Non-regulated emissions speciation in reference gasoline and gasoline-EtOH blend on passenger vehicles exhaust

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In order to reduce the emissions of air pollutants, engine, fuel formulation and engine management design have changed. Ultra clean vehicle technologies started to be used in increased number. As a result, the emissions composition is expected to change as well. A large number of comparative studies report results on regulated pollutants emitted by gasoline and gasoline blends, but there is a lack of data for the unregulated pollutants. The use of new technologies and new fuels require new emissions tests especially for non-regulated compounds.

In this study, the emissions characteristics of a reference gasoline fuel in comparison with reference fuel blended with EtOH, by different operating conditions are reported. The effects of the EtOH blend (10% and 20%) to a reference gasoline fuel on the exhaust emissions (NMVOC, CO₂, NOₓ, particles) and from an internal combustion engine gasoline passenger car equipped with catalyst respecting the Euro 4 emission norm, and direct injection system is presented.

The measurements were conducted on a roller test bench using different driving cycles: ARTEMIS real world driving cycle and additionally a driving cycle consisting in idle, 30, 50, 90 km/h.

The sampling positions were directly after the engine, an intermediary position and in the tailpipe exhaust.

The off line NMVOC (non methane volatile organic compounds) were sampled using cold traps, active carbon tubes, DNPH tubes and analysed by use of GC-MS and HPLC (high performance liquid chromatography), respectively. The particles were monitored by use of an EEPS (Engine Exhaust Particle Sizer). Other 22 components, were monitored by use of an on line FTIR (MEXA 6000 FT).

The investigations reveal that among the oxygenated compounds 15 species were found in engine out exhaust and only 3 in tailpipe emissions (formaldehyde, acetaldehyde and acroleine). The hydrocarbons emissions decrease by increased EtOH content. Total particle concentration, mass and diameter decreased substantially after catalyst and filter by increased ethanol blend. The nitro-compounds, while unregulated are also known to pose health and environmental problems. The nitro-phenols and nitro-cresolos in the combustion process of vehicles were reported by Nojima et al. (1983), Bolzacchini et al. (2004) in the gasoline exhaust. Their presence in the blended gasoline exhaust was also investigated.

The investigation of the unregulated compounds in the exhaust from conventional and alternative fuels allows the evaluation of alternative fuel usage effects.


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Influence of Ethanol (EtOH) blend in gasoline fuel on passenger car non regulated emissions was investigated.

Roller test bench measurements

Figure 1: BMW vehicle, 2006, Euro 4, gasoline fuelled, direct injection system, series vehicle.

Sampling positions:
The sampling positions were direct after engine (position 1), intermediary (position 2) and in the tailpipe exhaust (position 3).

Reference Fuel:
Gasoline: CEC RF-02-03, Oxygen Content 0.1% Additive: Bioethanol (10 and 20 % w/w)

Analytical instrumental
Off line NMVOC: DNPH tubes, active carbon tubes, cold trap On line Particles: EEPS CO, CO2, NO, NO2, N2O, H2O, HCHO, HCN, CH3CN, CH3OH, 1.3 C6H6, iso-C4H8, C6H6, C7H8, NH3, SO2, HCHO, HCOOH, THC, FTR Nexa 6000 FT.

Driving cycles:
-ARTEMIS cycle- real world driving cycle -Idia, 50, 90 km/h – driving cycle

Figure 2: Variation of total particle concentration with fuel composition, for different vehicle operation conditions.

Table 1: Variation of particle mass and diameter with fuel composition by 50 and 90 km/h

Table 2: Variation of particle mass and diameter with fuel composition by 50 and 90 km/h. Emissions indices variation with fuel composition by 50 and 90 km/h for the oxygenated compounds in the tailpipe exhaust.

Emission index (g/kg fuel)
Ei = (mi, emitted)/(mf, burned)
m= mass of species i; mf = mass of fuel burned

Calculating by multiplying the CO2 emission index c 3134 g/kg fuel with the emission ratio of the component relative to CO2 (mg/mg).

CO2 emissions are estimated based on fuel consumption only, assuming that the carbon content of the fuel is fully oxidised into CO2.

Figure 3: Emissions indices variation with fuel composition by 50 and 90km/h for the oxygenated compounds in the after engine exhaust.

Figure 4: Emissions indices variation with fuel composition by 50 and 90km/h for the oxygenated compounds in the tailpipe exhaust.

Figure 5: Identified nitro-compounds molecules in the after engine exhaust.

Figure 6: Profiles of selected NMVOC relative to benzene (p/p/p/p/p), in the after engine exhaust.

Conclusions
-Total particle concentration, mass and diameter decreased substantially after catalyst and filter by increased ethanol blend.
-During and after filter regeneration, tailpipe exhaust gas particle emissions are similar to emissions measured after engine.
-15 oxygenated species were found directly in the after engine position and only 3 at the end of the after treatment system (formaldehyde, acetaldehyde and acroleine).
-The nitro-compounds found in the after engine position by increased EToH were no more found in the exhaust gas.
-The hydrocarbons emissions decrease by increased EToH.
-Highest emission ratios related to benzene were found for toluene, ethylbenzene, xylenes, 1,3,5 TMB, 1,2,4 TMB, 1,2,4,5 tetramethylbenzene, 1,2,3,4 tetra-methylbenzene and naphthalene
-Vehicle emissions are strongly influenced by the vehicle operating conditions.
-The experiments showed that the BMW after treatment system works very well with increased ETOH.
-More studies with systems from other manufactures are required in order to asses the influence of the new technologies and the new alternative fuels on vehicles emissions.

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