THE EFFECT OF GASOLINE ADDITIVES ON BTEX EMISSIONS FROM LIGHT-DUTY VEHICLE

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Abstract: Gasoline additives are broadly applied for improving vehicle performance or solving specific problems. Based on their type of claims, six gasoline additive products were randomly selected to run FTP-75 test, and gaseous emissions in the exhaust of the test vehicle were collected to determine the concentrations of CO, HC, NOx, and BTEX. The results showed that all tested gasoline additives were able to reduce the emissions of regulated pollutants averaging a 7.1% deduction for CO, 25.6% for HC, and 11.9% for NOx. The use of GA1 additive, an octane booster, could enhance 19.3 % of benzene emission, 30.8 % for toluene, 17.1 % for ethylbenzene, and slightly reduce 1.8% of xylene emission in the engine exhaust. In this study, it is suggested that the use of gasoline additives should be carefully controlled to avoid imposing more BTEX emissions to the environment.

Key Words: Additive, FTP test, BTEX, Exhaust

1. Introduction

Tetraethyl lead was first introduced as fuel additive to reduce engine knocks in 1921 [1], however their continual use was banned later because of the resulting air pollution from vehicle exhaust. Instead of alkyl lead additives, methyl tert-butyl ether (MTBE) has become the most widely used unleaded gasoline additive since the late 1970s. MTBE and ethanol belonging to oxygenates are most commonly employed to enhance or maintain the adequate octane rating [2]. Moreover, the reformulated gasoline (RFG) was mandated to add either 11% MTBE or 5.7% ethanol, and limit benzene and aromatic levels to less than 1% and 27% by volume [1]. All oxygenated fuels were found able to reduce the emission of carbon monoxide (CO) and unburned hydrocarbons (HC) from automobile exhausts [3], and the reported reductions of CO emission were from 10 to 46.5% [4-6].

In order to satisfy a host of regulatory requirements and consumer needs, gasoline is changing to make it cleaner. The properties of commercial gasoline are influenced by the origin of the crude oil, the refinery operation, and the additive blending. Both gasoline composition and engine design can influence the emission of organic compounds and affect the amount and location of engine deposits. Thus, engine cleanliness is a vital factor of performance improvements on consuming less fuel and producing fewer emissions. The fate of engine operation is pointed to carbonaceous deposits that would form in precision fuel metering devices and throughout the engine's induction system to impair drivability, reduce power, increase fuel consumption, and increase exhaust emissions. Besides of blending their formula additives in commercial gasoline by oil companies, some car divers were used to add the retail gasoline additives for improving vehicle performance or solving specific driving problems such as hesitation, knocking and rough idle. There are more than fifty gasoline additives on the retail markets in Taiwan, and their label claims include restoring lost horsepower, maintaining octane requirement, cleaning fuel injector, cleaning carburetors, cleaning intake valve, cleaning combustion chamber deposits, reducing hesitation, reducing stalling, reducing rough idle, reducing knocking, lubricating engine, helping cold engine start, removing water content, reducing emissions, …etc. The packages of gasoline additives are evolving to be more powerful, customized and more cost-effective nowadays, and they are expected to prevent and control deposits in the fuel metering and intake systems, and concurrently improve performance in the combustion chamber.

Several active ingredients has been identified in different types of gasoline additives, including polyetheramine (PEA), Polyether pyrolidone (PEP), polyisobutylene (PIB) amine, and methylcyclopentadienyl manganese tricarbonyl (MMT) [7]. According to supplier literature, the lowest recommendations for one tank clean-up were 140 ppm PIB or 375 ppm PEA for fuel injectors or ports, 166 ppm PIB or 375 ppm PEA for intake valve, and 2000 ppm for combustion chamber deposits. Nonetheless, we don't know much regarding the impact of exhaust emissions imposed by other active ingredients in gasoline additives such as PEA, PEP, and PIB. Usually, Gasoline was formulated with alcohols and other oxygenates for the purpose of reducing CO, oxides of nitrogen (NOx) and particulate matter emissions, but they can increase the emission of formaldehyde or decrease those of the other aldehydes [8]. Thus, the overall quality of the fuel after blending is often a compromise among its various properties, such as volatility, anti-knocking, solvence, oxygen, sulfur, and aromatic contents.

Based on our survey, 30% of car drivers have experienced the use of retail gasoline additives in Taiwan. The environmental impacts of exhaust emissions imposed by gasoline additives have raised our concerns. The aromatics such as benzene, toluene, ethylbenzene, and xylene (BTEX) are recognized as both toxic pollutants and precursors of photochemical contamination, and their presence in exhaust emissions should be confirmed with the use of assorted gasoline additives. This study employed the FTP-75 test to simulate an urban driving condition of gasoline engines, and the concentrations of CO, HC, NOx, and BTEX in vehicle exhaust were determined as adding selected gasoline additives. In this study, the effect of gasoline additives on BTEX emissions was investigated.

2. Materials and Methods

2.1 Gasoline Fuels and Additives

Taiwan-produced commercial fuel 95-LFG was used as target fuel for the gasoline engine. According to more than ten types of label claims, the retail products of gasoline additives were sorted into two main classifications as engine cleaning and performance enhancement. Six gasoline additives were randomly selected out of thirty brand products for test, and the selection of tested gasoline additives should avoid focusing on single label-claim category or few brand products. Among tested gasoline additives, octane booster GA1 and multi-purpose additive GA 6 fall into the label-claim category of performance enhancement, while the others belong to the label-claim category of engine cleaning. The detailed label claims of the tested gasoline additives are summarized in Table 1. Prior to each set of experiment, the additives were separately premixed with 95-LFG at the suggested mixing ratio according to each product's applying description.

Table 1. Type and label claims of tested gasoline additives

No.	Type	less fuel use	restore horsepower	help starting	remove water	clean intake manifold	clean fuel injector	clean carburetor	reduce knocks	reduce rough idle	lubricate engine
GA 1	**octane booster**		x						x		
GA 2	**intake valve cleaner**			x		x					x
GA 3	**fuel injector cleaner**		x		x		x				
GA 4	**fuel system cleaner**		x		x	x	x				
GA 5	**carburetor cleaner**	x	x					x		x	
GA 6	**combo**	x	x			x	x	x			x

2.2 Vehicle Test

The tested gasoline powered engine was Nissan New Sentra1.6L jet engine with four cylinders, four stokes, natural-aspirated, PFI injection, bore and stroke (76 × 88 mm^2), total displacement of 1597 ml, maximum horsepower 110 HP at 6000 rpm and maximum torque 15 kg-m at 4000 rpm. The Schenck W-130 chassis dynamometer at Refining and Manufacturing Research Center, Chinese Petroleum Corp., Taiwan was used for this study. The chassis dynamometer is capable of switching promptly from negative to positive torque values, and it can be operated in both transient cycle and steady-state modes.

Light-Duty vehicle tests were conducted by following the 1975 Federal Test Procedure (FTP-75) to simulate an urban driving condition of gasoline engines. The basic FTP driving schedule is LA-4 urban cycle consisting of cold start phase for 505 seconds, stabilized phase for 867 seconds and hot start phase for 505 seconds [9]. Before testing a gasoline additive, the entire engine system was first cleaned, including gas tank, fuel filling route, cylinder, and the manifold of inlet air and exhaust. After changing both lubricating oil and oil filter, the test engine was set overnight for the preparation of each experiment.

2.3 Exhaust Collection

Sampling method of collecting gaseous emission in the exhaust of the test vehicle during the FTP-75 transient cycle is referred to USEPA testing method NVFEL 730E [10]. The Horiba 9000 series constant volume sampling system was used to collect the exhaust emissions. A portion of the exhaust gas mixtures were separately collected in 1 liter tedlar bags during each phase of the FTP-75 test, and the ambient air was collected as well. After the sample has been collected, it is transferred to analyzers where the concentrations of HC, CO, and NOx in the sample bag are determined. For BTEX analysis, the collected exhaust gas samples are ready for subsequent analysis.

2.4 Sample Analysis

Each BTEX-containing gas samples were analyzed using a combined automatic thermal desorption unit (Tekmar Aerotrap 6000) with gas chromatograph (HP5890) fitted with MSD (HP5971). The thermal desorption unit equipped with tenax TA internal trap was operated as the following sequence: (1) initial sample desorption at 250 for 10 min, (2) cryofocusing sample at -150 , (3) trap desorption at 250 for 4 min, (4) trap bake at 280 for 10 min, (5) subsequent injection of samples into the GC-MS system. The injected samples were then separated on J&W

DB-1 capillary column (60m L × 0.32 mm I.D. × 1 μm thick) and detected by MSD.

2.5 Data Interpretation

The concentrations are converted into grams per kilometer for each of the target pollutants measured by calculating the mass emission rates collected during each phase of the FTP-75 tests. The cold start and hot start bags are weighted 0.43 and 0.57 respectively. Once the mass emissions for each test phase are determined, the emissions of the target pollutants in grams per kilometer based on a 12 km test are calculated using the following formula:

$$M_i = (0.43M_{ict} + 0.57M_{iht} + M_{is}) \div 12 \qquad (1)$$

where, M_i: weighted mass emissions of each pollutant in grams per vehicle kilometer.

M_{ict}: mass emission as calculated from the transient phase of the cold start test, in grams per test phase.

M_{iht}: mass emission as calculated from the transient phase of the hot start test, in grams per test phase.

M_{is}: mass emission as calculated from the stabilized phase of the cold start test, in grams per test phase.

Table 2. Emissions of regulated pollutants HC, CO and NOx during FTP-75 testing of gasoline additives

No.	HC (g/km)	CO (g/km)	NOx (g/km)
95-LFG*	0.219	1.3	0.27
GA1	0.168	1.3	0.26
GA2	0.169	1.2	0.23
GA3	0.156	1.17	0.25
GA4	0.16	1.16	0.21
GA6	0.161	1.21	0.24

*95-LFG is the blank test without adding any commercial additives

3. Results and Discussion

3.1 Emissions of Regulated Pollutants

The emissions of all regulated pollutants including HC, CO and NO_x in the engine exhaust during the FTP-75 test for each tested gasoline additive and the fuel 95-LFG were summarized in Table2.

The emissions of HC, CO and NOx are 0.219 g/km, 1.3 g/km and 0.27 g/km when using the fuel 95-LFG only, and this measurement is regards as the result of the blank test. For all tested gasoline additives, the emissions of HC in the engine exhaust range between 0.156 g/km and 0.169 g/km with an average 25.6% reduction efficiency. The measurements of CO emissions in the engine exhaust were between 1.16 g/km and 1.3 g/km with an average 7.1% reduction efficiency, while the emissions of NOx were between 0.21 g/km and 0.26 g/km with an average 11.9% reduction efficiency. As compared with the measurements of 95-LFG, all tested gasoline additives appear capable of improving combustion efficiency of the engine, and reducing the emissions of regulated pollutants from vehicle exhaust. In addition, the improvement on reducing HC emissions was especially notable with the use of gasoline additives.

3.2 Emissions of BTEX

As applying each tested gasoline additives and the fuel 95-LFG, the emissions of benzene, toluene, ethylbenzene and xylene in the engine exhaust during the FTP test were compared in Fig. 1 to 4, respectively. In the blank test, the emissions of benzene, toluene, ethylbenzene and xylene are 2.69 mg/km, 6.17 mg/km, 1.81 mg/km, and 7.13 mg/km as using the fuel 95-LFG only. For the tested gasoline additives, the emissions of benzene were determined in the range of 0.63 and 3.21 mg/km, toluene ranging 2.89 and 8.07 mg/km, ethylbenzene ranging 1.29 and 2.23 mg/km, and xylene ranging 3.85 and 7.0 mg/km. It is observed from the figures that the enhancement of BTEX emissions by adding GA1 additive is predominant among all tested gasoline additives. Adding GA1 additive could enhance 19.3 % of benzene emission, 30.8 % for toluene, 17.1 % for ethylbenzene, and slightly reduce 1.8% of xylene emission in the engine exhaust. In Fig. 3, a slight enhancement (6.1 %) of ethylbenzene emission was also observed as applying GA6 additive. Among all tested gasoline additives, GA 4 additive has shown its superiority on suppressing BTEX emissions from the combustion engine.

Our concerns regarding gasoline additives' environmental impacts were confirmed that some gasoline additives do enhance the BTEX emissions from vehicle exhaust. For example, GA1 additive aiming at restoring lost horsepower could contain more aromatic contents than other types of gasoline additives. In 2007, Taiwan EPA plans to introduce more stringent standards for automobile gasoline. The 2007 Control Standards for the Composition of Gasoline and Diesel (draft) has added control standards of aromatic hydrocarbons levels and olefin levels in gasoline, which sets the upper bound of volume content at 36 % for aromatic hydrocarbons and 18 % for olefins. From this point of view, the level of aromatic hydro- carbons within gasoline additives has to be regulated because their abundance of aromatic hydrocarbons may impose an adverse impact on BTEX emissions.

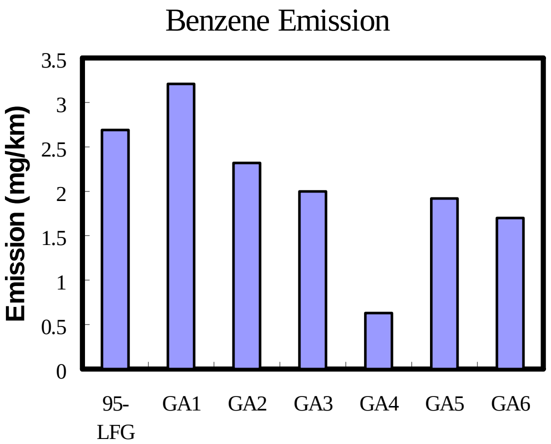

Fig. 1 Benzene emissions of the fuel and tested gasoline additives during FTP-75 testing

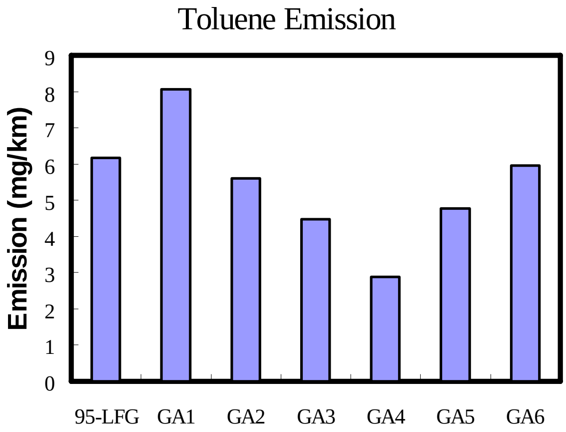

Fig. 2 Toluene emissions of the fuel and tested gasoline additives during FTP-75 testing

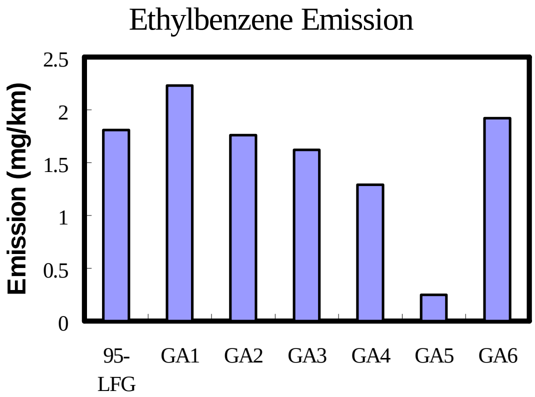

Fig. 3 Ethylbenzene emissions of the fuel and tested gasoline additives during FTP-75 testing

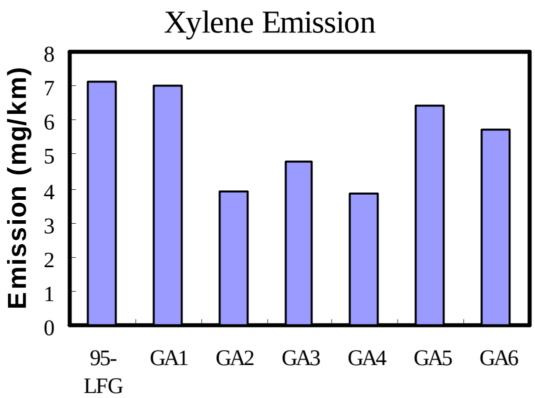

Fig. 4 Xylene emissions of the fuel and tested gasoline additives during FTP-75 testing

4. CONCLUSION

This study employed FTP testing to examine the gaseous emissions from the vehicle exhaust with the use of six selected gasoline additives. All tested gasoline additives have shown their effectiveness on depressing the emissions of regulated pollutants CO, HC, and NOx. Some gasoline additives were confirmed to enhance the BTEX emissions from vehicle exhaust, and the greatest augmentation of BTEX emissions was found 19.3 % for benzene, 30.8 % for toluene, and 17.1 % for ethylbenzene. Our concerns regarding environmental impacts imposed by gasoline additives were identified as the increase of the toxic release, including benzene, toluene, and ethylbenzene. The shift from the use of leaded to unleaded gasoline was associated with an increase in BTEX emissions, a trend probably attributable to the increased aromatics content of the lead replacement fuels. The use of gasoline additive also demonstrates a similar result, most likely, due to the abundance of alcohols and aromatic hydrocarbons in gasoline additives.

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