Impact of fuel and driving cycle on the chemical composition of particulate matter emitted by various automobile engines

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Ultrafine particles released by internal combustion engines are considered to constitute a substantial part of aerosols loading in urban areas of high traffic and population (Stolcpartova et al. 2015). Campaigns including simulations and test runs of modern combustion engines offer a powerful tool for investigation of chemical composition of particulate emission in dependence on engine technology, combustion processes, fuel, operation conditions, and driving cycles (Popovicheva et al., 2015).

In this study, the effects of commonly used fuels were examined on three representative engines. Blends of diesel (B0), 30% biodiesel with diesel fuel (B30), and neat biodiesel (B100) were tested in an Iveco Tector heavy-duty diesel engine operated on engine dynamometer over a World Harmonized Transient Cycle (WHTC) and steady-state conditions (1500 rpm and 30% load). Blends of 15% ethanol, 25% of n-butanol, and 25% of isobutanol with gasoline were tested in a Ford Ecoboost 1.0 direct injection gasoline engine (DISI) in a Ford Focus car, and in a Škoda 1.4 multi-point injection (MPI) engine in a Škoda Fabia car. The cars were tested on a chassis dynamometer using the Artemis driving cycle (urban, rural and highway).

Particulate matter collected on PTFE and quartz fiber filters was subjected to comprehensive chemical investigation, including thermo-optic analyses, capillary electrophoreses, FTIR spectroscopy, and mass spectrometry. We studied the differences in organic carbon (OC) to elemental carbon (EC) ratio, water-soluble ionic content, organic/ inorganic functionalities, and surface chemical composition with special focus on polycyclic aromatic hydrocarbons, PAH, content by changing diesel, gasoline and alcohol fuels, operation conditions, and the driving cycle.

The increase of biofuel fraction leads to an increase in OC/EC ratio for two operation conditions of diesel engine, WHTC and 1500 rpm 30 %, as following: 0.45 and 0.93 for B0, 1.1 and 1.9 for B30, 2.5 and 5.7 for B100. Spectra obtained with laser desorption/ionization mass spectrometry (L2MS) are in agreement with this measurements, where the WHTC diesel samples contain less PAHs and/or alkylated PAHs (four rings) than 1500 rpm 30 % samples which contain PAHs up to six member rings and additional alkylated PAHs. Furthermore, the increase of organic carbon relates to the higher abundance of acetate $CH3COO^-$ ions in biofuel emission, together with Na^+, Ba^{2+} and Ca^{2+} ions. Oxygenated fragments and alkaline metals were detected with secondary ion mass spectrometry (SIMS), enforcing the results from FTIR spectroscopy where higher relative concentrations of C=O carbonyls was detected for 1500 rpm 30% load.

DISI gasoline engine produces OC/EC ratio of ~1 with both fuels (gasoline and gasoline + 15% ethanol). The ratio is increased to ~2 when the amount of ethanol in the fuel is increased to 25%. Even if gasoline emission particulates have a lower OC/EC ratio they contain a wide distribution of PAHs, starting from lower masses and going up to eight member rings PAHs. Nevertheless gasoline samples contain less aliphatic fragments in comparison with diesel samples. The addition of alcohol in gasoline reduces the emission of alkylated PAHs (less pronounced petrogenic character). The largest difference is found for total ion concentrations between urban and highway Artemis cycle. In addition SIMS measurements showed a large contribution of sulfate and ammonium ions for highway Artemis cycle compared to the other tested cycles.

MPI gasoline engine produces high OC/EC (~5) even with pure gasoline fuel, demonstrating less soot production during the combustion of homogeneous air-fuel mixture when compared to direct injection engine system. These results present a complete picture of the chemical composition of particulate matter emitted by diesel and gasoline engines.

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Stolcpartova, J., Pechout, M., Dittrich, L., Mazac, M., Fenkl, M.,Vrbova, K., Ondracek, J., and Vojtisek-Lom, M., (2015) *Atmosphere* 6, 1714-173

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