



# Regulated and unregulated emissions from an internal combustion engine operating on ethanol-containing fuels

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## Abstract

In the present work, the effect of ethanol addition to gasoline on regulated and unregulated emissions is studied. A 4-cylinder OPEL 1.6L internal combustion engine equipped with a hydraulic brake dynamometer was used in all the experiments. For exhaust emissions treatment a typical three-way catalyst was used. Among the various compounds detected in exhaust emissions, the following ones were monitored at engine and catalyst outlet: methane, hexane, ethylene, acetaldehyde, acetone, benzene, 1,3-butadiene, toluene, acetic acid and ethanol. Addition of ethanol in the fuel up to 10% w/w had as a result an increase in the Reid vapour pressure of the fuel, which indicates indirectly increased evaporative emissions, while carbon monoxide tailpipe emissions were decreased. For ethanol-containing fuels, acetaldehyde emissions were appreciably increased (up to 100%), especially for fuel containing 3% w/w ethanol. In contrast, aromatics emissions were decreased by ethanol addition to gasoline. Methane and ethanol were the most resistant compounds to oxidation while ethylene was the most degradable compound over the catalyst. Ethylene, methane and acetaldehyde were the main compounds present at engine exhaust while methane, acetaldehyde and ethanol were the main compounds in tailpipe emissions for ethanol fuels after the catalyst operation. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Ethanol was first suggested as an automotive fuel in USA in the 1930s, but was widely used only after 1970. Nowadays, ethanol is used as fuel, mainly in Brazil (Rossilo-Calle and Corte, 1998), or as a gasoline additive for octane enhancement and better combustion, mainly in USA and Canada.

As gasoline price increases and pollutant emissions restrictions become more stringent, ethanol could be given more attention as a renewable fuel or gasoline additive. Although ethanol addition into fuel may contribute to a reduction in hydrocarbon and carbon

monoxide emissions, higher ethanol and acetaldehyde emissions could be emitted.

Furey and King (1981) investigated the exhaust and the evaporative emissions from cars running on unleaded gasoline, gasohol (10 vol% absolute ethanol in gasoline) and adjusted gasohol (gasohol with the same Reid vapour pressure (RVP) with gasoline). Three cars were tested: (a) a 1978 production car with a 5.7L engine and an oxidizing catalytic converter, (b) a prototype closed-loop dual-bed catalyst car with a 4.3 L engine, and (c) a prototype closed-loop three-way catalyst car with a 4.3 L engine. The evaporative emissions were 50% higher for ethanol fuels than for gasoline, while the total engine-out and the tailpipe hydrocarbon, carbon monoxide and nitrogen oxides emissions from the production car without closed-loop fuel control were significantly lower with oxygenated fuels than with gasoline. The changes in the exhaust

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emissions from one fuel to another in the closed-loop dual-bed catalyst car and the closed-loop three-way catalyst car were quite small.

Bata and Roan (1989) studied the effect of ethanol addition into gasoline on the exhaust emissions from a 1978 Ford 2.3 L engine, operating under fixed conditions. They observed lower hydrocarbon emissions and a 40–50% decrease in carbon monoxide concentration compared to the base fuel. On the other hand, aldehyde emissions were increased by 60–100%. Evaporative emissions were also increased for ethanol-containing gasoline.

Rice et al. (1991) studied the exhaust emissions from a Chrysler 2.2 L engine running on gasoline-butanol/ethanol/methanol (20% by volume alcohol) at three operating conditions. Carbon monoxide emissions for alcohol fuels relative to gasoline at a given air-to-fuel ratio were decreased due to the “leaning” effect related to the lower stoichiometric air-to-fuel value for alcohols. This effect, coupled with lower combustion temperature for alcohol blends also accounted for a modest lowering of nitrogen oxides emissions when using alcohols. In contrast, unburned fuel emissions were higher for alcohol containing fuels than for gasoline at intermediate load, but almost equal or lower at high load.

Reuter et al. (1992) estimated the effect of oxygenate addition in gasoline on exhaust and evaporative emissions from 20 1989 vehicles. The fuels used were gasoline containing 10 vol% ethanol or 15 vol% methyl tertiary-butyl ether (MTBE) or 17 vol% ethyl tertiary-butyl ether (ETBE). The addition of oxygenates decreased exhaust mass emissions of total hydrocarbons by 5.4% and CO emissions by 12.5%. Nitrogen oxides emissions were increased by oxygenates by 4.8%. No significant differences between oxygenates were identified for these effects. Benzene exhaust mass emissions were reduced by 10.5% with the oxygenated fuels while acetaldehyde emissions were increased for ethanol and ETBE blends.

Stump et al. (1996) examined the tailpipe and the evaporative emissions from three pre-1985 passenger motor vehicles operating on an ethanol (9 vol%) and a non-oxygenated fuel. A general reduction in hydrocarbon, carbon monoxide, benzene and 1,3-butadiene emissions was observed when the ethanol fuel was used. Both formaldehyde and acetaldehyde (almost double) emissions were increased with the ethanol blend. Most emissions occurred during the first 2 min of vehicle start-up. Diurnal evaporative emissions were less from the oxygenated fuel, while hot soak evaporative emissions were greater.

Mulawa et al. (1997) evaluated the impact of switching from regular gasoline to an E-10 fuel (gasoline with 10% ethanol) in Fairbanks (Alaska). Particulate matter emission rates for the E-10 fuel were lower than those for base gasoline.

Although some work has been done related to regulated emissions from ethanol-containing fuels, more attention should be given on unregulated emissions, such as ethanol and acetaldehyde.

In the present study, the effect of ethanol addition to gasoline on the exhaust emissions from an internal combustion engine, equipped with a three-way catalytic converter, is presented. Beyond the regulated emissions, i.e. total hydrocarbons (HC) and carbon monoxide (CO), some important unregulated compounds as methane, n-hexane, ethylene, acetone, acetaldehyde, acetic acid, benzene, toluene, 1,3-butadiene and ethanol were measured at the engine exhaust and after the catalytic treatment in order to define the organic compound pattern in exhaust gases in each case.

## 2. Experimental section

### 2.1. Test fuels

Three test fuels were used in this study. The first one was unleaded gasoline without any oxygenated additives, with an octane number of 95.5, that was used as a reference fuel and as a base fuel for the preparation of gasoline/alcohol blends and it is called hereinafter as “Base”. The second and the third fuels were gasoline–alcohol mixtures containing 3% (Eth3%) and 10% (Eth10%) w/w, respectively. Ethanol addition in gasoline had as a result an increase in research octane number (RON) and RVP of the fuel. The increase in the RVP of the fuel is an indication of increased evaporative emissions, although such measurements were not conducted in this study. The properties of the fuels used are presented in Table 1.

### 2.2. Test vehicle and procedure

A four-cylinder OPEL 1.6 L engine equipped with a hydraulic brake dynamometer (Clayton, CAM-250E)

Table 1  
Fuel properties

% w/w	Base fuel	Eth3%	Eth10%
Oxygen	0.16	1.10	3.58
Aromatics	43.7	43.4	42.9
Saturated	49.7	46.2	38.1
Alkenes	5.7	6.0	7.8
Benzene	2.52	2.45	2.25
Xylene	10.7	10.5	9.9
Toluene	11.1	11.0	10.7
RON	95.5	96.9	98.9
MON	86.0	86.3	87.0
RVP (100 F) kPa	61.4	62.6	65.9

for changing the engine load was used. The engine torque was measured using a hydraulic load cell. A typical commercial three-way catalytic converter (Pt/Rh: 5/1) with ceramic monolithic support was used. The power of the engine was increased in the range of 0–20 HP according to a specific time program by imposing selected pairs of engine speed (1000–2500 rpm) and torque (0.1–40  $\text{lb}_f \times \text{ft}$ ). The experimental set-up and procedure are described in a previous work (Pouloupoulos and Philippopoulos, 2000).

### 2.3. Analysis

A SUN MGA-1200 analyser was used to measure continuously the concentrations of HC (total unburned hydrocarbons, ppm, v/v), CO (vol%), CO<sub>2</sub> (vol%) and the air-to-fuel ratio ( $\lambda$ ). Specifically, total hydrocarbons, carbon monoxide and carbon dioxide were analysed by non-dispersive infrared and oxygen by chemiluminescence. The analyser provided a CO measurement range of 0–10% with a resolution of 0.01%, CO<sub>2</sub> range of 0–20% with a resolution of 0.01% and HC range from 0 to 9999 ppm with a resolution of 1 ppm.

Samples, which were collected from the engine and the catalytic converter exhaust gases at each engine power, were analysed by gas chromatography with flame ionisation detection (GC-FID) and by gas chromatography-mass spectrometry (GC-MS). Methane and ethylene were detected with GC-FID while rest of the hydrocarbons were analysed with GC-MS. The column (HP-PLOT Q) used in GC-MS permitted the detection of polar and non-polar compounds simultaneously. All the concentrations of the various compounds are expressed as ppm (v/v). Analysis details are presented in Table 2.

The presented data are the average of the data received from 3–4 repeatable tests for each fuel and

three measurements for each compound concentration at each engine power. The standard error of the mean value of HC and CO concentration (as % percentage of the mean) is below 7% in the most cases. The standard error of the mean value of each compound concentration is 10–15% in the majority of the measurements although higher standard errors are observed for concentrations below 10 ppm.

## 3. Results

### 3.1. Regulated emissions

At the start of the engine operation, HC emissions were about 100 ppm (Fig. 1) for all fuels used. Tailpipe emissions were almost the same as the engine-out emissions at 0.14 and 1.43 HP, since the required temperature for catalyst operation was not achieved (250–270°C). The highest engine hydrocarbon emissions were observed at 1.90 and 3.81 HP, around 600 ppm. It must be noted that at 1.90 HP the highest tailpipe HC emissions were also observed due to increased engine emissions and catalyst low activity. Hydrocarbon emissions were gradually decreased with increasing engine power because of higher engine operation temperatures. At those operating conditions, HC tailpipe emissions were below 50 ppm. At low engine powers, no significant changes from one fuel to another for HC engine-out and tailpipe emissions were observed except 1.90 HP, where the half HCs were emitted from engine for Eth3%. This effect was not observed at tailpipe indicating lower catalytic activity for Eth3% at these conditions. At engine powers above 1.90 HP, less HC emissions were observed for Eth3%.

Carbon monoxide engine-out emissions ranged in 0.40–0.60% v/v and were increased at 1.90 and 3.81 HP

Table 2  
Analysis details

	GC-MS	GC-FID
Apparatus	Hewlett Packard GC 6890-MSD 5973	SIGMA 3B Perkin-Elmer
Column	HP-PLOT Q	Poropak Q
Length	30 m	3 m
Internal diameter	$0.032 \times 10^{-3}$ m	$3.2 \times 10^{-3}$ m
Carrier gas	Helium	Nitrogen
Total flow	$25 \text{ ml min}^{-1}$	$20 \text{ ml min}^{-1}$
Mode	Splitless-Scan	Splitless
Injector temperature	250°C	150°C
Detector temperature	MS Quad: 150°C Ms Source: 230°C	250°C
Oven temperature	Initial: 60°C for 4 min 60°C → 190°C with $25^\circ\text{C min}^{-1}$ Final: 190°C for 7 min	160°C

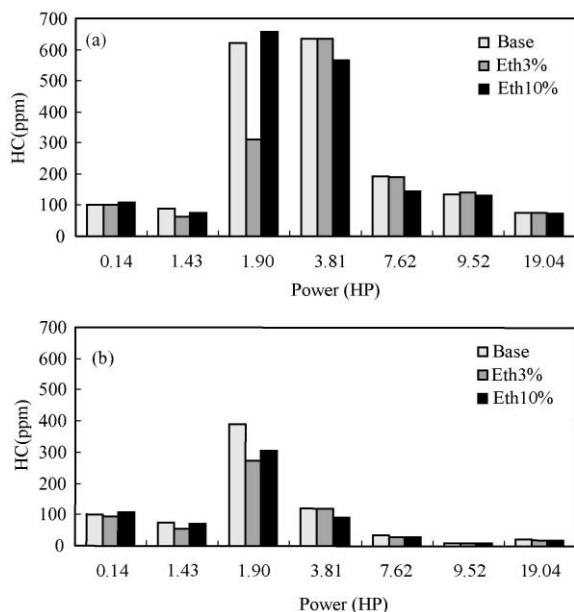


Fig. 1. HC emissions at (A) engine and (B) tailpipe exhaust.

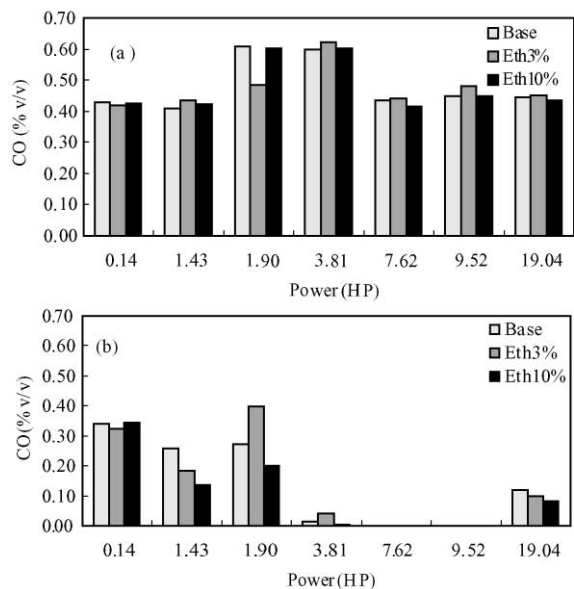


Fig. 2. CO emissions at (A) engine and (B) tailpipe exhaust.

for all test fuels (Fig. 2). Moreover, they were almost independent from the test fuel. CO tailpipe emissions were below 0.40% v/v and were less in the whole range of engine operation conditions for Eth10%. It is remarkable that at 3.81 HP, CO emissions were extremely low at the exit of the catalytic converter and were zero at 7.62 and 9.52 HP, while CO was present

again in tailpipe emissions at the maximum engine power.

### 3.2. Hydrocarbon speciation

Among the various compounds detected in exhaust emissions, the following ones were measured: methane, hexane, ethylene, acetaldehyde, acetone, benzene, toluene, 1,3-butadiene, acetic acid and ethanol.

Methane and hexane were selected because as alkane compounds they were expected to be quite resistant to oxidation according to literature while methane is also very potent in greenhouse effect. Ethylene was chosen since it is present in great amounts in vehicle exhaust and it is very drastic in ozone formation (Grosjean et al., 1998; Hirota et al., 1992). Acetaldehyde and acetone are involved in the photochemical smog generation cycle while acetaldehyde is also a toxic compound. Furthermore, a possible increased acetaldehyde emission is the main disadvantage of the use of alcohol fuels and consequently acetaldehyde emissions measurements are essential. Benzene and toluene belongs to aromatics, compounds accused of cancer generation, and 1,3-butadiene is a well-known toxic compound. Acetic acid has a very characteristic and annoying odour and it is mainly composed over the catalyst. Finally, unburned ethanol emissions related to the presence of ethanol in fuel were also examined.

Methane concentration in engine exhaust emissions for base fuel were the same or higher than for Eth10%. No specific pattern is observed in the case of Eth3%. In tailpipe exhaust emissions, methane concentration was higher for base fuel at low engine power, while at higher engine power, higher methane emissions were observed for Eth10%.

Hexane engine-out emissions ranged in 5–25 ppm and were higher for base fuel at 1.90–7.62 HP. Hexane tailpipe emissions were lower for Eth10% at low engine power, while above 3 HP the observed differences were insignificant.

Ethylene engine-out emissions were the highest among those measured in this study. They were increased at intermediate loads, especially for Eth10%, while no trend in the whole experimental cycle was observed due to fuel change (Fig. 3). Ethylene concentration in tailpipe exhaust emissions was decreased for Eth10% at low engine power.

Concerning acetaldehyde concentration in engine exhaust gases, it was elevated for ethanol fuels, especially at intermediate loads of 1.90–7.62 HP (Fig. 4), owing to acetaldehyde formation on catalyst due to partial oxidation of ethanol. It is noteworthy that acetaldehyde emissions in the case of Eth3% were higher related to Eth10%, whereas a linear connection between acetaldehyde engine-out emissions and ethanol content in the fuel would be expected (Zervas et al., 1999).

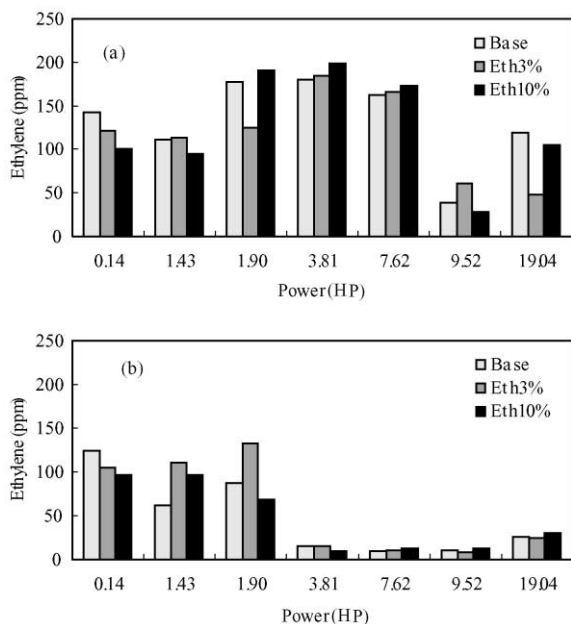


Fig. 3. Ethylene concentration at (A) engine and (B) tailpipe exhaust.

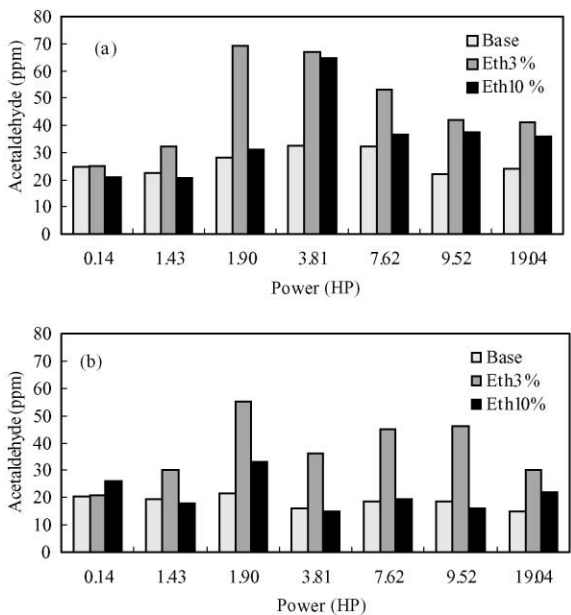


Fig. 4. Acetaldehyde concentration at (A) engine and (B) tailpipe exhaust.

Acetaldehyde production through the partial oxidation of ethanol seems to be highly dependent on oxygen concentration. In the case of Eth10%, the oxygen content of the fuel favours the oxidation of the produced acetaldehyde during the combustion process. Moreover,

ethanol seems to be converted preferably to ethylene (typical dehydration process of ethanol) than to acetaldehyde, since generally higher ethylene engine-out emissions were observed for Eth10%. After the catalytic converter the differences in acetaldehyde emissions between base and Eth10% fuel were insignificant, while low catalytic efficiency in acetaldehyde oxidation was observed for Eth3%.

Acetone engine-out emissions were increased for Eth10% at low engine loads, while at higher loadings the highest acetone emissions were observed for Eth3% (Fig. 5). In contrast, after the catalytic treatment the lowest acetone emissions were observed for Eth10% fuel.

Benzene emissions from engine were decreased with ethanol addition into gasoline (Fig. 6). The lowest benzene concentrations were observed with Eth10%. This beneficial effect was diminished after the full catalytic activity had been achieved.

Toluene engine-out emissions were also significantly decreased by ethanol addition into fuel. The tailpipe toluene emissions were decreased only for Eth10% (Fig. 7).

1,3-Butadiene was detected in the engine outlet only at low engine loads and its concentration (5–6 ppm) was slightly decreased only for Eth10%. Despite the low catalyst temperature at these conditions, 1,3-butadiene was significantly reduced over the catalytic converter.

Acetic acid was identified in the engine exhaust gases only for base and Eth3% fuels at 9.52 and 19.04

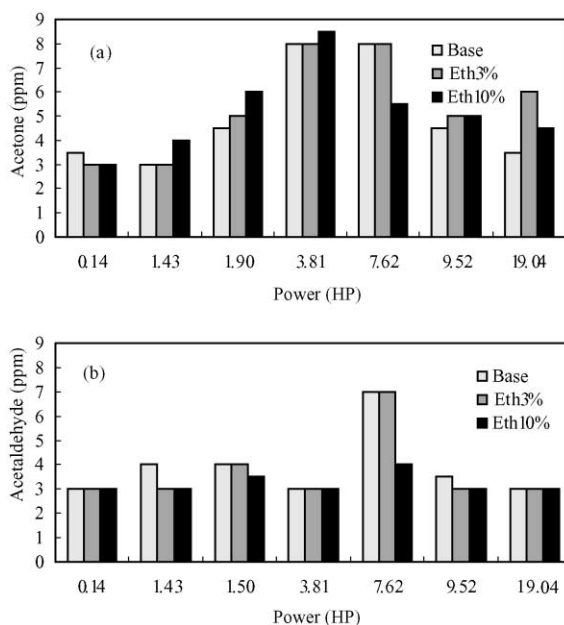


Fig. 5. Acetone concentration at (A) engine and (B) tailpipe exhaust.

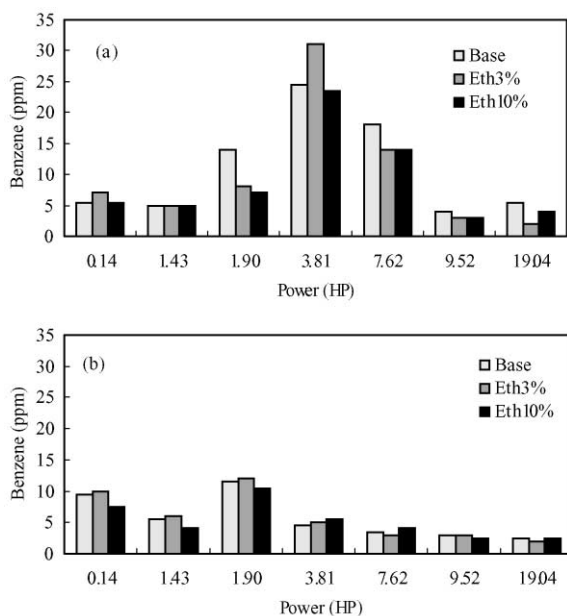


Fig. 6. Benzene concentration at (A) engine and (B) tailpipe exhaust.

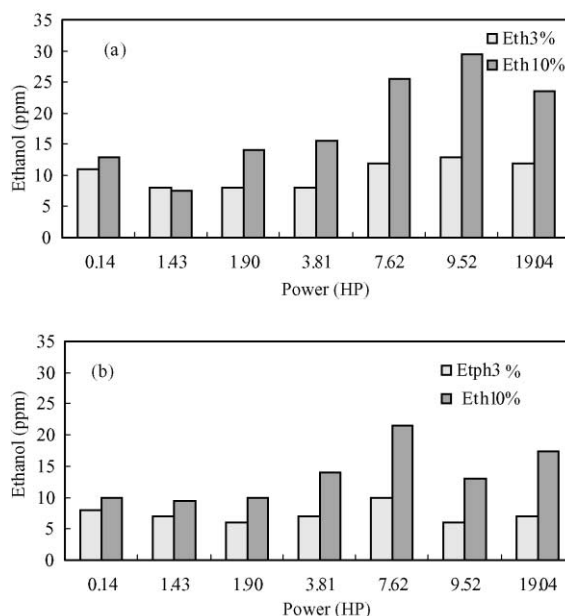


Fig. 8. Ethanol concentration at (A) engine and (B) tailpipe exhaust.

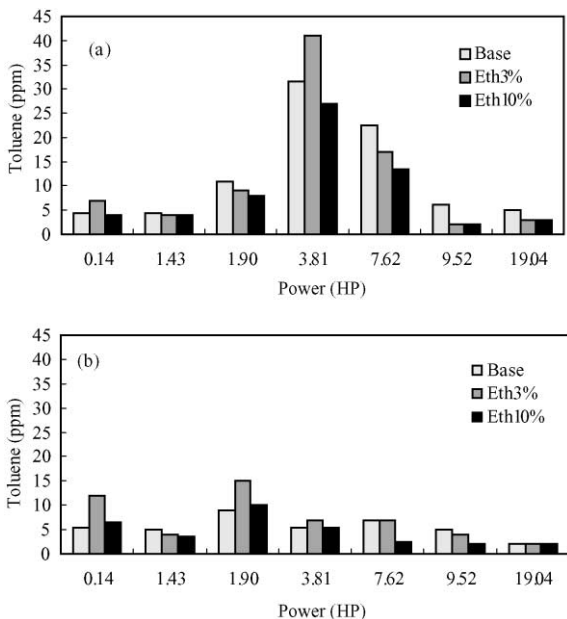


Fig. 7. Toluene concentration at (A) engine and (B) tailpipe exhaust.

(7–10 ppm). The same pattern was observed in the exhaust emissions after the catalytic converter (3–5 ppm). No acetic acid emissions were observed for Eth10%.

Finally, ethanol was detected in the engine exhaust gases only for gasoline/ethanol blends. In the case of Eth10%, ethanol engine-out emissions were 20–100% higher than these in the case of Eth3%. Low conversion of ethanol for both fuels over the catalyst was achieved. As expected, higher ethanol tailpipe emissions were observed for Eth10% (Fig. 8).

### 3.3. Catalytic converter efficiency for each compound

For the specific position of the catalytic converter in the experimental apparatus, its operation was achieved at an absorbed engine power higher than 2 HP. In that case, the temperature of the catalytic converter became higher than 260°C and the start up of its auto-thermal operation was sufficient.

The catalytic converter was more effective on carbon monoxide than HC oxidation. For the engine power range of full catalyst operation, the conversion of HC was 70–80% and of CO was 90–100%. For Eth10% fuel higher conversions and at lower engine power were achieved, especially in the case of carbon monoxide.

Ethylene, methane and acetaldehyde were the main compounds present at engine outlet and at tailpipe among those detected before catalyst operation. The catalyst operation changed that pattern. After its operation methane, acetaldehyde and ethanol (when it was present in fuel) were the main compounds in tailpipe exhaust HC emissions (Fig. 9). The highest engine emissions, the start of catalyst operation and the highest

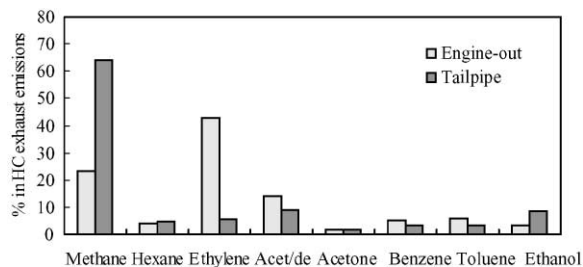


Fig. 9. The percentage of each compound in total engine-out and tailpipe HC emissions (as estimated from GC-analysis) in the case of Eth10% fuel at 3.81 HP.

catalytic activity were observed at 3.81 HP. Ethylene was the most easily oxidized compound while methane was the most resistant compound. The order from the most resistant to the easiest to oxidation compound was:

Methane < Ethanol < Hexane < Acetaldehyde < Acetone  
< Benzene < Toluene < Ethylene.

Ethylene and aromatics, i.e. benzene and toluene, were easily decomposed over the catalytic converter. Acetaldehyde conversion over the catalyst was higher when Eth10% was used as fuel. Negative methane conversions are explained by methane formation over the catalyst because of HC decomposition. At higher engine loadings hexane conversion was extremely minimized, probably due to decomposition of aromatics to hexane. So, taking into account the whole engine operating range, hexane is resistant to oxidation almost as much as ethanol is. It is noteworthy that ethanol proved to be quite resistant over the catalytic converter. Acetic acid was present in a few cases in exhaust gases and was mainly composed over the catalyst.

#### 4. Conclusions

In the present work, the effect of ethanol addition to unleaded gasoline on regulated and unregulated exhaust emissions from an internal combustion engine, before and after their treatment from a typical commercial three-way catalytic converter is studied. The main results obtained are:

- The addition of ethanol to the fuel up to 10% w/w resulted in a decrease in carbon monoxide tailpipe emissions in the whole operating range. On the other hand, an increase in the Reid vapour pressure was observed, indicating increased evaporative emissions for ethanol fuels.
- Acetaldehyde engine-out emissions were significantly increased for ethanol fuels, almost the double in some cases. The catalytic converter

operation decreased acetaldehyde emissions to a great extent in the case of Eth10%, while low catalytic efficiency on acetaldehyde was observed for Eth3%.

- Generally, benzene and toluene emissions were decreased by ethanol addition to gasoline although this beneficial effect of ethanol was eliminated after the operation of the catalyst. Acetic acid was detected in exhaust gases in some cases only for the base and the Eth3% fuel.
- Ethanol was identified in exhaust gases only when it was present in the fuel. In the case of Eth10%, almost double the ethanol emissions were observed than for Eth3% as engine power was increased.
- Concerning the catalytic converter efficiency, major differences were observed from one compound to another. Acetone, benzene, toluene and ethylene were easily decomposed while ethanol, hexane and acetaldehyde were quite resistant. Methane emissions after the catalytic converter were sometimes higher than after the engine, confirming results obtained in previous work (Pouloupoulos and Philippopoulos, 2000). As a result of the different catalytic efficiency for each compound, ethylene, methane and acetaldehyde were the main compounds present at engine outlet and at tailpipe before catalyst operation, while methane, acetaldehyde and ethanol were the main compounds in tailpipe exhaust emissions for ethanol fuels after the catalytic converter operation.

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