EEFECT OF TWO OXYGENATED FUELS ON GENOTOXIC EMISSIONS OF GDI VEHICLES

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Introduction/Background:

Gasoline Direct Injection has been introduced in the market due to their enhance efficiency, low fuel consumption and lower CO_2 emission. However, a large number of particles are emitted from GDI vehicles exceeding the current Euro 6 limits ($6x10^{11}$ particles/km). It is expected that 30% of the EU fleet will be GDI in 2020 and this will induce changes in the exhaust composition and with it may produce new health risks for humans. Some of the critical pollutants are polycyclic aromatic hydrocarbons (PAHs), alkyl-PAHs and nitro-PAHs with many of them being genotoxic. The use of alternative fuels such as ethanol or butanol could be a solution to lower the emissions of toxic pollutants. It has been reported[1, 2]that the concentration of some regulated pollutants (CO, HC and NOx) decreases with the use of ethanol. These findings are from port-fuel injection vehicles and effects on GDI-vehicles might differ due to higher injection pressures and different form of mixing the fuel with air, where a less homogeneous mixture can contribute to particle formation.However the impact of biofuel blendings on non-regulated pollutants like PAHs is contradictory on the literature.

PAHs are products of incomplete combustion of carbon-containing fuels and organic matter (Fig. S1). PAH emissions from internal combustion engines[3, 4] depend on parameters like fuel type, vehicle technology, and whether the engine has been warmed up or not and is operated in steady or transient conditions. It has been reported elsewhere [5-7] that ethanol addition may increase PM. PAH are usually released with PM. Then, the higher heat of evaporation of ethanol compared to gasoline causes cooling in the combustion chamber and therefore reduces vaporization of less volatile compound resulting in residual fuel which promotes PM formation by diffusion burning.

Methodology:

In this study, complete exhaust samples, including solid, condensed and gaseous fractions, have been collected in all-glass sampling devices from 2 Euro 6b-GDI vehicles (Golf VII and Citröen C4)) at the chassis dynamometer of the UASB (Biel, Switzerland). Vehicles were driven following the WLTC under hot (hWLTC) and cold start (cWLTC) conditions. See scheme in Fig. S2 Three fuels were tested: gasoline (E0), an ethanol-gasoline blend with 10% ethanol (E10) and a butanol-gasoline blend at 15% butanol (B15). Results are also compared to already published data with a different vehicle tested with E10 and E85[8]. Diluted exhausts were sampled from a CVS tunnel. In the laboratory, samples were processed following several extraction and cleanup procedures. Final extracts were analyzed by HRGC-HRMS and concentrations of PAH, alkyl-PAHs and nitro-PAHs were determined.

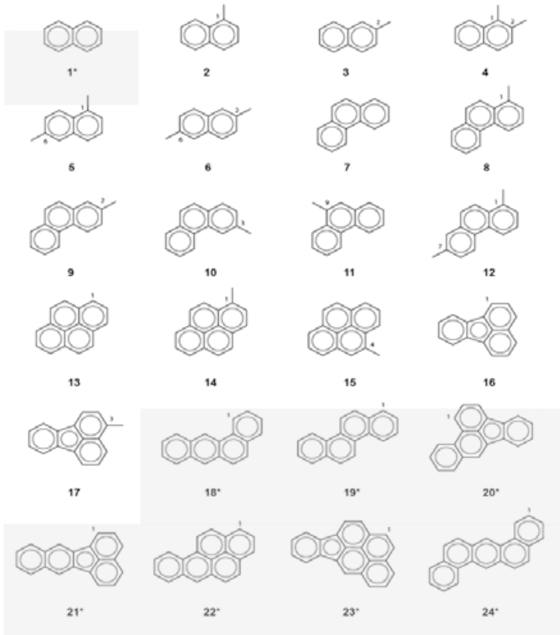

Fig. S1. Naphthalene (**1***), 1-methylnaphthalene (**2**), 2-methylnaphthalene (**3**), 1,2-dimethylnaphtphalene (**4**); 1,6-dimethylnaphthalene (**5**), 2,6-dimethylnaphthalene (**6**), phenanthrene (**7**),1-methylphenanthrene (**8**), 2-methylphenanthrene (**9**),3-methylphenanthrene (**10**), 9-methylphenanthrene (**11**), 1,7-dimethylphenanthrene (**12**), pyrene (**13**), 1-methylpyrene (**14**), 4-methylpyrene (**15**), fluoranthene (**16**), 3-methylfluoranthene (**17**), benzo(a)anthracene (**18***), chrysene (**19***), benzo(b)fluoranthene (**20***), benzo(k)fluoranthene (**21***), benzo(a)pyrene (**22***), indeno(1,2,cd)pyrene (**23***), dibenz(ah)anthracene (**24***)

Toxicity evaluation assessment

Toxicity equivalency factors (TEFs) can be used to compare the cumulated toxicity of multi-compound mixtures with similar mode of action. Several authors reported different PAH TEFs, often applied are those proposed by Nisbeth and LaGoy[9] which we and others used [10-12]. The toxic concentration is calculated by multiplying the concentration (ng/m^3) of each individual PAHs by its TEF value. We focus on the genotoxic PAHs which are those listed as group 1, 2A and 2B carcinogens[13]. TEF associated to these compounds are displayed in the poster together with the chemical structure and the carcinogenic group.

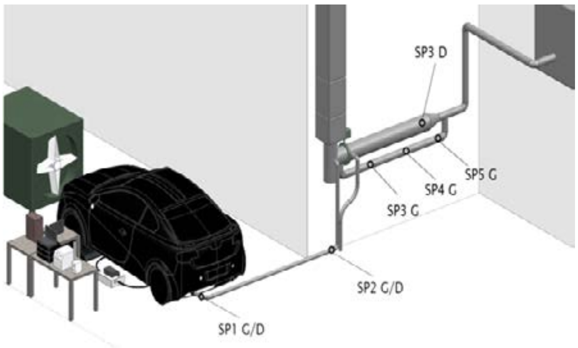

Fig. S2. Scheme of the sampling

Results/Conclusions:

A total of 34 PAH and alkyl PAHs were identified in the exhaust. The most prominent are shown in the figure on the right (Fig. S1) ordered according to increasing ring-number and molecular weight. Fig. 2 in the poster shows the effect of the different fuels on the concentration (ng/Nm^3) of PAHs under cWLTC (blue) and hWLTC (red) for the 3 vehicles tested (Golf VII, Citröen C4 and Volvo V60). PAHs are grouped according to the ring number.
Fig. 3. shows the cumulated genotoxic concentration (ng TEQ/Nm^3) of the 8 genotoxic PAHs (framed) and the individual patterns. On the right, the chemical structures with the carcinogenic group and TEF numbers are shown.
The hypothesis that ethanol lowers GDI vehicle emissions seems to be very dependent on the engine type. According to these tests, as it is happening with the ethanol, the use of butanol does not always reduce emissions. The oxygen content in butanol is similar to that of the ethanol, however, the octane nr. is similar to that of gasoline (99 and 95 respectively) although the heat of vaporization is lower than that of ethanol, but higher than gasoline. Therefore, the butanol may behave like gasoline.
According to the results observed, the following conclusions can be made:

Fuel effect. E10 and B15 seem to increase emission concentrations of the higher molecular weight PAHs, with higher values in hWLTC in the GOLF VII. The effect is null or lower with the Citröen and with the Volvo (E10 and E85) where even decreases. However, emissions of the most volatile compounds are lowered with the use of biofuels.

Cold emissions. A significant cold-start effect is observed for the 2- and 3-ring PAHs (highest volatility). This effect is reduced, with hWLTC emissions being even higher for the 4-, 5- and 6-ring PAHs.

Genotoxic Potential. The highest genotoxic concentration (due to benzo(a)pyrene) is observed with B15 in the Golf VII under the hWLTC. Nevertheless, the use of E10, B15 and E85 seems to reduce genotoxic emissions when comparing with the emissions with E0 under the cWLTC.
Observing the pattern figure, the benzo(a)pyrene relative proportions is higher in the hWLTC and in some vehicles increase with the use of E10, B15 or E85.

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