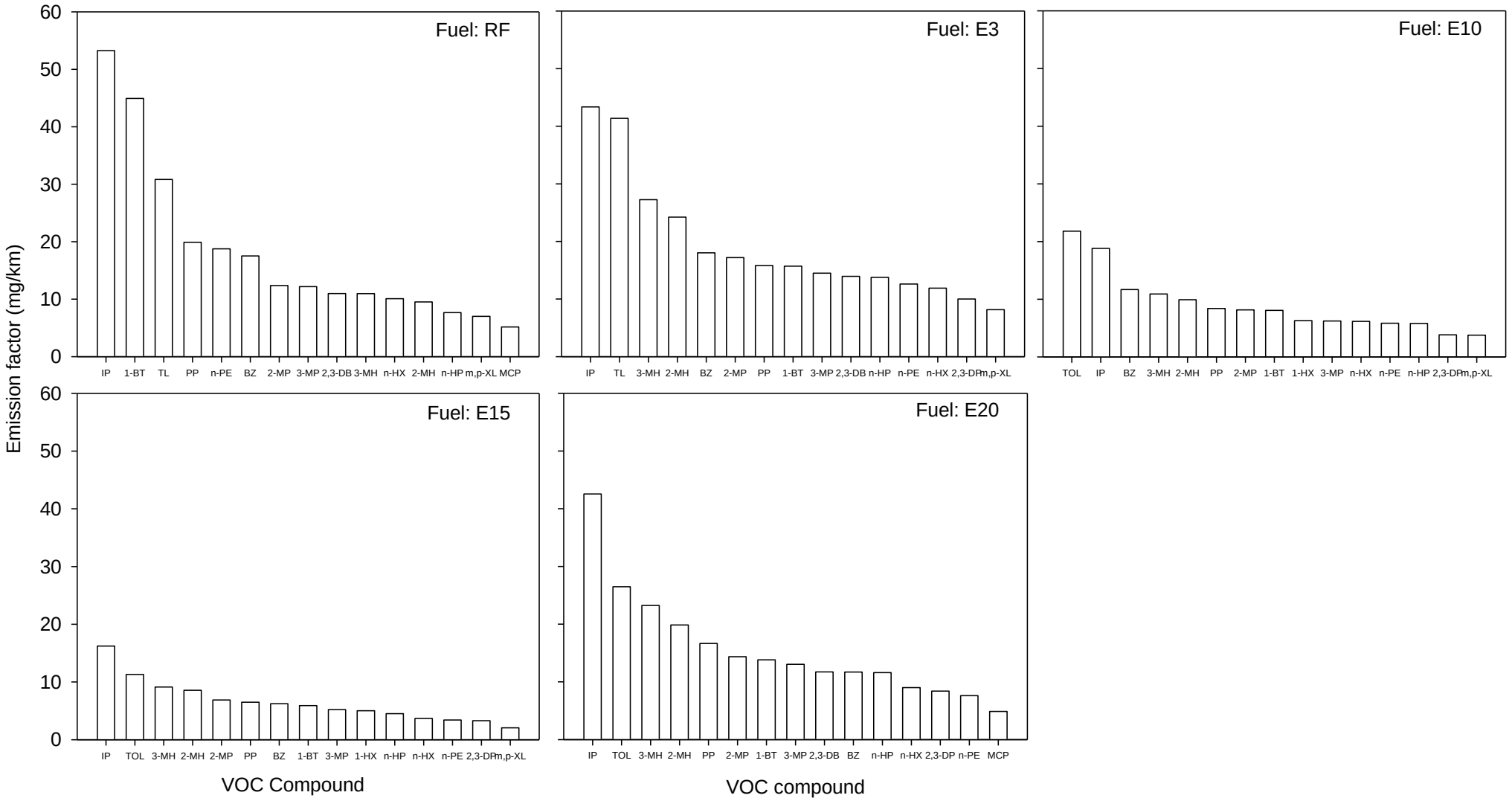


Fig. 1. Top 15 VOC species emission factors in four-stroke motorcycle exhaust for various ethanol blends. (1-BT: 1-butene; 1-HX: 1-hexene; 2-MH: 2-methlyhexane; 2-MP: 2-methylpentane; 3-MH: 3-methylhexane; 3-MP: 3-methylpentane; 2,3-DB: 2,3-dimethylbutane; 2,3-DP: 2,3-dimethylpentane; BZ: benzene; n-HP: n-heptane; n-HX: n-hexane; IP: isopentane; MCP: methylcyclopentane; n-PE: n-pentane; PP: propylene; TL: toluene; *m,p*-XL: *m,p*-xylene)

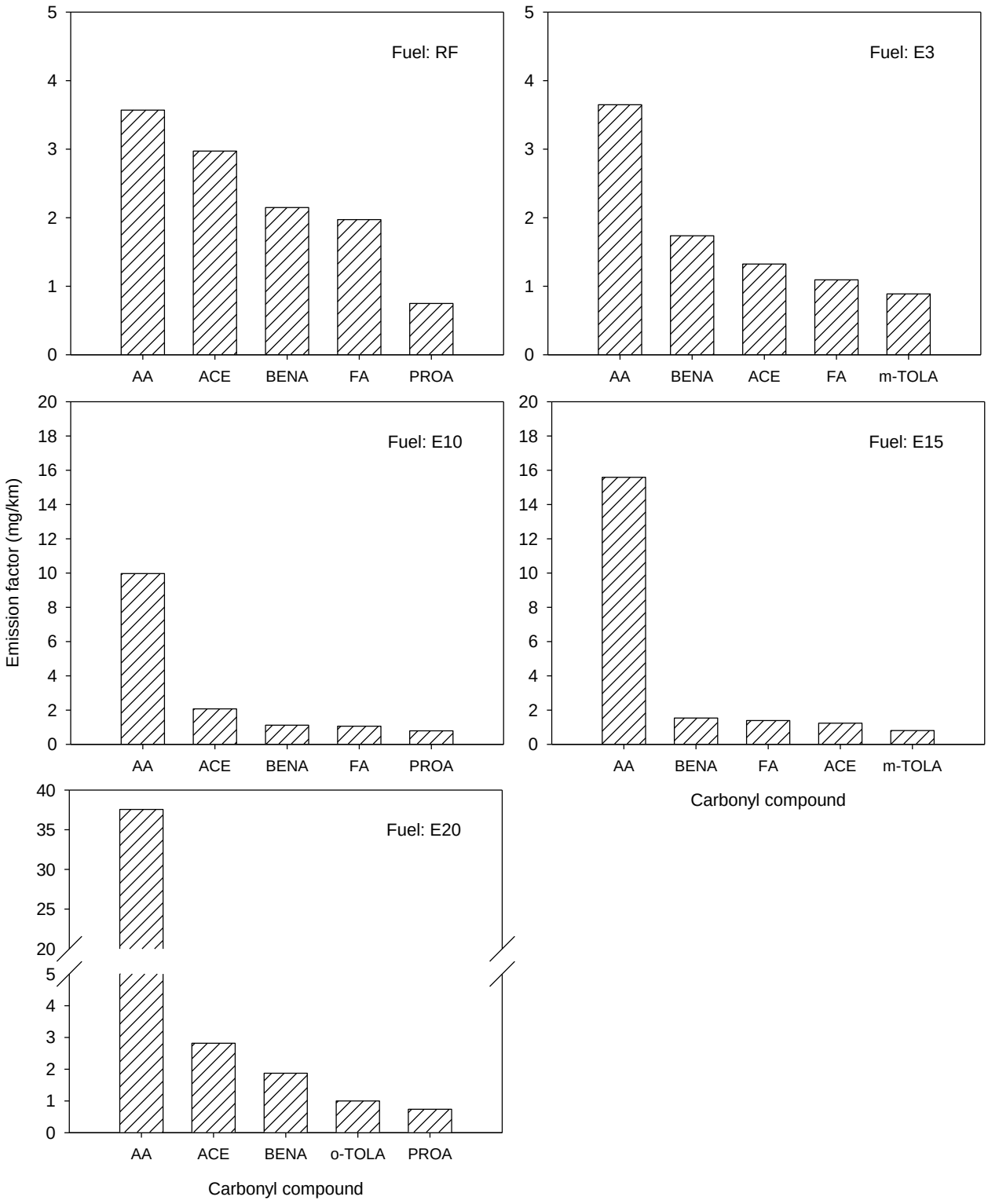


Fig. 2. Top five carbonyl species emission factors inf four-stroke motorcycle exhaust for various ethanol blends. (AA: acetaldehyde; ACE: acetone; BENA: benzaldehyde; FA: formaldehyde; PROA: propionaldehyde; *m*-TOLA: *m*-tolualdehyde; *o*-TOLA: *o*-tolualdehyde)

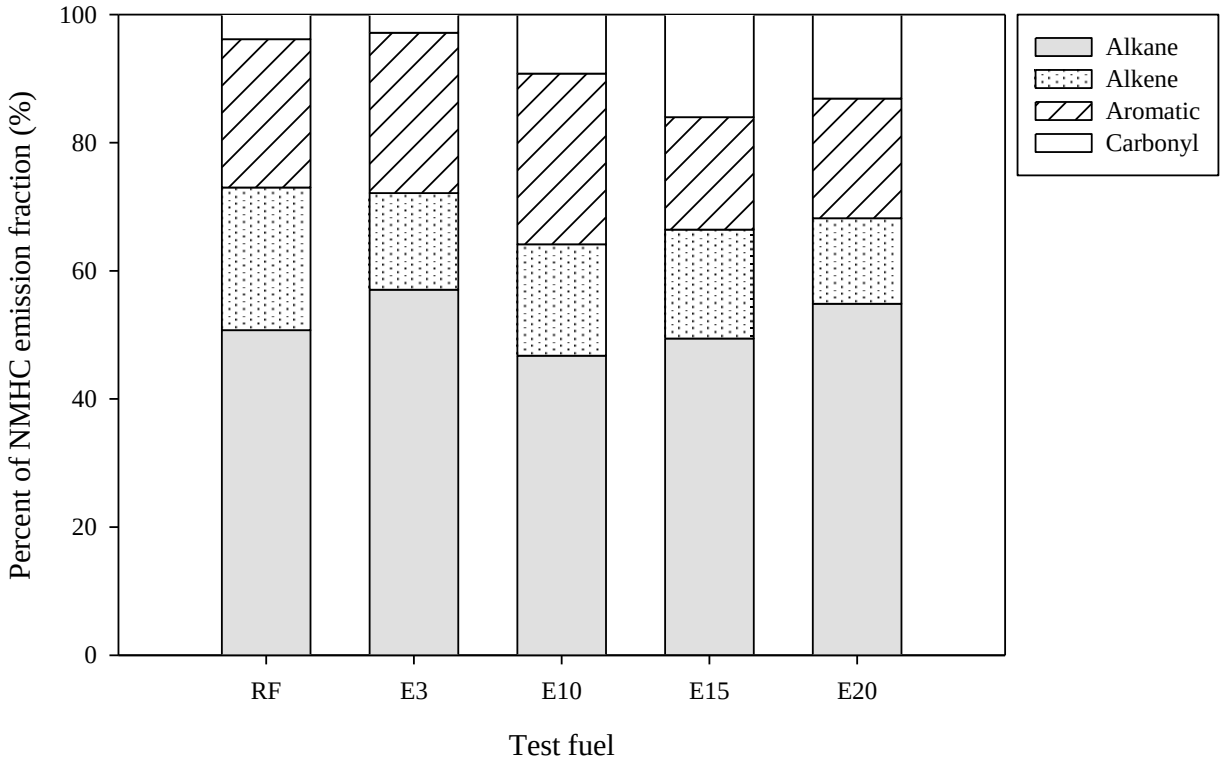


Fig. 3. Percentage contribution of four chemical groups to the analyzed VOCs for various ethanol blends. (The percentage is calculated based on emission factor per distance)

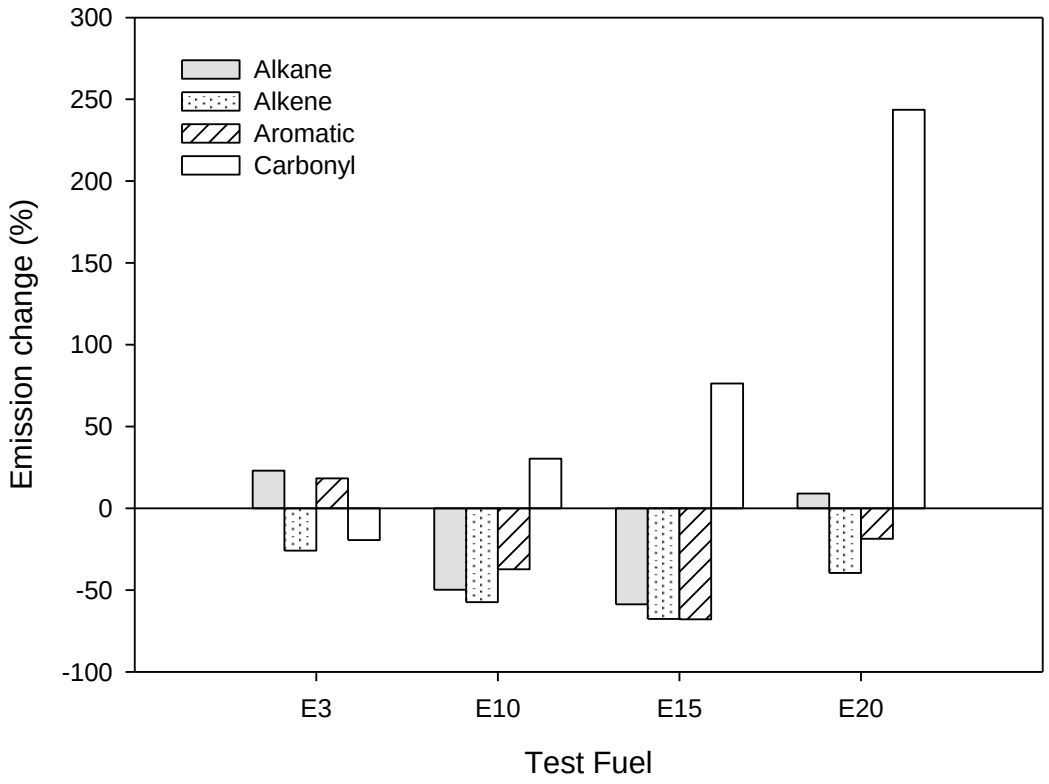
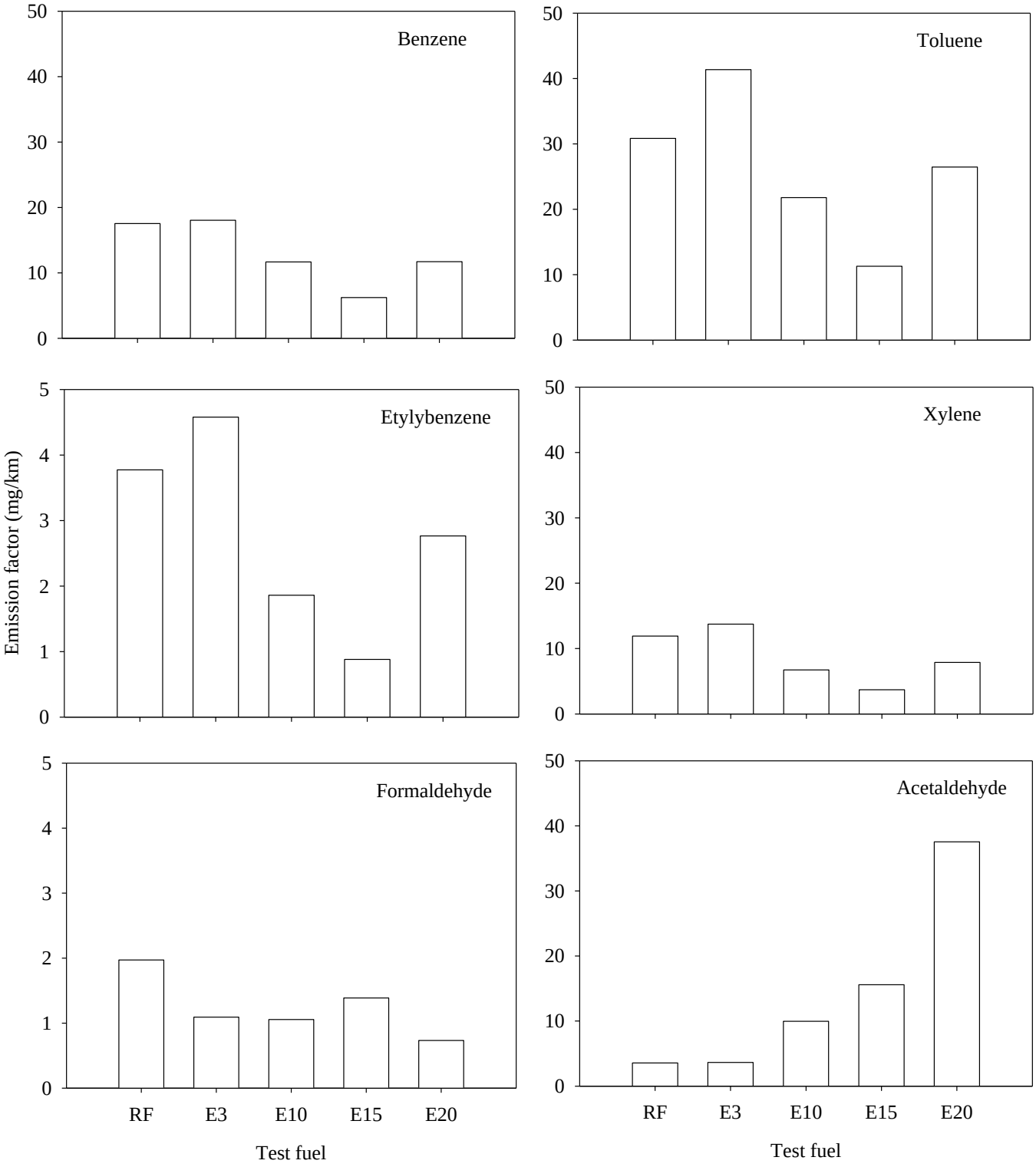


Fig. 4. Emission change (%) of four chemical groups to the analyzed VOCs for ethanol blends as compared to that of the RF. (The variance is calculated based on emission factor per distance)



*EF of xylene was the sum of m,p-xylene and o-xylene.

Fig. 5. Air toxics emission factors (mg/km) for the ethanol-blended gasoline.

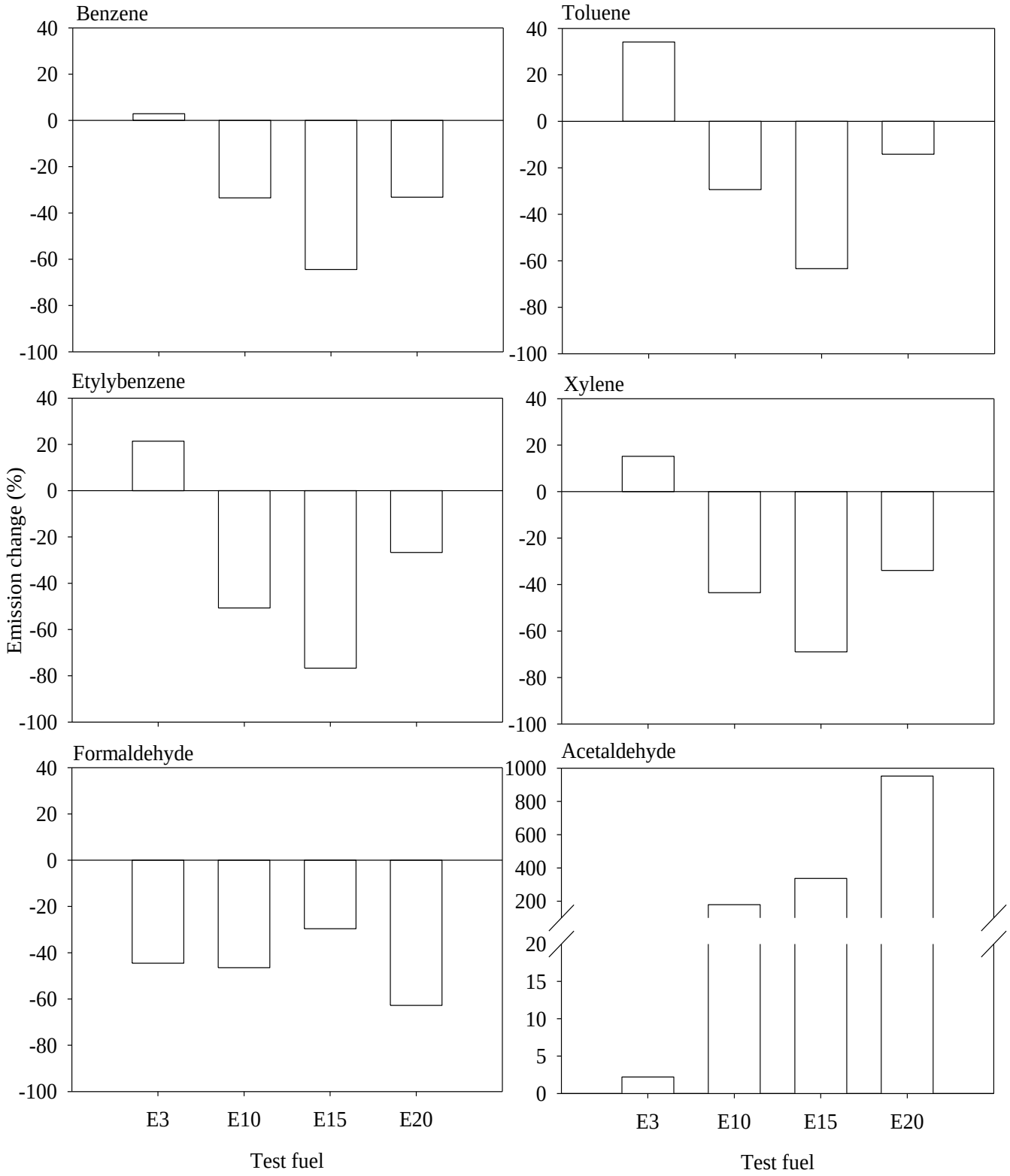


Fig. 6. Emission change (%) of the air toxics for ethanol blends as compared to that of the RF.