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Air Pollutant Emission Abatement using Application of Various Ethanol-gasoline Blends in High-mileage Vehicles

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ABSTRACT

The possibility of using ethanol-gasoline blends as fuel for vehicles as air quality management tools has been raised. In this study, two passenger cars with different accumulated mileage, i.e., low-mileage (35,000 km), and high-mileage (140,000 km) cars, were tested to investigate the ethanol-gasoline blend effect on emission abatement. Three ethanol-gasoline blends, containing 3, 10, and 20% ethanol by volume in gasoline, and one unleaded gasoline, were used as test fuels. Criteria pollutants (CO, THC, and NO_x), volatile organic compounds, and carbonyls were evaluated on a chassis dynamometer using the United States Federal Test Procedure. The exhausts of these criteria pollutants and BTEX (benzene, toluene, ethylbenzene, and xylenes) were lower while using ethanol-gasoline blends, even in the case of the high-mileage car fuelled with an E3 blend. However, formaldehyde and acetaldehyde emissions increased as the ethanol content in the gasoline was increased. The influence of ethanol blends on aldehyde emissions was more significant for the high-mileage car; there was an increase of 22–38% as compared to commercial gasoline. The results also showed that using ethanol-gasoline blends may lead to low ozone-forming potential (24–46%) as compared to using commercial gasoline. In terms of toxicity-based emissions, ethanol-gasoline blends ranked higher in cancer and acute-effects, especial for the high-mileage car. In brief, this study showed that ethanol-gasoline blends could be applied in in-use passenger cars without any engine adjustment in order to reduce the emission of criteria pollutants and the ozone-forming potential of VOCs as compared to using unleaded gasoline, but there may be an increase in some carcinogenic toxics emissions.

Keywords: Accumulated mileage passenger cars; Criteria pollutant; Volatile organic compound; Air toxics.

INTRODUCTION

As is well known, demands for fossil fuel in the transportation sector have increased in conjunction with growing economies. In order to reduce demand for petroleum as well as green house gas emissions resulting from vehicular transportation, alternative fuels have been evaluated as alternative energy sources; they include ethanol, methanol, natural gas, hydrogen, biodiesel and electricity as defined by the US Energy Policy Act of 1992. Ethanol is employed most widely, and many countries have established or have planned to promote ethanol gasoline (Niven, 2005). Brazil and the United States were responsible for 89% of the world's ethanol fuel production in 2009 (RFA, 2010). The use of 10% ethanol-blended gasoline is mandated in some U.S. states and cities, and in Brazil, the legal blend has been 25% ethanol-blended gasoline since 2007.

Many researchers have focused on the correlations between ethanol-gasoline blended fuels (3–85 vol%) and pollutant emissions. In general, exhaust total hydrocarbon and carbon monoxide emissions are lower with oxygenated fuels, but comparable or higher NO_x emissions are produced (Hsieh *et al.,* 2002; He *et al.,* 2003). The addition of ethanol also exhibits some adverse effects, e.g., increased fuel consumption (Al-Hasan, 2003) as well as the presence of unburned ethanol and increased aldehyde emissions (He *et al.,* 2003). Considering air toxics, addition of ethanol to gasoline has been observed to reduce benzene, 1,3-butadiene, toluene, and xylene emissions, but may increase acetaldehyde emission (Poulopoulos *et al.*, 2001; Leong *et al.*, 2002; Niven, 2005). Although there have been several studies examining emissions from in-use alternative fuel vehicles, it is worth noting that a traditional spark-ignition engine vehicle can safely use gasoline that contains up to 10% ethanol. Alcohol is completely miscible

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with water in all proportions. This may cause the blended fuel to contain water, and further result in corrosion problems on the mechanical components, especially on the components of older engines (Coetho *et al.,* 1996; Naegeli *et al.,* 1997). A flexible-fuel vehicle (FFV) is required that is equipped to sense the alcohol content of the fuel and make the necessary adjustment in order to use gasoline that has an ethanol content up to 85% (E85) (US DoE, 2008). In other words, E85 is used in engines modified to accept higher concentrations of ethanol.

Aged gasoline vehicles, most of which are not flexible-fuel vehicles, constitute more than 50% of the vehicles used and are responsible for 60–90% of the HC and CO and 50–80% of the NO_x in some megacities such as Mexico City and Bangkok (UNEP and OECD, 1999). The vehicles are also important contributor of the air pollution in urban areas (Srivastava *et al*., 2008; Tsang *et al*., 2008; Zhang *et al*., 2008; Chien *et al.*, 2009). In Taiwan, there are about six million passenger gasoline-using cars. Among these cars, over 40% of the vehicles in use are aged vehicles; their age ranged from 5 to 10 years and their odometer readings are over 85,000 km (Cheng *et al.,* 2005). Most of the on-road gasoline vehicles are not flexible-fuel vehicles. These high-mileage cars contribute to significant air pollutant emissions, as their emissions for CO, NO_x and HC are about 5 to 14 times higher than those of new vehicles (Chiang *et al.,* 2008). However, information related to ethanol blended fuel on the emission reduction of air pollutants for high-mileage (over 80,000 km) cars is rather limited.

Since the possibility of using ethanol-gasoline blends as fuel for vehicles as air quality management tools has been raised, an investigation of the blend effect on high-mileage cars is necessary. At present, biomass fuels cannot replace conventional fuels on a one-for-one basis in unmodified vehicles (Charles *et al.,* 2007). In addition, from the findings of the project that performed by State of Minnesota in 2008, using gasoline with up to 20 percent ethanol (E20) are generally considered non-corrosive and should not accelerate wear for newer engines (1995 and later). Consequently, this study was undertaken to evaluate the impact of ethanol-gasoline blends (3, 10, and 20% by vol) on engine emissions from both low- and high-mileage passenger cars without any engine adjustment. The results were then compared with a reference commercial gasoline. A comprehensive air pollutant emission evaluation, including criteria pollutants (CO, THC, and NO_x), individual volatile organic compounds (VOCs), and carbonyls, was conducted on a chassis dynamometer using the Federal Test Procedure (FTP-75). The ozone formation potential of VOC samples and an inhalation toxicity-based emission ranking for selected air toxics of each test fuel were calculated to provide useful information related to the potential impact of different ethanol-blended gasolines. The results of this study will provide a basis for regulatory agencies to plan an air quality control strategy for mobile sources where aged vehicles are responsible for urban air pollution.

EXPERIMENTAL METHODS

Test Fuels and the Vehicles

Four test fuels were used in this study. One fuel was commercial unleaded gasoline with a research octane number (RON) of 95 with methyl tert-butyl ether (MTBE) as the oxygenated additive; the corresponding fuel oxygen content was 1.6 wt%. The fuel used as the reference fuel (shown as G95 in Table 1) was purchased from a gasoline station operated by the largest petroleum refinery (China Petroleum Corporation, CPC) in Taiwan. The other three fuels, obtained also from the CPC, were ethanol-gasoline blends containing 3% (E3), 10% (E10), and 20% (E20) ethanol by volume; ethanol was added as the oxygenated additive, and the corresponding fuel oxygen contents were 1.1, 3.4, and 6.4% by weight, respectively. These blend samples were analyzed by CPC following the ASTM D2699 standard to obtain the designed RON value (ca. 95). The compositions of these fuels, measured by CPC, are presented in Table 1.

Table 1. Properties of the test fuels.

Test fuels	G95[a]	Ethanol-blended gasoline		
		E3[b]	E10	E20
Research Octane Number	95.4	95.3	95.1	95.2
Reid Vapor Pressure (kPa)	55.5	47.3	54.5	50.0
Gross Heating value (J/g)[c]	2574	2570	2524	2445
Ethanol (vol%)	-	2.9	9.9	18.5
MTBE (vol%)	10.15	0	0	0
Oxygen (wt%)	1.6	1.1	3.4	6.4
Paraffins (vol%)	10.6	8.1	8.8	8.0
Olefins (vol%)	9.9	15.3	13.6	11.6
Naphthenes (vol%)	5.9	6.5	5.7	6.1
Aromatics (vol%)	30.2	30.3	26.1	20.6
Isoparaffin (vol%)	32.7	36.3	35.5	34.9
Benzene (vol%)	0.51	0.58	0.45	0.36

[a] G95: commercial unleaded gasoline, MTBE as the oxygenated additive.
[b] E3, E10, and E15: gasoline containing 3, 10, and 20 vol% ethanol, ethanol as the oxygenated additive.
[c] The gross heating value is the sum of low heating value and latent heat of each test fuel.

Two passenger cars with different accumulated mileage were used in the experiments, including a low-mileage car with an odometer reading of 35,000 km and a high-mileage car with an odometer reading of 140,000 km at the time of testing. The displacements of the test vehicles were 2000 and 1800 cm^3, and the model years were 2005 and 2000 for the low- and high-mileage cars, respectively. The test passenger cars were without any engine adjustment, and the engine types were double overhead camshaft, variable valve timing with intelligence petrol engine, and four-cylinder inline. Both test cars were equipped with a three way catalytic converter (TWC).

Test Procedures

All selected vehicles were tested on a chassis dynamometer, housed in a certified laboratory, following the United State Federal Test Procedure (FTP-75) test cycle. Eight tests of various test fuels were conducted in this study. 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. For fuel changes, the tank fuel was drained; 2 L of the new fuel was added; the engine was idled for ten minutes to allow the new test fuel to flush the fuel supply system thoroughly, and the tank was drained again. 10 L of the new fuel were then added for the subsequent emissions test. The test car was left at room temperature for over 12 hour prior to the start of the testing process. All of the emission factors regarding air pollutants are presented for the entire test cycle.

Three samples of dilute exhaust gas from the constant volume-sampling system (CVS, Horiba, Japan) were collected during the FTP-75 corresponding to the cold start mode (Phase I), the hot stabilized mode (Phase II), and the hot start mode (Phase III). Exhaust samples, taken at the end of each individual phase as well as the end of the entire cycle of the FTP-75, were analyzed for CO, HC, NO_x and CO_2 by auto-monitors (HORIBA MEXA-9200). The background concentrations of these pollutants were also analyzed routinely and deducted from the test results. Background concentrations were about 2 ppm for CO, 3 ppm for THC (as carbon), 0.1 ppm for NO_x and 0.04% for CO_2, which were much lower than those of the sample gas.

VOC samples were also collected at the end of the entire cycle of the FTP-75 test using vacuum sampling cases containing a 10 L Tedlar bag. After samples were taken, the bags were carried within 24 hours to the analysis laboratory for hydrocarbon species analysis. Background samples from the air in the dynamometer laboratory were also collected. VOC samples were preconcentrated using a purge and trap system and then purged and analyzed by a gas chromatograph/mass spectrometer (GC/MS) (Varian 3600 GC, Varian Saturn 2000 MS). The GC was equipped with a fused silica capillary column (60 m at 0.32 mm i.d. with 1 pLm DB-1, J&W) and connected to the MS. All samples were calibrated by a working standard that was blended with standard gas (54 Environ-Mat Ozone Precursor, Matheson) and ultrahigh-purity nitrogen. Quality control samples also were analyzed in the procedure. The R-square (r^2) of the calibration curves of the 54 VOC species was generally higher than 0.995; the relative standard deviation (RSD) was less than 10%, and the accuracy was in the range of 89 ± 6% to 107 ± 9%. The method detection limit ranged from 0.13 μg/m^3 (cyclohexane) to 4.78 μg/m^3 (trans-2-butene).

Carbonyl compounds were collected by pumping exhaust gas through commercially available cartridges filled with 2,4-dinitrophe- nylhydrazine)-coated silica (Supelco). The cartridge was extracted with acetonitrile (Merck), which was applied as the solvent. The extraction solution was injected into a high performance liquid chromatography (Hewlett Packard 1100 series HPLC) equipped with an auto sampler (Hewlett Packard G1313A) and an infrared 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-dimethylbenzene- aldehyde).

Ozone Formation Potential and Toxicity Analysis

The maximum incremental reactivity (MIR) was used to measure ozone formation potential (OFP) from various VOC compounds. The ozone forming potential of a certain VOC mixture in the exhaust is calculated by summing up the concentrations of measured VOC and corresponding MIR factors. The scale developed by Carter (2009) was used to determine the MIR of the individual organic compounds. Since the MIR is a popular method to assess OFP, the detailed calculation method can be found in several previous studies (Kirchstetter *et al.,* 1999; Schmitz *et al.,* 2000; Tsai *et al.,* 2003).

The toxicity assessment was conducted using toxicity-based emission ranking. Six major air toxics, including benzene, toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde, were selected as target pollutants for evaluating the toxicity of the emissions of each test fuel. 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 (within the appropriate categories of cancer, acute, and chronic effects, as shown in Table 2). The total mass emission (g/year) of each pollutant was calculated using an emission factor based on vehicle kilometers traveled (VKT) (Yao *et al*., 2011), and the average VKT for passenger cars with 1801–2400 cm^3 displacement was set at 16,380 km per year in Taiwan (Cheng *et al.,* 2005).

RESULTS AND DISCUSSION

Effects on Criteria Air Pollutant Emission Factors and Fuel Consumption

The emission factors for the criteria air pollutants of the two test cars for the entire test cycle are presented in Table 3. As expected, the criteria air pollutant emissions of the

Table 2. Health benchmarks for cancer, acute, and chronic effects.

Air toxics	Cancer ($\mu g/m^3$)	Cancer data source[b]	Acute ($\mu g/m^3$)	Acute data source[b]	Chronic ($\mu g/m^3$)	Chronic data source[b]
Benzene	1.3E+00	IRIS[*2]	1.3E+03	CARB/OEHHA[*3]	60	CARB/OEHHA
Toluene	---[a]		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

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

[b] The health benchmarks were obtained from the US EPA Integrated Risk Information System (IRIS) (U.S. EPA, 2010); and from the California Environmental Protection Agency, California Air Resources Board and Office of Environmental Health Hazard Assessment (CARB/OEHHA, 2009)

Table 3. Criteria air pollutants and organic compound emissions factors for the ethanol-gasoline blend fuels.

Test vehicle	Test fuel	CO (g/km)	THC (g/km)	NMHC (g/km)	NO_x (g/km)	Total VOC[a] (mg/km)	Alkanes (mg/km)	Alkenes (mg/km)	Aromatics (mg/km)	Carbonyls (mg/km)
Low-mileage vehicle	G95	1.72	0.104	0.097	0.072	480	110	46	298	27
	E3	1.68	0.101	0.095	0.071	462 (4%)[b]	79	86	271	26
	E10	1.52	0.088	0.086	0.068	418 (13%)	189	32	173	24
	E20	1.19	0.074	0.072	0.061	348 (28%)	162	10	153	23
High-mileage vehicle	G95	1.75	0.185	0.164	0.471	1799	327	343	1077	52
	E3	1.73	0.182	0.162	0.472	1501 (17%)	481	141	831	48
	E10	1.62	0.163	0.145	0.451	1431 (20%)	423	122	839	48
	E20	1.32	0.140	0.132	0.417	1327 (26%)	446	132	702	47

[a] EF of total VOCs is the sum of alkanes, alkenes, aromatics, and carbonyls.

[b] Value in parentheses ( ) shows the emission reduction of each ethanol blend as compared to the emissions for the G95.

low-mileage car (LV) were found to be less than that of the high-mileage car (HV). A previous study has indicated that the gradual deterioration of these exhaust catalysts eventually leads to the increase of emissions from in-use passenger cars, especially on the cars above 80,000 km (Ntziachristos and Samaras, 2000). It may be caused by the malfunction of catalyst for high-mileage vehicles, even after warm-up, and result in higher air pollutant emissions than those from low-mileage car.

The highest CO emissions appeared in the G95 test fuel, for which the values were 1.72 and 1.75 g/km for LV and HV, respectively, followed by E3 (1.68/1.73 g/km), E10 (1.52/1.62 g/km), and E20 (1.19/1.32 g/km). CO emissions decreased by 8 to 31% for E10 and E20 compared to that of G95, however, the E3 blend shows no reduction, and the variances are only 1 to 2%. The THC LV and HV emission factors were 0.104/0.185, 0.101/0.182, 0.088/0.163, and 0.074/0.140 g/km for the G95, E3, E10, and E20 test fuels, respectively. The lowest THC emission was observed while using the E20 fuel. Except for the E3 blend, THC emissions decreased by 12 to 29% for ethanol-gasoline blends compared to that of G95. The LV and HV NO_x emission factors were 0.072/0.471, 0.071/0.471, 0.068/0.451, and 0.061/0.417 g/km for the G95, E3, E10, and E20 test fuels, respectively. The reduction of NO_x emissions was relatively smaller, about 4 to 15% for E10 and E20 blends compared to that of G95.

In general, there was a decreasing trend for the three criteria air pollutant emissions as the ethanol content was increased in both test cars, except for the E3 blend. The E20 blend emitted the lowest CO, THC, and NO_x emissions in the test cars. This was attributed to an improved combustion process as a result of the oxygen content in the blends. The more completely combustion lead to lower CO and THC emissions. Moreover, ethanol has a higher latent heat relative to that of the commercial gasoline. The gasoline-air mixture's temperature decreases at the intake stroke and causes low combustion temperature, which in turn affects thermal NO_x production (Poulopoulos *et al.,* 2001; He *et al.,* 2003). It is worth noting that the high-mileage passenger car operated well on ethanol blends up to 20 percent without any engine adjustment and may improve in terms of criteria air pollutant emission abatement.

In addition, it is very difficult to prepare fuels which only change the oxygen content while keeping the other parameters constant and maintaining a constant RON. Therefore, other fuel compositions may also influence exhaust pollutant emissions. According to previous study, CO emissions are related to the fuel aromatic content (Zervas *et al.*, 2003; Yao *et al.,* 2009), THC emissions are related to the aromatics and paraffins content (McArragher *et al.*, 1999), and the fuel aromatics and paraffin contents influence the NO_x emissions (Schuetzle *et al.,* 1994). The other parameters in the blended fuel (e.g., aromatic, paraffins, etc.) may also be one of the reasons for low CO, THC, and NO_x emissions observed in the present study.

Fuel consumption of the ethanol-gasoline blends and reference fuel in the test vehicle shows G95 provided the best fuel consumption, the values are 92.6 and 76.9 mL/km for LV and HV, respectively. E20 blend showed the highest fuel consumption for both test cars (105.3 mL/km for LV and 87.7 mL/km for HV); it increased approximately 14% relative to RF. E3 and E10 blends also showed 2.4 to 8.0% increasing as compared to that of G95. In general, there is a trend that the fuel consumption increases as the ethanol content increases. More fuel must be introduced into the engine cylinder as the content of ethanol increases due to ethanol having a low heating value. Table 1 data show that the heating values of the test fuels were 2574 and 2445 J/g for RF and E20, respectively. E20 shows the lowest heating value among the test fuels, it may contribute higher fuel consumption than other fuels.

Organic Compounds Emissions and Its Ozone Formation Potential

Organic Compounds Emissions

The 69 species of analyzed organic compounds were divided into four groups: alkanes (27 species), alkenes (11 species), aromatics (16 species), and carbonyls (15 species). The total organic compound emission factors, i.e., the sum of the four groups, for the low-mileage car were 480, 462, 418, and 348 mg/km for the G95, E3, E10, and E20 fuels, respectively, and the emission factors of the high-mileage car were 1799 (G95), 1501 (E3), 1431 (E10), and 1327 (E20) mg/km (Table 3). Total organic compound emissions decreased with increasing ethanol content. The results showed that the E20 fuel had the lowest total organic air pollutant emission among the test fuels in both the low- and high-mileage cars. The emission reductions of total organic compounds were 28% (low-mileage car) and 26% (high-mileage car) for the E20 blend as compared to those of the G95.

The organic compound group emissions for the test fuels used in the test cars are shown in Table 3. The ethanol-gasoline blends generally produced high alkanes emissions and low alkenes, aromatics, and carbonyls emissions as compared to those of the G95 fuel for both tested cars. The test results showed a large decrease in alkene emissions with increased ethanol level with the exception of the E3 blend used in the LV. The emission reductions ranged from 31–78% and 59–65% for the LV and HV, respectively.

Aromatic emissions also showed a large decrease with increasing ethanol levels; the reduction values ranged from 9 to 49% for the LV and from 22 to 35% for the HV as compared to those of G95 (298 mg/km for the LV and 1077 mg/km for the HV). Aromatic compounds show high emission fractions of total VOC in all test fuels, especial for the G95 and E3 fuels in the low-mileage car. The aromatics contributions for the G95, E3, E10, and E20 fuels were in order of 62, 59, 41, and 44% and 60, 55, 59, and 53% for the low- and high-mileage cars, respectively. The fuel properties in Table 1 show that the values of the aromatics content levels in the G95 and E3 fuels are around 30% by volume, higher than that of the other two fuels. The high aromatic compound emissions for the G95 and E3 fuels may be attributed to their heavy carbon content.

Carbonyl emissions decreased by 6–16% and 7–10% while using ethanol-blends as fuel; however, the fraction of the carbonyl group increased with increases of ethanol levels in the fuel. The values were 5.6/5.8/6.6% and 3.2/3.3/3.5% for E3, E10, and E20 in the LV and HV, respectively. E20 contributed the highest carbonyls emission fraction among all the test fuels; acetaldehyde and formaldehyde were the major carbonyl compounds with increasing emission of test vehicle exhaust.

In brief, the emissions of total organic compound and each organic compound group presented a reduction for both tested cars while using ethanol-gasoline blends as compared to those of G95. This implied that the ethanol-gasoline blends may also produce organic air pollutant emission improvement in high-mileage vehicles without any engine adjustment.

Ozone Formation Potential

In general, in our study, the use of ethanol-gasoline blends results in a more than 10% reduction in VOC emissions, and this evidence suggests that there may be a positive influence on ozone formation and air quality if there is a large-scale switch to ethanol blends, especially in highly motorized cities; therefore, the ozone formation potential of VOC samples also was investigated using maximum increment reactivity (MIR). Fig. 1 shows the ozone formation potential (OFP, in g-O_3 produced per km) of vehicle exhaust fueled with G95 and the ethanol-gasoline blends for both low- and high-mileage cars.

The ozone formation potentials in the low-mileage car (1.33–2.68 g-O_3/km) were lower than those of the high-mileage car (6.08–9.05 g-O_3/km). The aromatic chemicals showed the highest contribution of ozone formation regardless of fuel types or test car. These results indicated that the sequence of ozone formation potential in the test cycle was E3 > G95 > E10 > E20 for the low-mileage car and G95 > E10 > E3 > E20 for the high-mileage car. Ozone formation potential for low- and high-mileage cars generally decreased while using ethanol-gasoline blends as compared to the OFP of G95, with the exception of the E3 blend used in the LV (which increased by 7%). The results indicated that the use of ethanol-gasoline blends may lead to low ozone-forming potential as compared to commercial gasoline. Both test cars fuelled with E20 showed the lowest ozone formation potential, with the reduction being about 46% (2.48 to 1.33 g-O_3/km) and 33% (9.05 to 6.08 g-O_3/km) for both the low- and high-mileage cars while using the E20 blend fuel. In brief, the data indicated that the ozone-forming potential decreased with the use of ethanol-gasoline blends, with the reduction ranging from 35–46% and 24–33% for the low- and high-mileage cars, respectively.

Emission Factors of Selected Air Toxics

Fig. 2 and Fig. 3 show the organic air pollutant emission factors for each test fuel for the low- and high-mileage cars, respectively. Six major air toxics, including benzene,

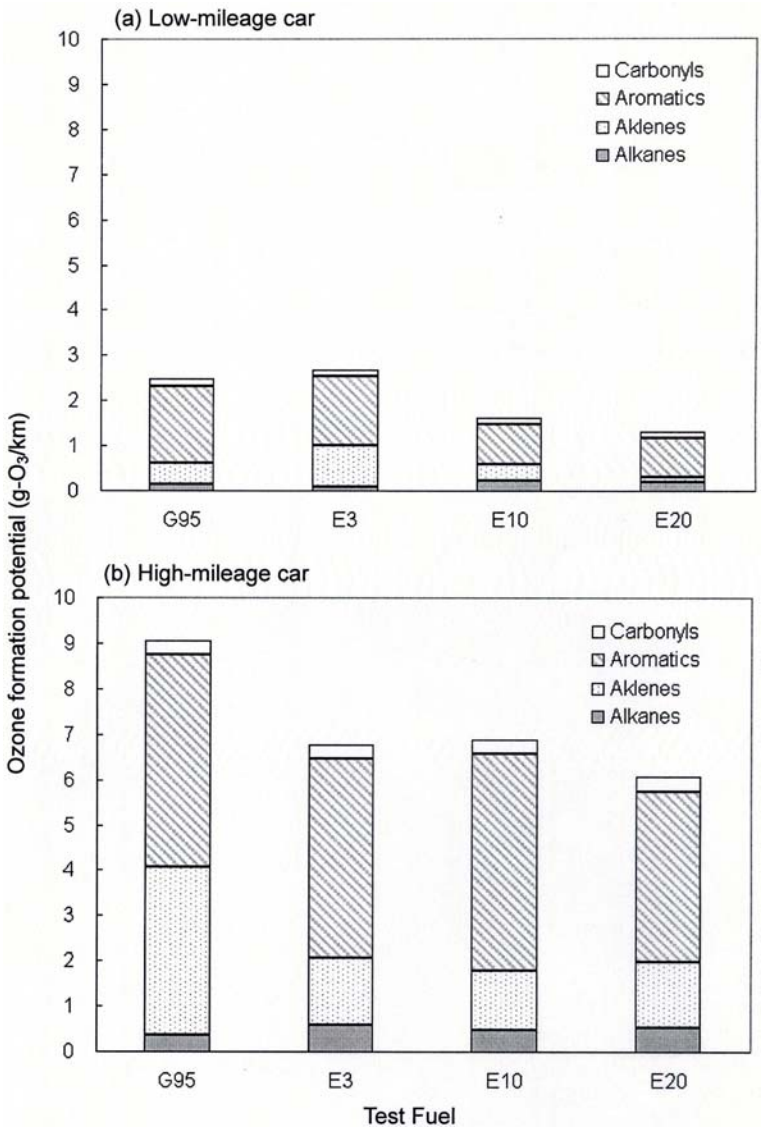

Fig.1. Ozone formation potentials (g-O_3/km) of vehicle exhaust using the unleaded gasoline (G95) and ethanol-gasoline blend fuels (E3, E10, and E20)

toluene, ethylbenzene, xylene (BTEX), formaldehyde, and acetaldehyde, were selected as target pollutants according to the results of previous studies (Tsai *et al*., 2003; Jia *et al*., 2005). Toluene represents the highest emissions among the target air toxics in all the test fuels for both the low- and high-mileage cars. Toluene emissions accounted for 18–24% and 19–26% of the total organic compound emissions for the low- and high-mileage cars, respectively. The emission factors for the low- and high-mileage cars were 109/80/62 mg/km and 386/329/250 mg/km for E3, E10, and E20, respectively, and were 111 and 391 mg/km for G95. In general, benzene, xylene, and ethylbenzene also showed a higher emission than other detected aromatic compounds for all test fuels in the test car exhaust. The emission of benzene, xylene, and ethylbenzene ranged from 19–28, 32–43, and 10–12 mg/km for the low-mileage car, and from 46–61, 81–100, and 40–47 mg/km for the high-mileage car while using ethanol-blended gasoline as fuel. The values for G95 were 29 (benzene), 45 (xylene), and 12 (ethylbenzene) mg/km for the LV and 63 (benzene), 102 (xylene), and 48 (ethylbenzene) mg/km for the HV.

Fig. 4 shows the six toxics emission reduction for each test fuel. Compared to the G95 emissions, the highest emission reduction appeared in toluene, followed by benzene, xylene, and ethylbenzene. Emission reductions for toluene were 28/44% and 16/36% while using E10 and E20 for both the low- and high-mileage passenger cars, respectively, and were 23/34% and 16/27% for benzene, 22/28% and 11/21% for xylene, 13/16% and 6/15% for ethylbenzene. BTEX, as aromatic compounds which can cause harmful effects to bones and blood, presented in large quantities in gasoline vehicle exhaust. These aromatic compounds were reduced by 15–44% while the test cars were fuelled with E20. This indicates that the ethanol in ethanol-gasoline blend fuels plays a significant effect on aromatic emissions, as compared to G95.

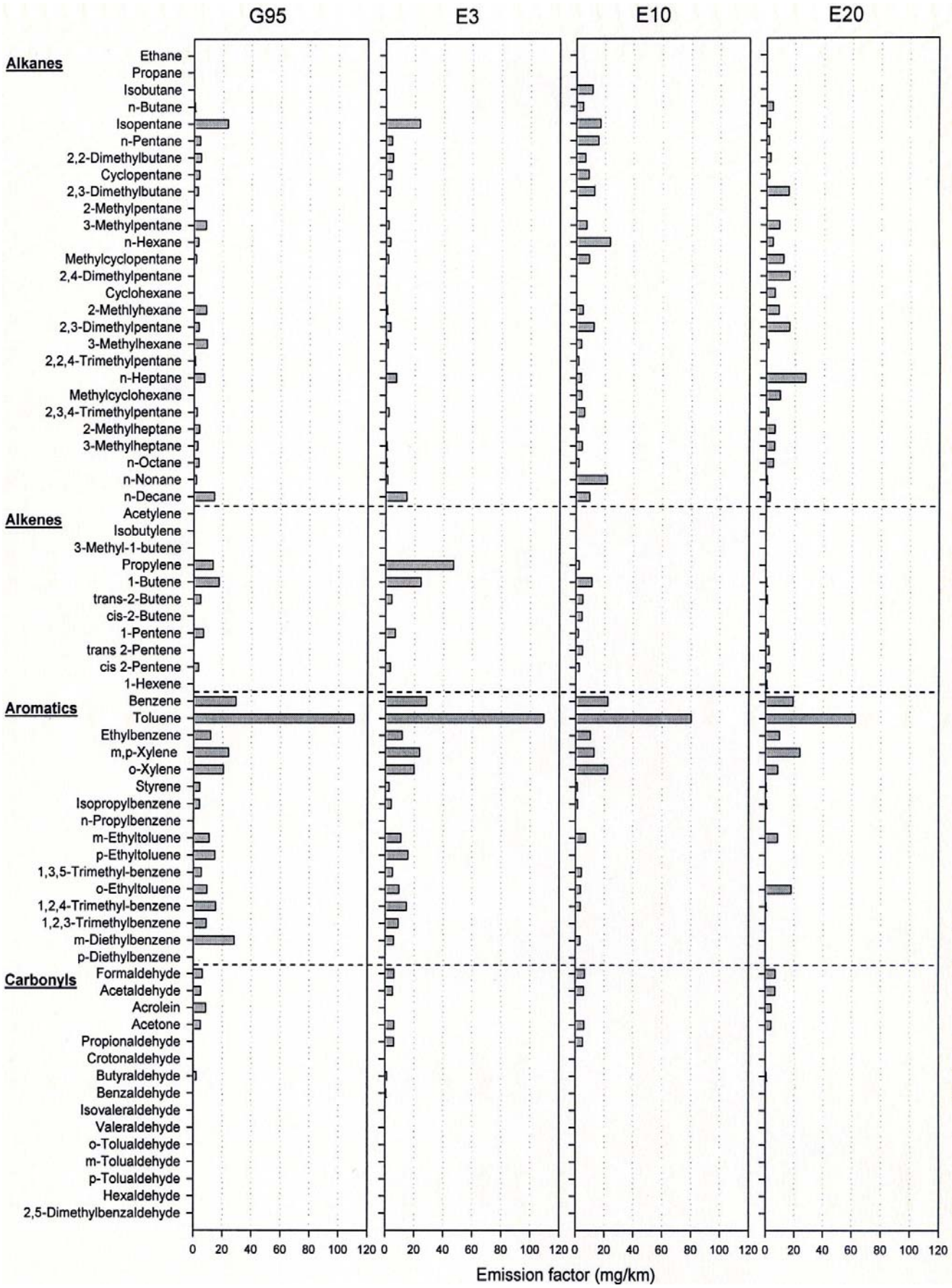

Fig. 2. VOC profile of the test fuels used in the low-mileage vehicle.

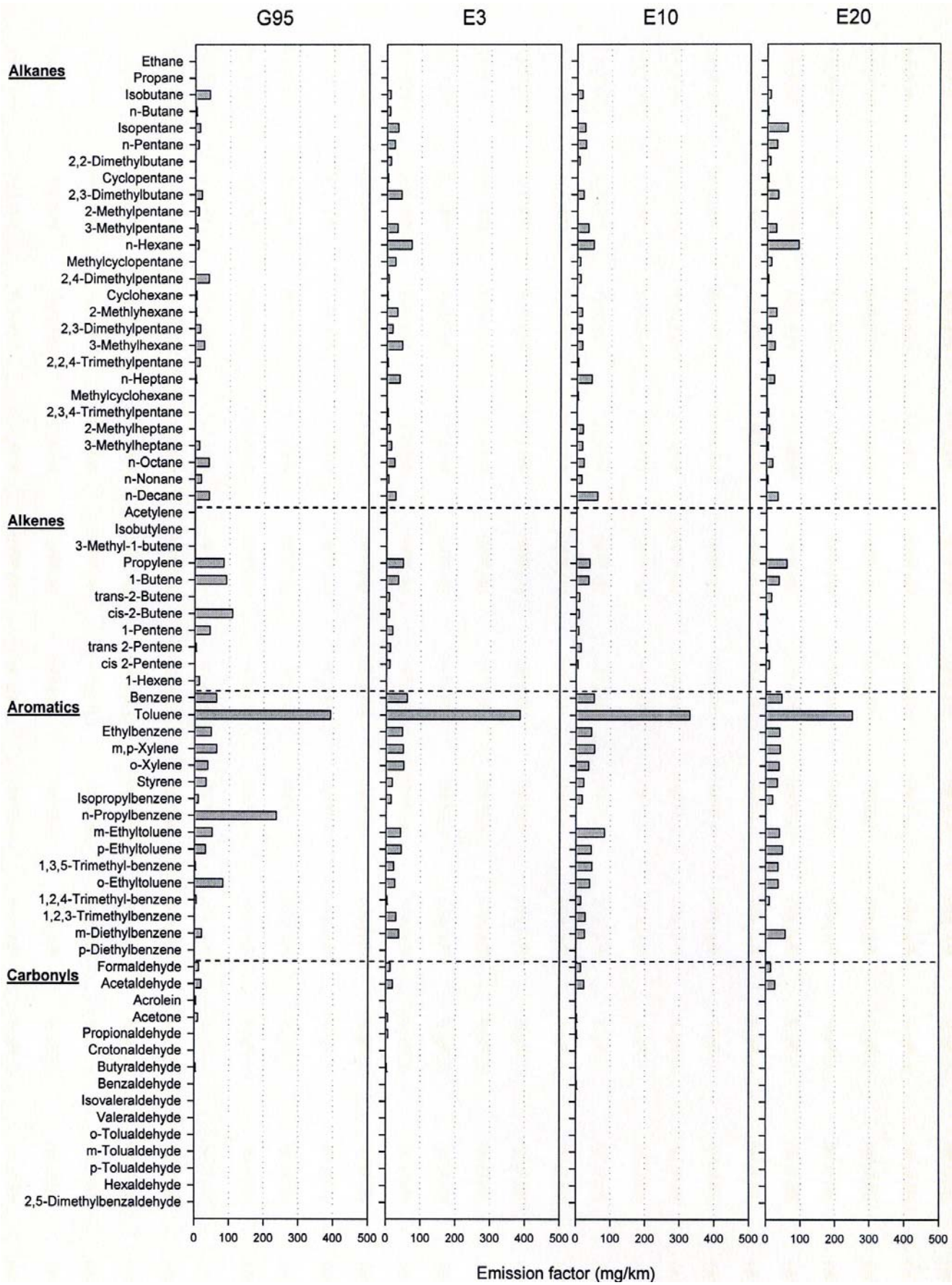

Fig. 3. VOC profile of the test fuels used in the high-mileage vehicle.

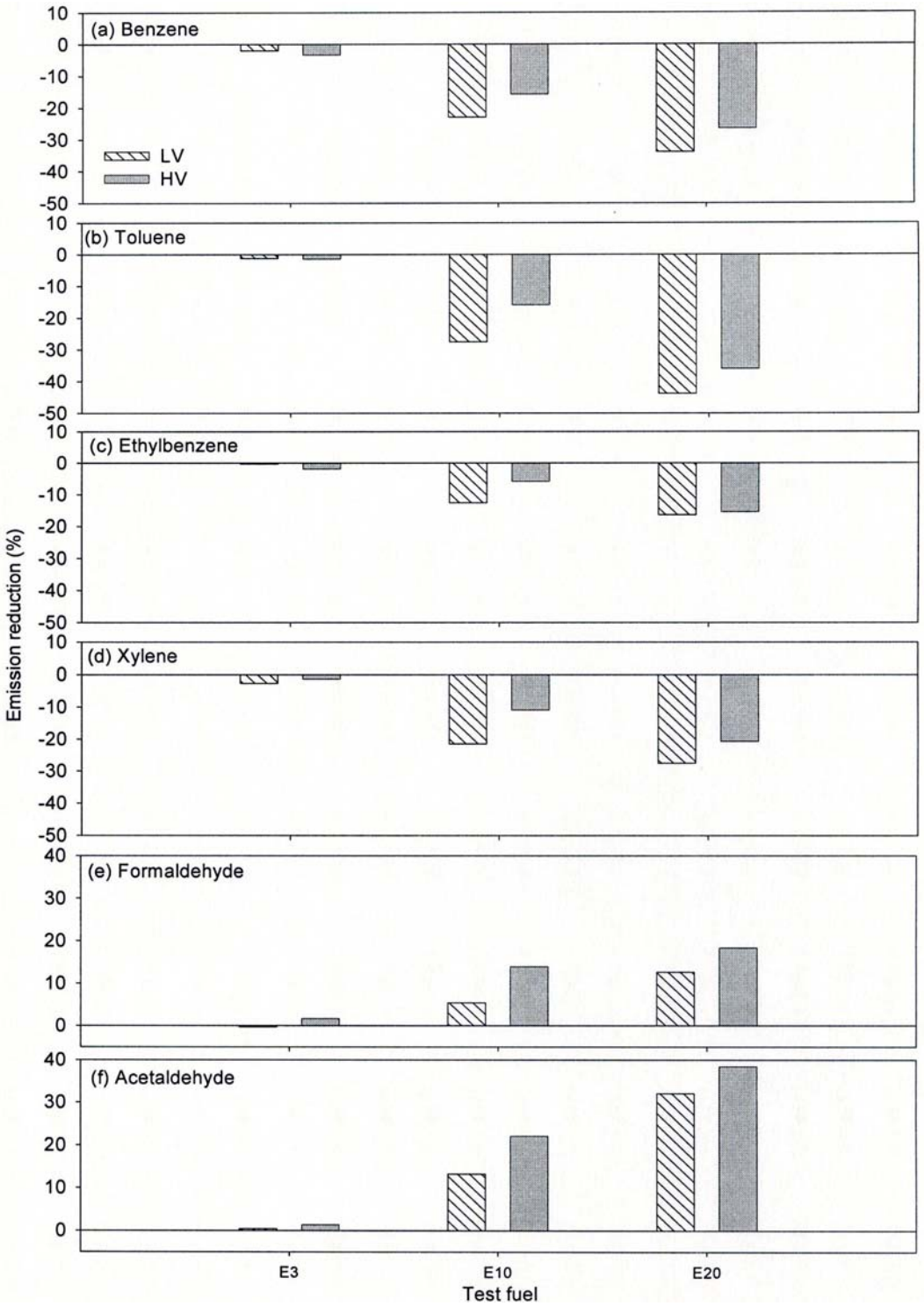

Fig. 4. Emission reduction (%) of major air toxics of the ethanol-gasoline blend fuels as compared to those of the commercial fuel (G95). (The reduction is calculated from emission factor per distance; - implies reduction, + implies increasing)

However, formaldehyde and acetaldehyde emissions increased as there was an increase in the ethanol content in the gasoline. Among all the test fuels, the highest aldehydes emissions can be seen in E20; the emission factors were 7.0/15.3 mg/km of formaldehyde and 6.9/27.3 mg/km of acetaldehyde in the LV and HV, respectively. The aldehyde emission increased by 5–32% and 14–38% for both the low- and high-mileage passenger cars, respectively, since it may be produced through the partial oxidation of ethanol in ethanol-gasoline blend fuel. In addition, alkenes play a significant role in the formation of aldehydes (Altshuller 1991; Grosjean *et al.*, 1996). As mentioned previously, a

large decrease in alkene emissions with increasing ethanol level was found; this may offset some of the increases in direct aldehyde emissions and secondary aldehyde formation from emissions of ethanol-gasoline blends, especially in the case of formaldehyde and acetaldehyde. It is worth noting that the influence of ethanol-gasoline blends on aldehyde emissions was more significant for the high-mileage passenger car.

Preliminary Toxicity Assessment

Six major air toxics, BTEX, formaldehyde, and acetaldehyde, were selected as target pollutants for evaluating the inhalation toxicity-based emissions of each test fuel. Table 4 shows the air toxics mass-based and toxicity-based emissions ranking for the four test fuels. It should be noted that the evaluation of the toxicity-based emissions were limited to the inhalation routes 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 health-effect risk assessment because the emission factor does not equal an exposure estimate.

Both the mass-based and toxicity-based emissions for the six toxics for the test vehicles showed the high-mileage car to have a higher ranking than the low-mileage car. In contrast, the ranking of the test fuels were not consistent between the mass-based and toxicity-based emissions. The mass-based emission of the test fuels showed that the RF had the highest rankings, following by E3, E10, and E20. For three carcinogenic toxics, i.e., benzene, formaldehyde, and acetaldehyde, the ranking of the cancer effects of the test fuels was inconsistent based on the emission ranking. The results show that the fuel with the highest emissions in terms of carcinogenic effects was E20, and the higher mass emission as compared to those of the other test fuels as

Table 4. Ranking of air toxics emissions based on mass and toxicity for ethanol-blended gasolines.

Test Fuel	Low-mileage vehicle				High-mileage vehicle			
Mass-based emission (g/year-car)	G95	E3	E10	E20	G95	E3	E10	E20
Benzene	476	466	367	314	1029	995	867	756
Toluene	1813	1791	1313	1019	6410	6315	5390	4097
Ethylbenzene	192	192	168	161	783	768	737	662
Xylene	732	712	574	530	1670	1647	1486	1323
Formaldehyde	102	102	107	115	211	215	241	250
Acetaldehyde	85	86	97	113	323	328	395	448
Total[a]	3400	3348	2626	2252	10427	10267	9116	7537
Ranking by mass emission								
Benzene	5	6	7	8	1	2	3	4
Toluene	5	6	7	8	1	2	3	4
Ethylbenzene	5	6	7	8	1	2	3	4
Xylene	5	6	7	8	1	2	3	4
Formaldehyde	7	8	6	5	4	3	2	1
Acetaldehyde	8	7	6	5	4	3	2	1
Total[a]	5	6	7	8	1	2	3	4
Ranking by cancer effects								
Benzene	5	6	7	8	1	2	3	4
Formaldehyde	7	8	6	5	4	3	2	1
Acetaldehyde	8	7	6	5	4	3	2	1
Total[a]	7	8	6	5	4	3	2	1
Ranking by acute effects								
Benzene	5	6	7	8	1	2	3	4
Toluene	5	6	7	8	1	2	3	4
Xylene	5	6	7	8	1	2	3	4
Formaldehyde	7	8	6	5	4	3	2	1
Acetaldehyde	8	7	6	5	4	3	2	1
Total[a]	7	8	6	5	4	3	2	1
Ranking by chronic effects								
Benzene	5	6	7	8	1	2	3	4
Toluene	5	6	7	8	1	2	3	4
Ethylbenzene	5	6	7	8	1	2	3	4
Xylene	5	6	7	8	1	2	3	4
Formaldehyde	7	8	6	5	4	3	2	1
Acetaldehyde	8	7	6	5	4	3	2	1
Total[a]	5	6	7	8	1	2	3	4

[a] Total is the sum of six air toxics based on either mass or toxicity.

well as the low cancer health benchmark of formaldehyde and acetaldehyde were responsible for this. The total cancer-based emissions for E20 were higher than those of the other test fuels by 1.04–1.06 times for the low-mileage car, and 1.03–1.13 times for the high-mileage car.

The emission rankings for acute effects were the same as those for the carcinogenic effects because E20 had the highest ranking; the acute-effects-based emissions of E20 were 1.05 to 1.06-fold higher than those of the other test fuels for the low-mileage car, and were 1.03–1.12 times for the high-mileage car. The high emissions and low acute-effect values of formaldehyde and acetaldehyde may be responsible for the high acute effects of E20. However, the highest total chronic-effect emissions of the six air toxics appeared in the RF, following by the E3, E10, and E20 fuels.

In brief, toxicity-based emission rankings for the six air toxics show that E20 had high emissions in terms of cancer and acute effects while the RF had the highest emissions in terms of the chronic effects. Notably, E20 had the lowest total mass-based emissions of the air toxics, but it ranked highest based on cancer and acute-effects among all the tested fuels, especial for the high-mileage car. The results of toxicity-based emission also implied that contributions of BTEX to the acute effects were small in comparison to those of formaldehyde and acetaldehyde for ethanol-blended gasoline but did not indicate distinct effects on chronic-effect emissions. It should be noted that the toxicity-based emissions only considered inhalation exposure; therefore, the emission ranking is not intended to replace health-effect risk assessment, because the emission factor does not equal an exposure estimate. However, this method does provide a simple way to evaluate emission data within a context of toxicity.

CONCLUSIONS

In this study, the effect of ethanol-gasoline blends on air pollutant emissions from different accumulated mileage vehicles was investigated. Two passenger cars with different accumulated mileage, i.e., low-mileage (35,000 km), and high-mileage (140,000 km) cars, were tested. Four test fuels (unleaded gasoline, E3, E10, and E20) were used. The emissions of CO, THC, NO_x, benzene, toluene, xylene, and ethylbenzene were lower with ethanol-gasoline blends, especially in the case of the low-mileage passenger car fuelled with the E20 blend. The high-mileage car also showed a reduction in these emissions while using ethanol-gasoline blends. However, formaldehyde and acetaldehyde emissions increased as the ethanol content in the gasoline was increased. The aldehyde emission increased by 13–32% (low-mileage car) and 22–38% (high-mileage car) while using E10 and E20 as compared to those from commercial gasoline, respectively. The influence of ethanol-gasoline blends on aldehyde emissions was more significant for the high-mileage passenger car.

The emission ranking for the six air toxics showed that E20 had the lowest total mass-based emissions of the air toxics, but it ranked high based on cancer and acute-effects among all the tested fuels, especially in the case of the high-mileage car. The high mass-based emissions and low health benchmark values of formaldehyde and acetaldehyde possibly contributed to the high toxicity-based emissions for E20. The results of ozone-forming potential shows that using ethanol-gasoline blends may lead to low ozone-forming potential (24–46%) as compared to commercial gasoline, even in high-mileage cars.

In summary, the two test inflexible-fuel vehicles, having both low- and high-mileage, operated well on ethanol blends up to 20 percent. Ethanol-gasoline blends may result in a mitigation effect on exhaust emissions of the criteria pollutants, most organic compounds and on ozone-forming potential. The high-mileage car also showed an emission decrease while using ethanol-gasoline blends. In contrast, the toxicity-based emission ranking for the six air toxics of ethanol-gasoline blends showed high emission based on cancer and acute-effects. For the purpose of criteria air pollutant emission reduction and ozone air quality improvement, the ethanol-gasoline blends are recommended for use as an alternative fuel in in-use passenger cars; ethanol content up to 20% in gasoline (E20) still suitable to be used in car. However, in view of toxicity, the use of ethanol-gasoline blends needs more evaluation, especially in the case of high ethanol content.

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