THE EMISSION OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR BAPeq FROM A MOTORCYCLE ENGINE FUELED LEAD-FREE GASOLINES BLENDED ALKYLATE ADDITIVES

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Abstract
Emission characteristics from a new four-stoke motorcycle engine fueled lead-free gasoline [including 92-lead-free gasoline (92-LFG) and 95-lead-free gasoline (95-LFG) both provided by two petroleum companies in Taiwan] blended various fraction (10 ~ 50%, v/v) of alkylate additives were investigated at different cruising speeds on a chassis dynamometer. The concentrations of 21 individual polycyclic aromatic hydrocarbons (PAHs) emitted from the exhaust of engines were primarily analyzed by a gas chromatography/mass spectrometry (GC/MS). The total PAHs and their corresponding benzo[a]pyrene equivalent (BaPeq) emission amounts were estimated and calculated in this study. The results show that adding various fractions of alkylate in gasoline-powered engines would basically decrease the both emission of total PAHs and BaPeq in the exhaust. Adding alkylate in lead-free gasolines, the total PAHs average depletion ratios were between 4.72~ 51.2% and 9.22 ~ 30%, respectively for 92-LFG and 95-LFG powered engines. Simultaneously, BaPeq average depletion ratios were between 20.0 ~ 40.2% and 16.2 ~ 25.0%, respectively for 92-LFG and 95-LFG powered engines. The alkylate blended lead-free gasoline can somewhat improve emissions of the hazardous air pollutants.

Introduction
Two kinds of lead-free gasoline, including 92 lead-free gasoline (92-LFG) and 95 lead-free gasoline (95-LFG) are the major fuels currently used in Taiwan area for spark-ignition engine vehicles. Furthermore, motorcycle also is the widespread used traffic tool and its estimated number will exceed 18 millions until the end of 2007 in Taiwan[1]. PAHs and their derivatives are associated with the incomplete combustion of organic materials, such as the burning of gasoline in motor vehicles also including motorcycles. For gasoline-powered engines, the emission of PAHs occurs through many factors, including the chemical compositions of fuels. Alkylate is one of popular compositions which to be recognized as “the perfect gasoline” to be adding in gasoline. It is revealed that replacement of conventional petroleum with alkylate should have a higher priority for small engines than cars[2]. The purpose of this study was to use different fractions of alkylate as gasoline additive to assess the effect on PAH emissions and their BaPeq. The results obtained from this study will enhance further examination of appropriate type of lead-free gasoline to reduce the risk from motorcycles.

Materials and Methods

1. Fuels and Alkylate additive.
Two kinds of commercial gasoline, including 92-LFG and 95-LFG from China Petroleum Corporation (CPC) and Formosa Petrochemical Corporation (FPCC), were adopted as test and base fuels in this study. blended. Three different fractions of isooctane as alkylate, 10%, 30% and 50% by volume, was adding in C92-LFG, F92-LFG, C95-LFG and F95-LFG, respectively, named C92-I10 ~ F95-I50. The compositions and specifications of eight test gasolines are shown in Table 1.

Table. 1 .Properties of the test fuels.

Fuel parameter	C92-I10	C92-I30	C92-I50	C95-I10	C95-I30	C95-I50	T92-I10	T92-I30	T92-I50	T95-I10	T95-I30	T95-I50	Analytical method ASTM
RVP (kPa)	50.4	43.3	35.8	50.0	43.3	35.0	46.2	39.9	32.8	48.8	41.0	33.2	D5191
Distillation (at 15 ℃, g/ml)	0.7386	0.7290	0.7195	0.7481	0.7366	0.7248	0.7350	0.7263	0.7176	0.7357	0.7266	0.7177	D4052
Net Heat Value (cal/g)	10287	10437	10475	10219	10306	10356	10428	10522	9571	10397	10417	10474	D240
Octane Number (RON)	93.1	95.0	96.7	96.1	97.1	98.3	93.2	94.8	96.5	95.7	97.1	98.2	D2699
MTBE (wt%)	8.43	6.61	4.74	8.65	6.76	4.75	1.74	1.37	0.99	6.91	5.39	3.89	D4815-E
Total O (wt%)	1.59	1.25	0.89	1.57	1.23	0.86	0.32	0.25	0.18	1.25	0.98	0.70	D4815-E

2. Motorcycle and dynamometer

The motorcycle tested in this study for the investigation of PAH emission is a new four-stroke injection motorcycle produced by Sang-Yang Motor, which is one of the most popular type in Taiwan. A testing gasoline-powered motorcycle engine, total displacement of 124.6 mL, compression ratio 8.6:1, was installed on a MAHA LSP2000 chassis dynamometer to simulate 3 driving modes including idling, 30 km/hr and 50 km/hr cruising speeds. Each mode was operated 3 times for 12 different fuels.

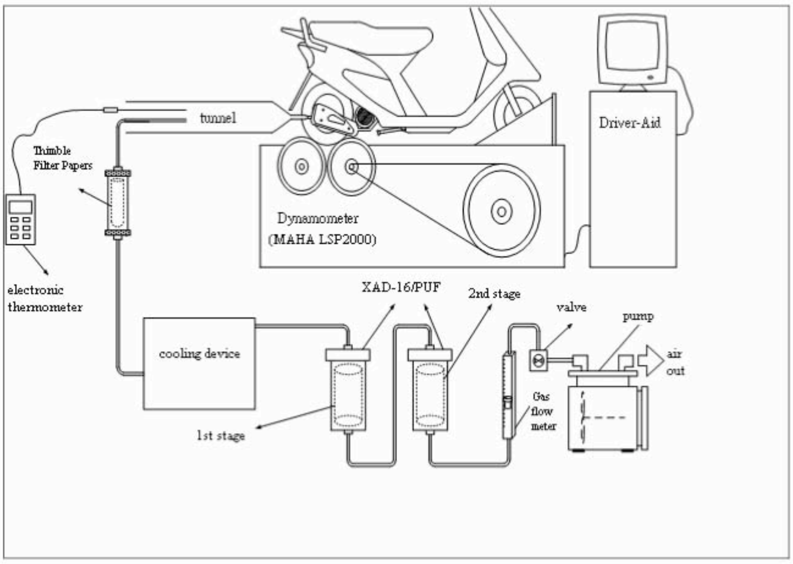

Fig. 1 .Schematic diagram of the test equipment and gas sampling system.

3. PAH analysis

After sampling, both glass fiber filter and cartridge were Soxhlet extracted with a mixed solvent (*n*-hexane and dichloromethane, v:v = 1:1, 500 mL each) for 24 hrs. The extract was concentrated by purging with ultrapure nitrogen (flow rate 1.0 L/min) to 2 mL, which was followed by the cleanup procedure to remove pollutants that would coelute with PAHs from the gas chromatography (GC) column. The cleanup procedure was done in a cleanup column. The column (internal diameter 1 cm) contained approximately 5 g of glasswool at the bottom, filled by 17 g of 6% deactivated silica gel (mixed with 60 mL *n*-hexane) in the middle section, and topped with 1 cm of anhydrous sodium sulfate. Before cleanup, we added 60 mL *n*-hexane to wash the sodium sulfate and the silica gel. Just before the sodium sulfate layer was exposed to the air, the elution of *n*-hexane was stopped and the eluant was discarded. During cleanup, the concentrated sample was transferred onto column, and the wall of the vessel was rinsed twice with 2 mL of *n*-hexane which was also added to the column. Then, 200 mL 6% ethylether in *n*-hexane was added to the column and allowed to flow through the column at a rate of 3–5 mL/min, and the effluent was collected. The collect effluent the cleanup procedure was reconcentrated to 0.5 mL with nitrogen. We used a GC (model 5890A; Hewlett-Packard, Wilmington, DE, USA) coupled with a Hewlett-Packard capillary column (HP Ultra 2, 50 m ×0.32 mm ×0.17 μm), a mass selected detector (MSD) (Hewlett-Packard model 5972), and a computer workstation for the PAH analysis. We determined the masses of molecular and fragment ions of PAHs using the scan mode for pure PAH standards. We identified PAHs using the selected ion monitoring (SIM) mode. The GC/mass spectrometer (MS) was calibrated with a diluted standard solution of 16 PAH compounds (PAH Mixture-610M; Supelco, Bellefonte, PA, USA) plus five additional individual PAHs obtained from Merck (Darmstadt, Germany). These 21 PAH compounds grouped by the number of rings are as follows: naphthalene(Nap) for 2-ring; acenaphthylene(AcPy), acenaphthene(Acp), fluorene(Flu), phenanthrene (PA), and anthracene (Ant) for 3-ring; fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), and chrysene (CHR) for 4-ring; cyclopenta[c,d]pyrene (CYC), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo(a)pyrene(B[a]P), perylene(PER), dibenzo[a,h]anthracene(DBA), benzo[b]chrycene(BbC) for 5-ring; indeno[1,2,3,-cd]pyrene(IND), benzo[ghi]perylene (Bghip) for 6-ring; and, coronene (COR) for 7-ring.

Results and Discussions

1. PAH emission concentration from 92-gasoline-powered motorcycles. Figure 2 showed the total-PAHs emission concentration in the exhaust of motor engines fueled by various 92-gasolines. For CPC fuels, the total-PAHs emission concentration including C92-LFG, C92-I10, C92-I30, and C92-I50 gasoline-powered engines are 7750, 7640, 2900, and 1700 µg/Nm^3. For Another four FPCC based gasolines including F92-LFG, F92-I10, F92-I30 and F92-I50, the total-PAHs Emission concentration in the exhaust are 6030, 5940, 5180, and 5020 µg/Nm^3, respectively. By the comparison of CPC and FPCC based gasolines, adding alkylate in C92-LFG would reduce the total-PAHs emission more significant than FPCC based gasolines. Under the parameters in table 1, the only two parameters for CPC and FPCC based gasoline-powered engines, the content of MTBE and total oxygen are quite different. Raising the content of alkylate will reduce the emission of PAH in the exhaust of motorcycles.

2. PAH emission concentration from 95-gasoline-powered motorcycles. The total-PAHs emission concentration in the exhaust of motor engines fueled by various 95-gasolines. For CPC fuels, the total-PAHs emission concentration including C95-LFG, C95-I10, C95-I30, and C95-I50 gasoline-powered engines are 8060, 7270, 7100, 6570 µg/Nm^3. For Another four FPCC based gasolines including F95-LFG, F95-I10, F95-I30 and F95-I50, the total-PAHs Emission concentration in the exhaust are 7550, 6900, 5380, 5330 µg/Nm^3, respectively (Figure 3). The same trend of reducing PAH emission concentration are found in 95-gasoline-powered engines as 92-gasoline-powered engines. However, less PAH emission concentration reduction in the exhaust of motorcycles than CPC 92-gasolines.

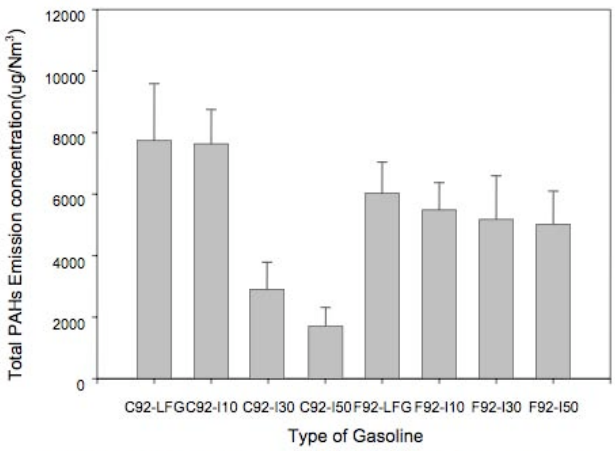

Fig. 2 .Total PAH Emission Concentration from 92-Gasolime-Powered motorcycles.

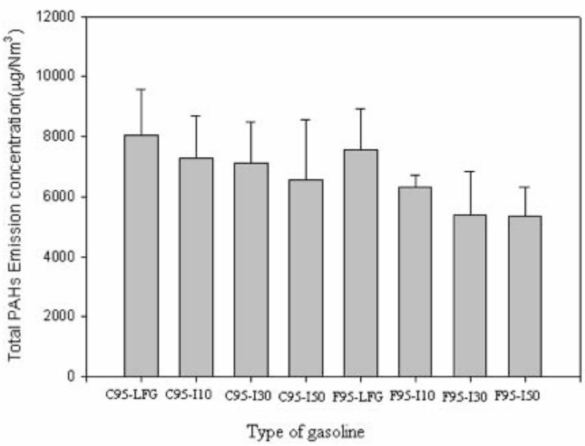

Fig. 3 .Total PAH Emission Concentration from 95-Gasolime-Powered motorcycles.

3. PAH and BaPeq depletion percentage in the exhaust of motorcycles (Figure 4 and 5). Adding alkylate in 92- and 95-gasoline-powered motorcycle is to exam the possible depletion of “perfect gasoline” than common commercial gasolines did. For 92-LFG motorcycle engine, adding alkylate will raise the PAH emission depletion percentage from 5% to 55%. Furthermore, the adding ration of alkylate is proportioned as PAH emission depletion. However, for 95-LFG engines, adding alkylate is also to reduce the PAH emission concentration. The depletion of PAH emission is found from 10% ~ 22% and also is proportioned as adding ratios of alkylate. The result reveals that adding alkylate will help to reduce PAH emission and contribution in the exhaust of motorcycle engine. However, using BaPeq to evaluate the content of alkylate in gasoline, for 92-LFG motorcycle engine, adding alkylate will raise the BaPeq emission depletion percentage from

20% to 40% for I10 to I50. For 95-LFG motorcycle engine, the better reduction of BaPeq is under adding 30% of alkylate.

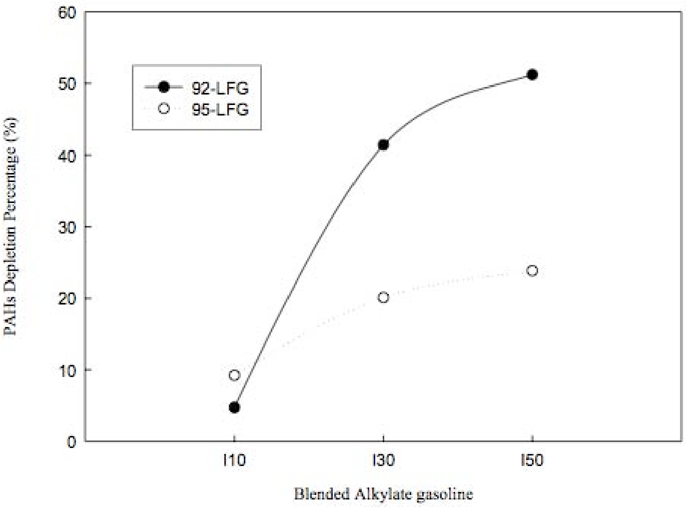

Fig. 4 .The Average PAH Depletion Percentage for the different Alkylate Adding fractions.

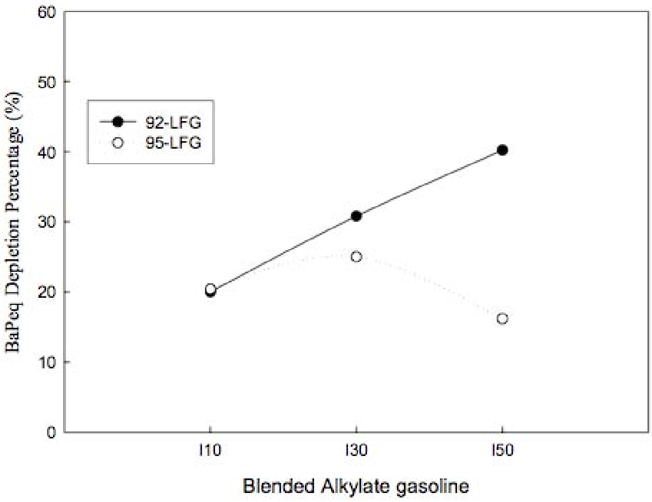

Fig. 5 . The Average BaPeq Depletion Percentage for the different Alkylate Adding fractions.

Conclusions

In this study, emitted by C92-LFG engine had highest total PAHs concentration for 7750 ug/Nm^3 between the six gasolines with and two gasolines without adding isooctane additive. The other gasoline-powered engines had 7640 ug/Nm^3 (C92-I10), 6030 ug/Nm^3 (T92-LFG), 5490 ug/Nm^3 (T92-I10), 5180 ug/Nm^3 (T92-I30), 5020 ug/Nm^3 (T92-I50), 2900 ug/Nm^3 (C92-I50) and 1700 ug/Nm^3 (C92-I30). The total PAHs emission from C95-LFG had highest concentration (8060 ug/Nm^3). The PAH emission concentration of other 95-motorcycle engines had 7550 ug/Nm^3 (T95-LFG), 7270 ug/Nm^3 (C95-I10), 7100 ug/Nm^3 (C95-I30), 6900 ug/Nm^3 (T95-I10), 6570 ug/Nm^3 (C95-I50), 5380 ug/Nm^3 (T95-I30) and 5330 ug/Nm^3 (T95-I50). For most different engines, the PAH was depleted during the processes of engine combustion. Moreover, the isooctane additives will reduce the health risk caused by BaPeq, also has adverse effect for the use in the two gasolines.

Acknowledgements
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