



Effects of Blending Ethanol with Gasoline on the Performance of Motorcycle Catalysts and Airborne Pollutant Emissions

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ABSTRACT

This study investigated the effects of blending ethanol with gasoline on the exhaust emissions of fuel-injected motorcycles. Regulated gasoline (RF), and 15 (E15) and 30 (E30) vol% ethanol fuel were used as test fuels. Measurements of several air pollutants (CO, HC, and NO_x) and organic air pollutant groups were conducted for two new fuel-injected four-stroke motorcycles. In addition, various catalysts were inserted into the motorcycles' tailpipes to determine the characteristics and performance of the catalysts in treating the exhaust.

Compared to using RF, we found that using blended fuel potentially reduced the CO and HC emissions by 30–37% and 19–28%, respectively. New catalytic systems, in conjunction with using different fuels, reduced CO, HC, and NO_x emissions in the tailpipe exhaust by 12–61%, 32–39%, and 81–85%, respectively. The CO and HC emissions were directly proportional in quantity to the running mileage of the catalyst, but the NO_x emissions were unaffected by this mileage, although they increased as the catalyst aged.

We also discovered that at identical running mileages for a catalyst, the fuel consumption increased by –1.7–6.5% and 4.1–15% when using E15 and E30 fuel instead of RF. Furthermore, the specific surface area and pore volume of the catalyst decreased with the aged catalyst the phosphorus and sulfur content in the catalyst increased with the catalyst's running mileage; adding ethanol to the fuel decreased emissions of paraffins, olefins, and aromatics but increased those of carbonyls; and the ozone formation potential of volatile organic compounds (VOCs) in the tailpipe exhaust was 16.7–17.2% for paraffins, 22–33% for olefins, 26–45% for aromatics, and 4.9–25% for carbonyls.

Keywords: Criteria air pollutant; Fuel consumption; VOC species; Catalyst.

INTRODUCTION

Because of the depletion of fossil fuels, searching for alternative fuels has become essential. Transportation is a major fraction of global energy consumption with an energy demand of around 25–27% (Conti *et al.*, 2016; World Energy Council, 2016). This demand is increasing by 1.4% annually (U.S. EIA, 2016a). In the transportation sector, 90% of greenhouse gas is being emitted by the use of gasoline and diesel fuels in the United States (U.S. EPA, 2019). The developing countries are contributing to 94% of the growth in the transportation energy sector (de Assis Brasil Weber *et al.*, 2019). World transport energy consumption is set to reach 3906 Mtoe in 2040 (U.S. EIA, 2016a). In places where

traffic is busy and intensively crowded or in urban areas, motorcycles are much more convenient and flexible (Durant *et al.*, 1996; Durant *et al.*, 1999; Lin *et al.*, 2019). Normally, the number of motorcycles around the world is approximately 350 million and increases with rises in the global metropolitan population (Chiang *et al.*, 2014; Alves *et al.*, 2015; Chernyshev *et al.*, 2018). In terms of the global distribution of motorcycles, Asia is in the lead, followed by Europe, Latin America, North America and Africa (DeMarini *et al.*, 2004; Costagliola *et al.*, 2014, 2016). Motorcycles are very suitable for Asia, particularly in Asia's developing countries because of their lower operating costs, lower rates of fuel consumption and higher convenience. In Vietnam, India, Indonesia, Thailand and China, motorcycles account for more than 60% of the number of passenger vehicles in use (Weiss *et al.*, 2015). Motorcycles are clearly a very important component of the transportation infrastructure in southern Asia.

Because of the inherent physicochemical characteristics of ethanol and isobutanol, it is possible for these fuels to

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spark ignition in an engine. This makes it possible to blend them with pure gasoline to reduce the dependency on petroleum fuels. The United States government is pushing ethanol fuel, and lately allowed the sale of E15 gasoline together with the long-approved E10 gasoline. A 10 vol% of anhydrous ethanol mixed with gasoline is widely used, without any need for engine modification, in almost all light-duty vehicles engines in the United States (U.S. EIA, 2016b). A higher ethanol blending such as 20–25% has been widely used in Brazil since the late 1970s after the 1973 oil crisis and an E85 blend is commonly used in the United States and Europe for flex-fuel vehicles (FFVs) (Rico, 2008; Larsen *et al.*, 2009). E100 has been introduced in Brazil for neat gasoline vehicles and most recently for E100 FFVs. This shows that ethanol can be an important alternative fuel for gasoline.

Due to fuel consumption, the transportation sector makes a significant contribution to air pollution and global warming (Clairotte *et al.*, 2013). The European Union (EU)'s Directive 2009/28/EC requires 10% of transport fuels to come from renewable energy by 2020 and this percentage will be increased in the following years (Clairotte *et al.*, 2013; Rodriguez *et al.*, 2015). Following the EU directive, the United States Environmental Protection Agency (U.S. EPA) has also set a target of 36 billion gallons of renewable fuel to be blended with gasoline by 2022 (Clairotte *et al.*, 2013).

Normally, ethanol contains less energy than gasoline, hence, motor vehicles using ethanol fuel have lower fuel economy. At the same time, the addition of ethanol fuel increase acetaldehyde and nitrogen oxide emissions and have a significant impact on air quality, especially in the photochemical components of air pollution and in ozone formation (Sarkar *et al.*, 2017; Kim *et al.*, 2018; Tsai *et al.*, 2018; Meng, 2019). Some researchers have investigated the torque, brake power and brake thermal efficiency of engines using an E20 ethanol/gasoline blend. Lower carbon monoxide and hydrocarbon emissions were determined for exhaust emissions from ethanol blending vehicles (Yao *et al.*, 2018; Yusoff *et al.*, 2018). NO_x emission change was generally insignificant (Yusoff *et al.*, 2018), but high speeds and torque could produce high NO_x. Hoang *et al.* (2019) found that when using E10 in the motorcycles which they tested there was a slight increase in engine power, and in NO_x and CO₂ emissions, while CO and HC emissions were lowered. When a wide-open throttle test was conducted under steady-state conditions using E30, vehicle power decreased by 10% and fuel consumption increased by 5% in comparison with E0 (no ethanol addition gasoline), because of the lower heating value of E30 (Sakthivela *et al.*, 2019). When E30 is used instead of E0, NO_x emissions increased by around 2.5 times, CO emissions decreased by 75% and HC emissions decreased by 66% (Sakthivela *et al.*, 2019). A clear trend of reduced hydrocarbons and CO emissions and increased NO_x emissions have been observed as the ethanol concentration in fuel increased from 0% to 20% (Agarwal, 2007).

The huge number of motorcycles in developing countries presents many challenges, such as safety issues, increasing fuel prices and air pollution. Although motorcycles have lower fuel consumption per individual relative to four-wheel

passenger cars due to their smaller engine capacity and lighter weight, motorcycles emit more pollutants per driving mileage (known as their emission factor), since the combustion of motorcycle engines is usually incomplete, and what is worse, they have poorer emission control/aftertreatment technologies. Vasic and Weilenmann (2006) observed that the ratios of mean emissions in g km⁻¹ from motorcycles and cars are very high, especially for HC in urban driving (factor of 222). When emissions were measured in terms of fuel-based emission factors (g L⁻¹), the fuel-based emission factors of LDMCs (light-duty motorcycles) and HDMCs (heavy-duty motorcycles) registered in or after the year 2000 were about 120 times higher than those of LDGVs (light-duty gasoline vehicles) in the same age group. In fact, the emission standards for motorcycles are 2–3 stages behind the emission standards applied to passenger cars (Sun *et al.*, 2016). Therefore, motorcycles exhaust emissions cannot be ignored in any examination of total motor vehicle emissions. When ethanol (EA), methyl *tertiary*-butyl ether (MTBE) and ethyl *tertiary* butyl ether (ETBE) percentages are increased, CO and NMHC concentration decreases. The emission of CO decreases by 0.363, 0.266 and 0.356 g km⁻¹ for light-duty vehicle when EA, MTBE and ETBE oxygenate blending ratios are increased (Lim *et al.*, 2019). When Euro III motorcycles are equipped with catalyst and electronic fuel injection systems the CO and hydrocarbons in their emissions can be significantly reduced in comparison with Euro I and II carbureted motorcycles (de Assis Brasil Weber *et al.*, 2019). There are certain potential hazards and unwanted side effects when using E10 fuel in a motorcycle. They will consume more fuel, especially if E85 is used. The ethanol industry states that engines that use E85 experience 25–30% less fuel power than they would be using regular gasoline. This is because ethanol contains less energy than gasoline despite having a higher natural octane number. Ethanol also is not effective in breaking up sludge in fuel tanks, which can lead to problems with clogged lines and filters as well as blocked carburetor jets and fuel injectors.

This study investigated the effects on exhaust emissions of ethanol blending in gasoline for fuel-injected motorcycles. Varied ethanol contents in gasoline, including 15 vol% and 30 vol% ethanol blends, were conducted as test fuels. Criteria air pollutants (CO, HC, and NO_x), and organic air pollutant groups were identified using two new fuel-injected four-stroke motorcycles with 125 cm³ displacements. The exhaust propelled through various catalysts in the motorcycle tailpipes was analyzed at different mileages to determine its characteristics, as well as the overall performance of the engines. The results were then compared with the results from the same test motorcycles using different fuels (RF, E15 and E30).

EXPERIMENTAL METHODS

Test Fuels and Motorcycle

In this study gasoline was blended with 15% (E15) and 30% (E30) ethanol by volume. We prepared the regulated gasoline (95 octane commercial gasoline), E15 and E30 under the same octane number. The largest petroleum refinery in

Taiwan (China Petroleum Corporation [CPC]) prepared the three types of gasoline used in this study. A commercial unleaded gasoline was used as the regulated gasoline (RF). This RF has an octane rating of 95. It includes a methyl *tert*-butyl ether (MTBE) oxygenating additive. By buying our fuel at a gasoline station operated by CPC we were able to get CPC to do composition analyses of the fuels, following American Society for Testing Materials procedures. The properties of the ethanol-blended gasolines and of the RF, measured by CPC, are presented in Table 1. The motorcycles (SYM-GR 125) being tested in the experiment weighed about 112 kg. Fuel injection was used as the fuel supply system. The engines were air cooled and used capacitive discharge ignitions in a single-cylinder arrangement. At their maximum power (10 ps at 8000 rpm), the compressor ratio of the engines was 8.6 and the maximum torque was 1.0 kg-m at 5500 rpm. The emissions which resulted from using different ethanol-gasoline blends were compared to the emissions produced by an untuned non-catalyst motorcycle in order to highlight the effect which catalysts had on emissions.

The three-way catalytic system is a stainless steel container including a honeycomb monolith structure (\varnothing 45 mm \times L 130 mm) and catalytic converter. Alumina is employed as a high surface area support, the mixed oxides, CeO₂-ZrO₂ added as the O₂ storage promoters, precious metals (Rh, Pt and Pd) are the active phases for exhaust reactions and BaO and/or La₂O₃ act as stabilizers of the surface area of support (Kašpar *et al.*, 2003). Catalyst system with different running mileage such as zero, < 500, 5000, 10,700 and 16,200 km was presented as C-0, C- < 500, C-5000, C-10700 and C-16200, respectively.

Test Procedures

Emission tests were executed using chassis dynamometers in the laboratory of a regional motorcycle manufacturer. The main system included a chassis dynamometer (20 kW; Meiden), a dilution tunnel, a constant volume sampler unit (CVS-51S; HORIBA), and an exhaust gas analyzer (MEXA-7200; HORIBA) for CO, HC and NO_x. Motorcycle

details (registration number, maker, category, and test weight) were loaded into the dynamometer system to estimate the appropriate inertia loading for the motorcycle during the testing process. The motorcycle testing followed the WMTC (World Motorcycle Test Cycle) driving cycle. The temperature of the test room ranged from 20°C to 30°C. The sampling equipment for organic air pollutants was similar to those we used in previous research (Tsai *et al.*, 2003; Tsai *et al.*, 2017). Following procedures recommended by the WMTC, a vacuum box containing a 10-L Tedlar bag was used to sample emissions. By setting a controlling flow rate of 150 mL min⁻¹, exhaust gas was drawn in through a sampling pump. In order to direct samples into the sample bag, three-way control valves were used. Due to the limitations of the sampling equipment, the sampling work was performed by manual operation. Before doing each emission test, strict fuel change protocols were used to ensure minimal crossover between test fuels took place so as to ensure that all the tests were done consistently. The process of changing fuel was as follows: The fuel tank was drained, 1 L of the new fuel was added in, the engine was idled for 5 min, the new test fuel was flushed through the fuel supply system thoroughly, and then the tank became empty again. For the remainder of the emission test, 2 L of the new fuel were then added. Next, the test motorcycle and fuel were conditioned taking the motorcycle out on the road for 10 min without measuring any emissions. Before the cold start testing process began, the motorcycle was parked at room temperature for more than 6 h. The three kinds of tests taken were all directed at detecting organic compounds. Two tests used E15, E30, and one test used regulated gasoline (RF).

Analytical Procedures

The testing bags were collected and put into a black container after sampling and underwent a hydrocarbon species analysis in the laboratory within 24 h. Using a purge and trap system (Varian), hydrocarbon species with a carbon number larger than 3 (> C3) were preconcentrated. Using gas chromatography/mass spectrometry (GC/MS; Star 3600

Table 1. Properties of the test fuels(regulated gasoline, E15 and E30).

Parameter	Regulated gasoline (RF)	E15	E30
RON	95	95.1	94.9
RVP (kPa)	55.3	49.8	44.6
Density (g mL ⁻¹)	0.74	0.75	0.73
Ethanol (wt%)	-	15.78	29.32
Ethanol (vol%)	-	14.21	26.15
Paraffins (vol%)	11.02	7.93	9.23
Isoparaffins(vol%)	29.38	36.53	42.81
Olefins (vol%)	10.10	10.50	9.05
Naphthenes(vol%)	7.31	5.65	6.24
Aromatics(vol%)	31.32	24.45	7.38
Benzene (vol%)	0.62	0.43	0.25
MTBE (vol%)	12.15	-	-
Oxygen content (wt%)	1.98	5.85	11.32
Heating value (kcal kg ⁻¹)	10841	10158	9985
Carbon (wt%)	83.96	81.71	75.63
Hydrogen (wt%)	11.83	12.78	14.15

GC plus a Saturn 2000 MS; Varian), the samples were quantified. Using liquid nitrogen, the temperature of the trap system was cooled down to 160°C. In order to purge, the thermal desorber was then preheated to 200°C. The GC was equipped with a fused silica capillary column (60 m L × 0.32 mm ID with 0.1 mm film thickness, DB-1) and connected to the MS. The certified standard gas (56 Environ-Mat Ozone Precursor; Matheson) was diluted with ultrahigh-purity nitrogen (99.995%) in dilution bottles to reach the calibration standards. For GC/MS, the R-squared (r^2) of the calibration curves of the 56 VOC species were generally higher than 0.995, the relative standard deviation (RSD) was less than 8%. Commercially available cartridges filled with 2,4-dinitrophenylhydrazine (Supelco) were used to collect carbonyl components in the exhaust. In the laboratory, the cartridge was first extracted from an aliquot of 2 mL acetonitrile (Merck). The extraction procedure was repeated with 5 mL acetonitrile. The extraction solution was injected into a high-performance liquid chromatographer (HPLC; 1100 series; Hewlett Packard) equipped with an auto sampler (G1313A; Hewlett Packard) 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 > 0.9999, the RSD was < 5%, the accuracy ranged from $98 \pm 2.6\%$ to $105 \pm 3.8\%$, and the method detection limit ranged from 6.23 (acetone) to 165 mg m^{-3} (2,5-dimethylbenzaldehyde). Background samples (room air) were also collected in the dynamometer laboratory and deducted from the test results. The results revealed that the VOC concentration was < 125 mg m^{-3} (toluene), and the VOC concentration of the dynamometer laboratory could be ignored being < 10 times that of the motorcycle exhaust.

Ozone Formation Potential of VOC Species

Generally, MIR is popular in identifying the ozone formation potential (OFP) in various VOC compounds. The equation is as follows (Russell *et al.*, 1995):

$$\text{MIR} = \max \{ [\partial(\text{O}_3)_p / \partial E_i] \} \quad (1)$$

for all VOCs/ NO_x , where $(\text{O}_3)_p$ is maximum ozone concentration, E_i is incremental of VOC concentration. The VOC species motorcycle exhaust emission factors associated with the maximum incremental reactivity factors (Carter, 2009) were applied to determine the OFP (in mg-O_3 produced per km) of the motorcycle exhaust.

RESULTS AND DISCUSSION

Criteria Pollutants

The study identified the following fuel effects: For regulated gasoline, the CO, HC, and NO_x emission was 3.4, 0.47, and 0.37 g km^{-1} , respectively, without catalyst treatment (shown as Fig. 1). When compared with regulated gasoline, E15 CO and HC emissions were reduced by 30% and 19%, respectively. When compared with regulated gasoline, E30 CO and HC emission were reduced by up to 37% and 28%,

respectively. However, NO_x emission increased 8.1% for E15 and showed only a slight reduction (2.7%) for E30. The NO_x emission trend seemed not to depend on the fraction of ethanol blended into the gasoline. Results indicated that gasoline blended with ethanol can reduce the CO and hydrocarbon emissions from tailpipe exhaust. The blending of ethanol in regular gasoline reduced NO_x using E30 and increased NO_x using E15. Ethanol blending increases the oxygen content in gasoline and the volatility of gasoline. As a result, ethanol blending can be an effective method for reducing CO and hydrocarbon emissions. However, the fact that blended gasoline burns at a lower temperature can lead to consequent NO formation. The hydroxyl functional groups present in the ethanol flame can reduce hydrocarbon production and lower NO formation (Bergthorson and Thomson, 2015). Some studies show conflicting results (i.e., an increase of NO_x with ethanol blending) (Najafi *et al.*, 2009), illustrating the inherent complexity in these studies created by the wide flexibility in operating parameters and by engine specific complications. Research shows that reductions can reach up to 30% of CO emissions, depending on the type and age of an engine/vehicle, the emission control system used, and the atmospheric conditions in which the vehicle operates (Agarwal, 2007).

This study identified the following catalyst effects: For regulated gasoline, when a new catalyst was used, the CO, HC and NO_x in emissions were reduced by 33%, 32%, and 81% (respectively) when compared with a non-catalyst tailpipe exhaust system (shown as Fig. 1); for E15 fuel, the CO, HC and NO_x emissions were reduced by 12%, 39%, and 85% (respectively) when a new catalyst was used when compared to a non-catalyst system. For E30 fuel, the CO, HC and NO_x emissions was reduced by 61%, 38%, and 81% (respectively) when using a new catalyst when compared to a non-catalyst system.

The study identified an aging effect: CO, HC and NO_x emissions could increase from 6.1% to 25%, 9.4% to 25% and 14% to 43%, respectively when the engines with catalysts were run from 5000 to 16,200 km on regulated gasoline (shown as Fig. 1); when engines with catalysts were run for 5000 to 16,200 km using E15, CO, HC and NO_x emissions could increase from 5.3% to 12%, 13% to 52% and 33% to 83%, respectively; and when engines with catalysts were run for the same distance using E30, CO, HC and NO_x emissions could increase from 81% to 104%, 4.8% to 29% and 14% to 57%, respectively. CO and HC emissions were directly proportional to the catalyst mileage. The running mileage of catalyst was between brand new and 16,200 km; in this range, the increase of CO emission rate was 37.4, 14.9 and $50.0 \text{ mg per } 1000 \text{ km}$, and that of HC emission rate was 4.59, 7.38 and $3.88 \text{ mg per } 1000 \text{ km}$ for RF, E15 and E30, respectively. However, the NO_x emission could increase after the catalyst aged, but the NO_x emission factor did not depend on the catalyst mileage.

The study acquired the following data related to fuel consumption. The fuel consumption of motorcycles with tailpipes without catalyst systems was 24.16 mL km^{-1} for regulated gasoline, 25.19 mL km^{-1} for E15, and 25.91 mL km^{-1} for E30. There was an increase of 7.2–10.5% in fuel

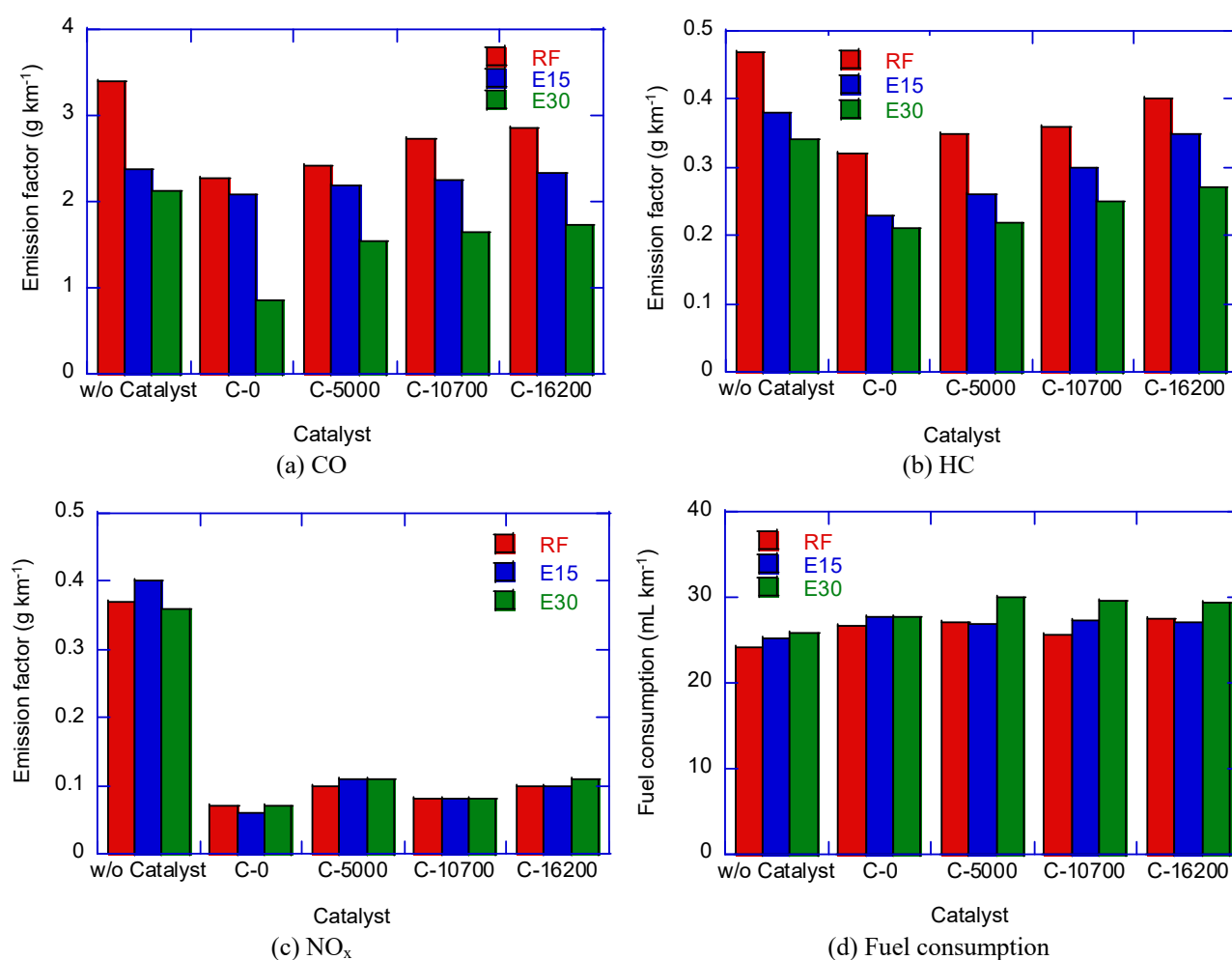


Fig. 1. CO, HC, NO_x emission and fuel consumption for different ethanol blending fuel of motorcycles without catalyst or with catalyst. (running mileage: 0, 5000, 10700 and 16200 km).

consumption when motorcycles had catalysts as compared to those that did not have catalyst systems.

The performance of fuel consumption could range from -3.6 to 3.0% for regulated gasoline, from -3.5 to -1.5% for E15, and from 5.6 to 7.9% for E30 in the catalyst mileage range of 5000 to 16,200 km. For the same catalyst mileage, the fuel consumption could be -1.7–6.5% different between E15 and regulated gasoline. Fuel consumption could increase 4.1–15% for E30 in comparison with the regulated gasoline. High ethanol addition in gasoline could increase fuel consumption due to the low energy content of ethanol in comparison with the gasoline.

Because ethanol has a high octane rating, the addition of ethanol to gasoline can lead to a reduction in the aromatic HCs (such as benzene), and other hazardous high-octane additives commonly used to replace tetraethyl lead in gasoline (Taylor *et al.*, 1996). The addition of ethanol can enhance the volatility of gasoline. However, some studies have identified divergent results about NO_x emissions, showing the ethanol concentration in the fuel increased anywhere from 0% to 20%. So, while the addition of ethanol can reduce CO and HC, aldehydes and unburned ethanol emissions, and decrease or increase NO_x, results can vary depending on

operating conditions, spark advance timing and other parameters (de Melo *et al.*, 2012).

Catalyst Characteristics

Fig. 2 shows the nitrogen adsorption-desorption isotherms and reveals representative Type IV isotherms with H2-type hysteresis for catalysts (Bumajdad *et al.*, 2006). Results indicated that mesoporous structures with ink-bottle type pores (Lan *et al.*, 2014), and the addition of noble metals, could have an effect on the pore types of the catalyst supporting materials. At lower relative pressure ($P/P_0 < 0.6$), monolayer nitrogen adsorption occurs on the walls of the mesopores. As the relative pressure rises, the isotherms exhibit capillary condensation at a relative pressure around 0.8. If higher relative pressures occur, multilayer adsorption occurs for catalyst support. For catalyst-5000, catalyst-10700 and catalyst-16200, the hysteresis loop observed was insignificant, revealing a blocking effect due to the formation of soot particles, and the ink-bottle-shaped pores became blocked. The specific surface areas of catalyst-5000 and catalyst-16200 decreased by 40–50% and 60–70%, respectively, of the catalyst materials (shown as Table 2). Moreover, the pore diameter increased significantly from

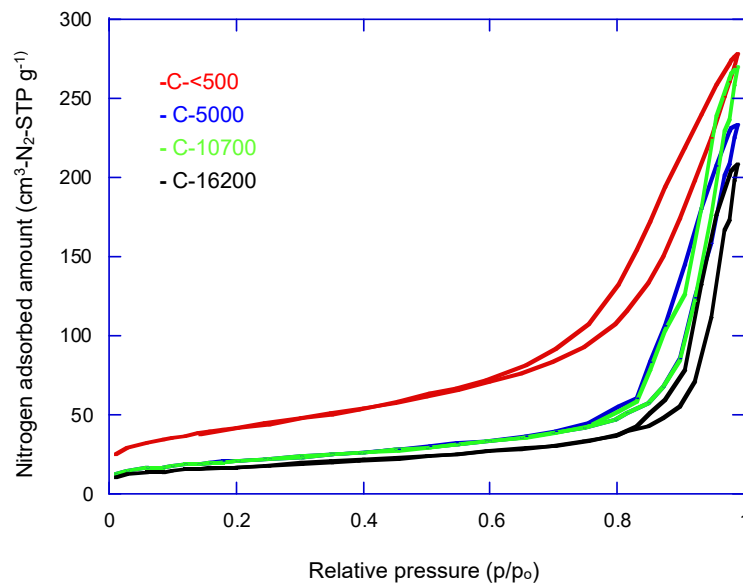


Fig. 2. Nitrogen adsorption and desorption isotherms for catalyst under different running mileage (mileage: < 500, 5000, 10700 and 16200 km).

Table 2. Specific surface area, pore volume and average pore diameter of catalyst.

Catalyst running mileage (km)	BET ($\text{m}^2 \text{g}^{-1}$)	PV ($\text{cm}^3 \text{g}^{-1}$)	PD (\AA)
< 500	163 ± 25	0.434 ± 0.065	113 ± 10
500	92.0 ± 35	0.362 ± 0.024	193 ± 36
10700	78.6 ± 13	0.354 ± 0.015	225 ± 41
16200	62.3 ± 15	0.346 ± 0.051	263 ± 21

BET: Specific surface area, PV: pore volume and PD: average pore diameter.

113 \AA (new catalyst) to 193 \AA (catalyst-5000) and 263 \AA (catalyst-16200). Total pore volumes of aging catalysts were reduced by 83% and 80% when compared to brand new catalysts (shown as Table 2). Incompletely consumed products (such as soot particles) were transported into the pores of the catalyst to decrease the specific surface area and pore volume. The catalyst supports, and noble metal particles, maintained a stable textural structure during the exhaust treatment and application of high temperatures. However, under certain conditions the noble metals could be transported into the inner pore and deposited on the wall of the pore, with the result that the pore became blocked by the noble metals, reducing pore volume and specific surface area, and the pore structures collapsed completely due to the encapsulation of noble metal particles (Monte and Kašpar, 2005).

In this study the element constituents of the catalyst were Al (19.5–22.3%), Ce (4.0–5.5%), Ni (4.5–5.5%), Fe (1.4–3.3%), Zr (1.2–1.8%), La (1.0–1.5%), Ca (0.10–0.36%) and Zn (0.008–0.216%) (shown as Fig. 3(a)). Three catalytic noble metals were determined to exist in the catalyst. These were Rh (1.0–1.5%), Pd (1.3–1.9%), and Pt (1.3–1.8%) (shown as Fig. 3(b)). Results indicated that the noble metals became reduced after the mileage increased. Some toxic elements were analyzed such as P (0.005–1.472%), and S (0.03–0.94%) (shown as Fig. 3(b)).

Some research has indicated that alkaline earth metals (Ca and Sr etc.) (Fernández-García *et al.*, 2002; Swatsitang *et*

al., 2016), rare earth metals (Y, La, Pr, Nd, and Sm etc.) (Tan *et al.*, 2015; Tan *et al.*, 2016) and transition earth metals (Cr, Mn, Fe, Co, Ni, and Cu etc.) can enhance thermal stability due to the electropositive promoters which they introduce into the lattice of solid solutions in catalysts (Li *et al.*, 2010; Alla *et al.*, 2017). Phosphate compounds such as phosphate esters, thiophosphate esters, metal thiophosphates and phosphorus-containing ionic liquids can be used as lubricant additives in antiwear or extreme pressure additives (Johnson, 2016). Phosphate additives can serve as a protective film and reduce friction in bearing material systems (Johnson, 2016). This may be the main reason for P accumulation in the catalyst system after an increase of running mileage.

This study determined that the materials used in the catalyst were these: Al_2O_3 was the support used to react with a CeO_2 - ZrO_2 solid solution to form alumina-ceria-zirconia complex oxide that has high thermal stability and reducibility (Acuña *et al.*, 2014; Piumetti *et al.*, 2016); catalytic novel metals, including Pt, Pd and Rh, were used to treat the exhaust because they can convert any incomplete combustion of CO and HC into CO_2 and H_2O . Rh was identified. It enhances the CO, H_2 , and NO reactants to form CO_2 , H_2O , and N_2 over the catalyst composite materials. Rh can dissociate NO better than Pt and Pd (Shelef and Graham, 1994). The Ce_2O_3 was used to capture excess O_2 to form CeO_2 for CO oxidation and this mechanism also enhanced the NO reduction to form N_2 (Ramanathan and Sharma, 2011).

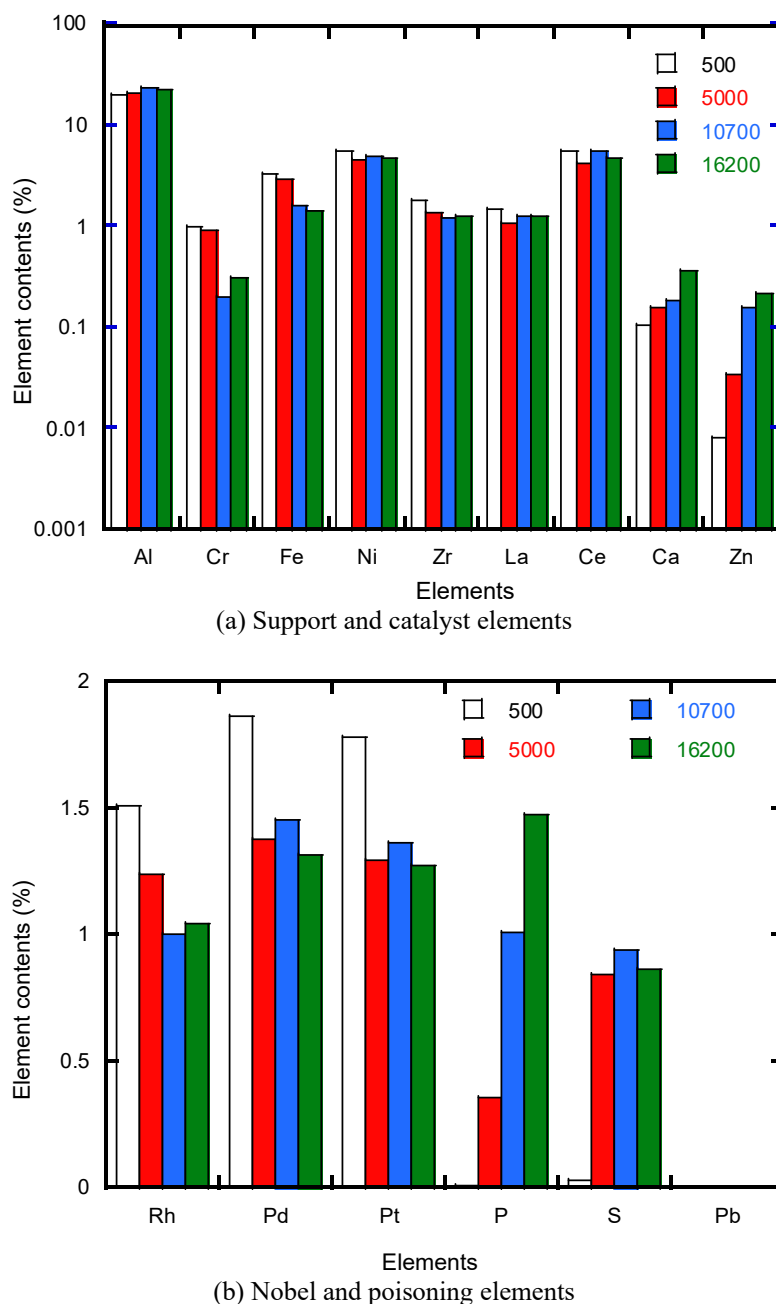


Fig. 3. CO, HC, NO_x emission and fuel consumption for different ethanol blending fuel of motorcycles with various running mileage of catalyst system (mileage: < 500, 5000, 10700 and 16200 km).

VOCs Characteristics

In this study an analysis of the VOC species was conducted. The major species of paraffins identified included isopentane, methyl hexane, 2,3-dimethylbutane, *n*-heptane, and cyclopentane, 1-butene, isoprene, and 1-hexene. These were the main olefin species. For aromatic species, toluene, benzene, xylene, ethylbenzene, 1,3,5-trimethylbenzene and ethyltoluene were found to be highly abundant in the exhaust. For carbonyls, the main species were acetaldehyde, acetone, formaldehyde, and benzaldehyde. For non-catalysts in the tailpipe, the analyzed VOCs emission factor was 116 mg km⁻¹ for regulated gasoline, 76.8 mg km⁻¹ for E15 and 51.5 mg km⁻¹ for E30. The VOC group fraction was 49–

52% paraffins, 9.5–14% olefins, 26–30% aromatics and 4.5–16% carbonyls in the tailpipe exhaust (shown as Fig. 4). The addition of ethanol reduced paraffins, olefins and aromatics emissions and increased the carbonyls emission. After the catalyst treatment the VOCs exhaust was reduced from 116 to 63.1 mg km⁻¹ (a 45.6% reduction) for regulated gasoline, from 76.8 to 40.5 mg km⁻¹ (a 47.3% reduction) for E15 and from 51.5 to 25.5 mg km⁻¹ (a 50.5% reduction) for E30. VOC emissions increased as catalyst mileage increased from 0 to 16,200 km. These VOC emissions increases were from 63 to 99 mg km⁻¹ for regulated gasoline, from 40 to 68 mg km⁻¹ for E15 and from 26 to 41 mg km⁻¹ for E30 (shown as Fig. 6(a)).

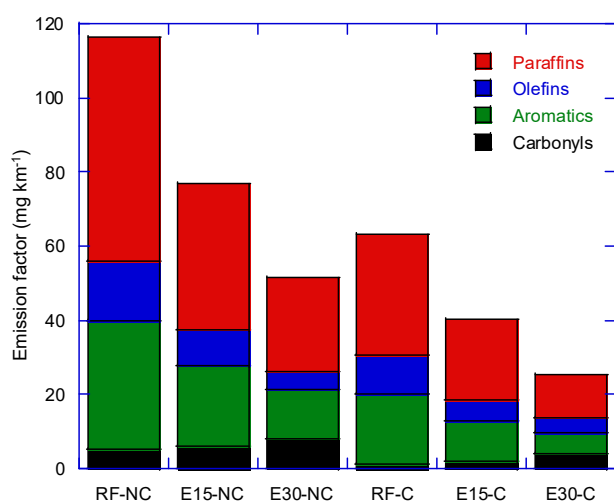


Fig. 4. VOCs emission factors for regulated gasoline (RF), E15 and E30 associated with non-catalyst (NC) and catalyst (C).

Ozone Formation Potential

VOCs are the important precursors in O₃ formation (Alvim *et al.*, 2018; Deng *et al.*, 2018; Jia *et al.*, 2018; Meng *et al.*, 2019) and most of them are the hazardous air pollutants (HAPs) (Widiana *et al.*, 2017; Hua *et al.*, 2018). For the olefin paraffin species, the major components with potential for ozone formation included isopentane, cyclopentane and 2-methylpentane, 1-butene, isoprene, 1-hexene and trans-2-pentene. For the aromatic species, xylene, toluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, and ethyltoluene were shown to be highly abundant. For carbonyls, the main ozone formation potential species were acetaldehyde, and formaldehyde. When there was no catalyst in the tailpipe, the analyzed VOCs ozone formation potential was 457 mg-O₃ km⁻¹ for regulated gasoline, 298 mg-O₃ km⁻¹ for E15 and 196 mg-O₃ km⁻¹ for E30. The fractions of VOC materials with ozone formation potential in the tailpipe exhaust were 16.7–17.2% paraffins, 22–33% olefins, 26–45% aromatics and 4.9–25% carbonyls (shown as Fig. 5). The addition of ethanol was shown to reduce paraffins, olefins and aromatics emissions and to increase the carbonyls emission. When the exhaust was treated using a catalyst system, the ozone formation potential of analyzed VOCs was reduced from 457 to 256 mg-O₃ km⁻¹ (a 44.0% reduction) for regulated gasoline, from 298 to 156 mg-O₃ km⁻¹ (a 47.7% reduction) for E15 and from 196 to 109 mg-O₃ km⁻¹ (a 44.4% reduction) for E30. As the catalyst mileage increased from 0 to 16,200 km, the ozone formation potential of VOCs increased from 256 to 407 mg-O₃ km⁻¹ for regulated gasoline, from 156 to 276 mg-O₃ km⁻¹ for E15 and from 109 to 183 mg-O₃ km⁻¹ for E30 (shown as Fig. 6(b)).

The potential strategy of emission reduction of motorcycle suggests the power supplied by the electricity or low airborne emission fuels, and improving the infrastructure of the transportation to eliminate the application of motorcycle.

In Taiwan, the 3% ethanol addition into gasoline as E3, it could be sold about 7834 kL in 2013. The E3 gasoline was executed in 2007, however, the fraction of E3 sales volumes

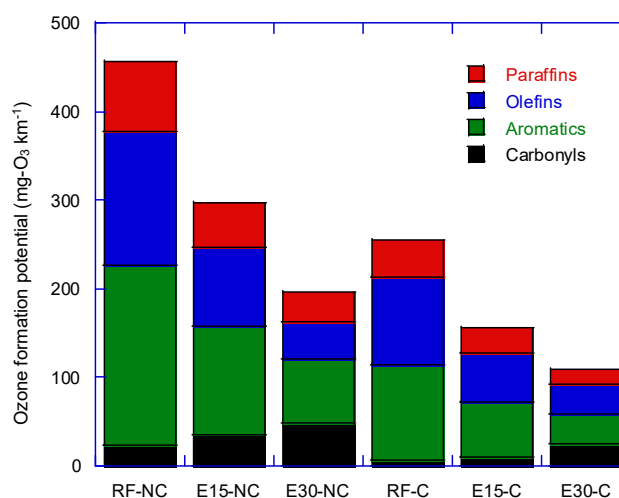


Fig. 5. Ozone formation potential of VOCs for regulated gasoline (RF), E15 and E30 associated with non-catalyst (NC) and catalyst (C).

were much less than that of regulated gasoline. The ethanol additive gasoline is not easy to promotion due to its sources of raw materials (most of ethanol is import from othercountries), high cost, fuel consumption, and corrosion of engine system. The government has to set up the long-term targets for the bio-ethanol development and emission reduction and integrated design a set of interrelated research, technology, development and innovation policies for the bio-ethanol application system (Chung and Yang, 2016) to enhance the growth of ethanol alternative fuels in Taiwan.

CONCLUSIONS

Using ethanol-blended fuel can significantly reduce CO emissions (by 30–37%) and HC emissions (by 19–28%) compared to using regulated gasoline, and adding a catalyst to the tailpipe exhaust system can decrease CO, HC, and NO_x emissions by 12–60%, 32–39%, and 81–85%, respectively, for various fuels. The results of this study showed that the specific surface areas for catalyst-5000 and catalyst-10700 were approximately 50% less than those for brand new catalysts. After the test engines reached a mileage of 16,000 km, the specific surface areas decreased to about one third of those of a new catalyst. Additionally, after the increase in mileage, the catalysts exhibited reduced quantities of three catalytic noble metals (Rh, Pd, and Pt) and increased quantities of P and S.

Adding ethanol to the gasoline decreased paraffin, olefin, and aromatic emissions but increased carbonyl emissions. The VOCs in the tailpipe exhaust consisted of 49–52% paraffins, 9.5–14% olefins, 26–30% aromatics, and 4.5–16% carbonyls. When the exhaust was treated with a catalytic system, the ozone formation potential of the analyzed VOCs decreased from 457 to 256 mg-O₃ km⁻¹ for regulated gasoline, 298 to 156 mg-O₃ km⁻¹ for E15, and 196 to 109 mg-O₃ km⁻¹ for E30. However, the VOC ozone formation potential of an aged catalyst (16,200 km) was 1.59–1.77 times higher than that of a brand new catalyst.

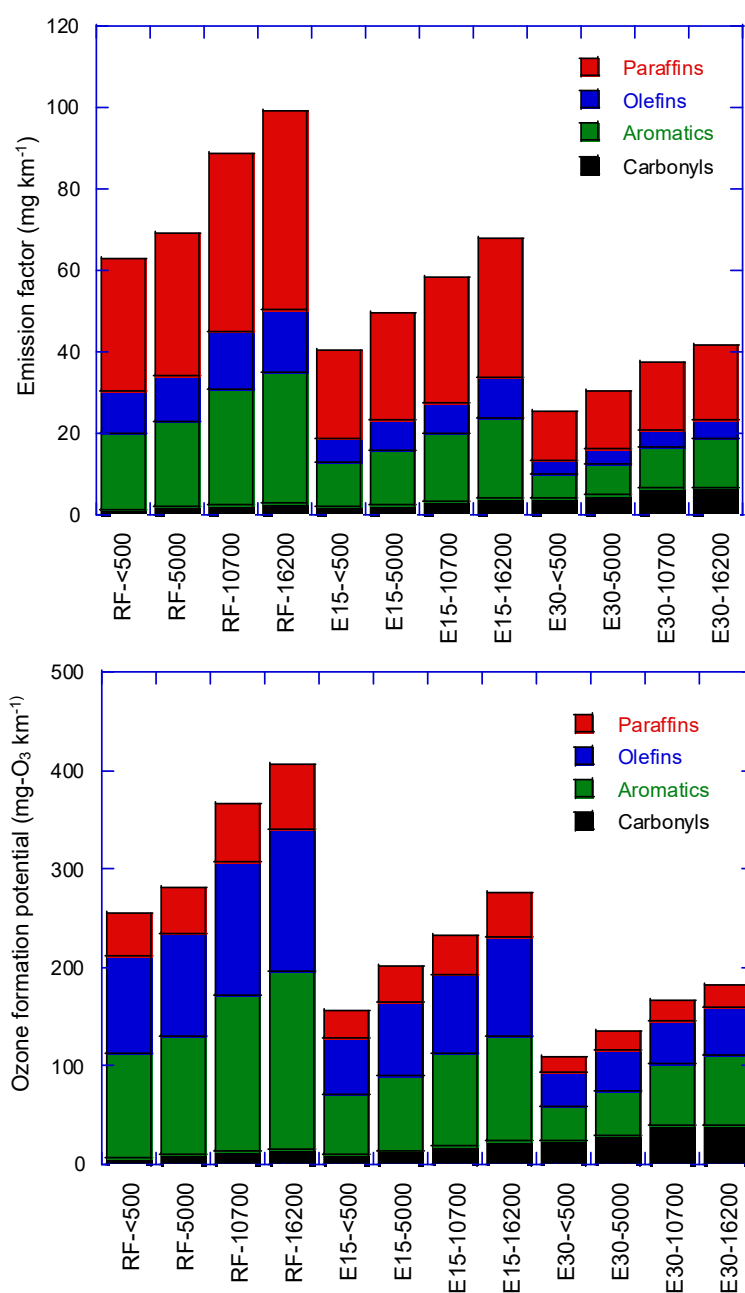


Fig. 6. VOCs emission factors and ozone formation potentials for regulated gasoline, E15 and E30 associated with catalyst aging (mileage < 500, 5000, 10700 and 16200 km).

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