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, CO_2, 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-cresols 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.

Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M.: Studies on photochemical reaction of air pollutants. X. Identification of nitrophenols in suspended particulates. Chemical and Pharmaceutical Bulletin 31, 1047–1051., 1983

Bolzacchini, E., Perrone, M.G., Gianelle, V., Rindone, B., Avella, F., Faedo, D., Ierardi, P., Astorga, C., Hjorth, J.: Nitrophenols in Milan atmosphere and urban particulate. Proceedings of the Eighth Symposium of the Environmental Chemistry Division, Italian Chemical Society, Siena, June 2004

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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, CO_2, NO, NO_2, N_2O, H_2O, NH_3, SO_2, HCHO, HCOOH, CH_4, C_2H_4, C_2H_6, 1,3 C_4H_6, iso-C_4H_8, C_6H_6, C_7H_8, NO+NO_2,
THC: FTIR MEXA 6000FT

Driving cycles

-ARTEMIS cycle- real world driving cycle
-Idle, 50, 90 km/h – driving cycle

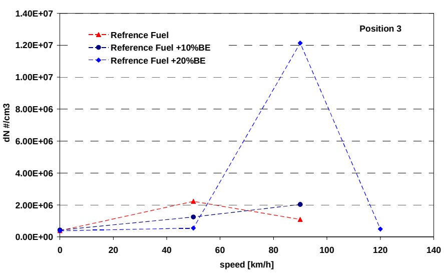

Figure 2: Variation of total particle concentration with fuel composition, for different vehicle operation conditions

		Position 1		Position 2		Position 3	
Fuel	Speed km/h	Dp [nm]	Mass [µg/cm³]	Dp [nm]	Mass [µg/cm³]	Dp [nm]	Mass [µg/cm³]
Reference fuel	Idle	37.22	12105.25	23.88	2388.33	18.50	141.28
	50	14.08	854.00	21.40	2140.00	21.72	260.60
	90	44.08	16894.00	13.04	1304.00	13.23	218.00
Reference fuel + 10% BE	Idle	14.21	102.74	20.19	2018.75	12.21	49.90
	50	17.82	464.64	18.35	1835.00	17.63	191.99
	90	18.90	428.88	18.95	1895.00	20.71	382.75
	120			16.14	1614.40		
Reference fuel + 20% BE	Idle	11.72	115.74	12.34	1234.00	11.37	26.80
	50	13.68	192.04	15.70	1570.00	17.82	182.00
	90	14.41	234.50	16.04	1604.29	43.30	2086.00

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

Emission index (g/kg fuel)

Ei= (mi, emitted)/(mf, burned)

mi- mass of species i; mf-mass of fuel burned

✓Calculated by multiplying the CO_2 emission index c 3134 g/kg fuel with the emission ratio of th component relative to CO_2 (mg/mg).
✓CO_2 emissions are estimated based on fue consumption only, assuming that the carbon conter of the fuel is fully oxidised into CO_2

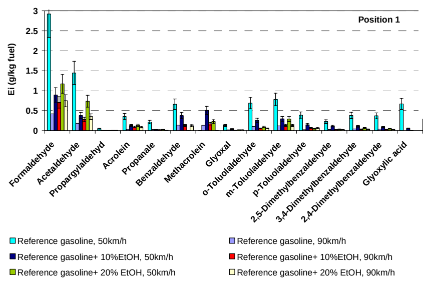

Figure 3: Emissions indices variation with fuel composition by 50 and 90km/h for the oxygenated compounds in the after engine exhaust

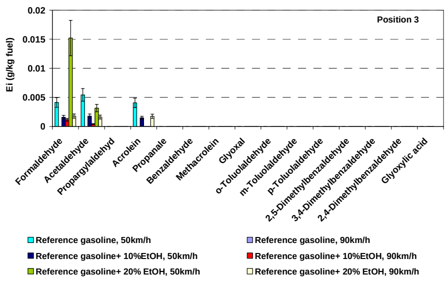

Figure 4: Emissions indices variation with fuel composition by 50 and 90km/h for the oxygenated compounds in the tailpipe exhaust.

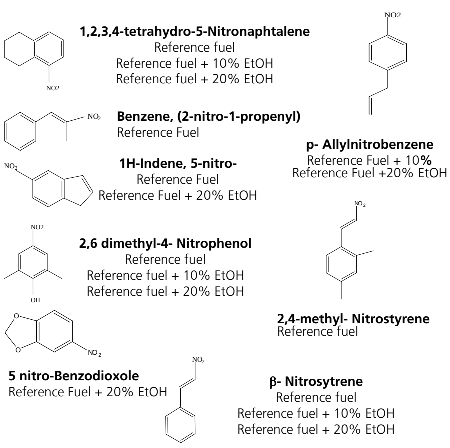

Figure 5: Identified nitro-compounds molecules in the after engine exhaust.

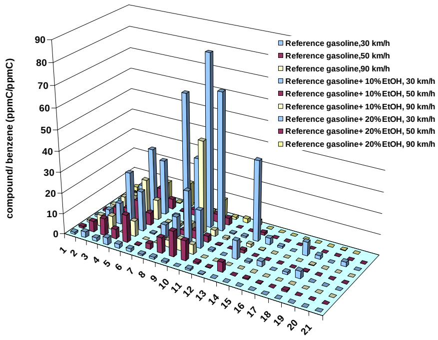

Figure 6: Profiles of selected NMVOC relative to benzene (ppbC/ppbC), in the after engine exhaust.

(1) Benzene, (2) Toluene, (3) Ethylbenzene, (4) o- Xylene, (5) m- Ethyltoluene, (6) p- Ethyltoluene, (7) 1.3.5TMB, (8) 1.2.4.TMB, (9) 1.2.4.5 Tetramethylbenzene, (10) 1.2.3.4 Tetramethylbenzene, (11) 2 Pentanolnitrate, (12) 2- Nitrophenol,, (13) 2- Methylnaphtalene, (14) 2,6- dimethyl- 4- Nitrophenol, (15) 1.2.3.4- tetrahydro- 5-Nitronaphtalene, (16) 3- methyl-Biphenyl, (17) 1-phenyl 2-Nitropropene, (18) p-Allylnitrobenzene, (19) 2.4-methyl-Nitrostyrene, (20) 5-nitro- Benzodioxole, (21) Dibenzofuran

The nitro-compounds were not found in the tailpipe exhaust samples

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 tetra-methylbenzene, 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 increase 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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