Effect of atmospheric ageing on volatility and ROS of biodiesel exhaust nano-particles

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Keywords: Diesel particulate matter, aging, ROS.
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Generally, the magnitude of pollutant emissions from diesel engines is ultimately coupled to the structure of fuel molecules. The presence of oxygen, level of unsaturation and the carbon chain length of respective molecules influence the combustion chemistry. It is speculated that increased oxygen content in the fuel may lead to the increased oxidative potential (Stevanovic, S. 2013). Also, upon the exposure to UV and ozone in the atmosphere, the chemical composition of the exhaust is changed. The presence of an oxidant and UV is triggering the cascade of photochemical reactions as well as the partitioning of semi-volatile compounds between the gas and particle phase. To gain an insight into the relationship between the molecular structures of the esters, their volatile organic content and the potential toxicity of diesel exhaust particulate matter, measurements were conducted on a modern common rail diesel engine. This research also investigates the contribution of atmospheric conditions on the transfer of semi-volatile fraction of diesel exhaust from the gas phase to the particle phase and the extent to which semi-volatile compounds (SVOCs) are related to the oxidative potential, expressed through the concentration of reactive oxygen species (ROS) (Stevanovic, S. 2013).

Methodology: A Cummins diesel engine runs on blends of four methyl ester biodiesels and conventional diesel on a variety of operating conditions. The exhaust produced by the engine passes through a multi-stage dilution system followed by a flow through reactor by which ageing process is induced. A Volatility Tandem Differential Mobility Analyser (VTDMA) measures the change in volatile content of particles. A profluorescent nitroxide molecular probe (bis(phenylethynyl) anthracene-nitroxide; BPEAnit) (Stevanovic, S. 2013) is used for assessing the oxidative potential of particles (i.e. potential of particles to induce oxidative stress).

Results and discussion: Figure 1 shows the volatility of 60nm particles from the 50% blends of four metyl-esters and diesel fuel. Overall, the organic content of the particles in all blends has increased after ageing. As the oxidative potential is related not only to the organic content but also to the portion of the oxidised organic fraction of PM (Stevanovic, S. 2013), particles are more potentially toxic after being exposed to oxidative agents i.e. ozone and UV light.

The results of VTDMA measurement are in good correlation with the oxidative potential measured by BPEAnit. It shows that in almost all cases, the oxidative potential of the particle phase increases after being exposed to ozone and UV light. It is also evident that there is a correlation between the level of saturation of the fuel and the organic content of the particles where the most saturated fuel produces the most volatile particles. In addition, the volatility of aged particles produced by saturated fuels increases more than those produced by less saturated blends.

The presented research shows that biodiesel, compared to the commercial diesel, emits more volatile particles with higher ROS concentrations, and interestingly, the matter is deteriorating over time as diesel exhaust is aged in the atmosphere. Also, an increase in organic fraction upon aging indicated that the greater amount of SVOCs is present after the combustion of biofuels. Since the organic fraction is tied to the oxidative capacity of particles, those particles produced by bio-diesel are likely to be more harmful than those produced by commercial diesel. Overall, the ROS measurements confirm the mentioned hypothesis.

It also sheds a light onto new aspects of particulate emissions that should be taken into account when establishing relevant metrics for health implications of emissions from various future fuels. While the common belief is in favour of a movement from conventional fuels to those extracted from animals and plants, findings of this research may argue the latter notation.

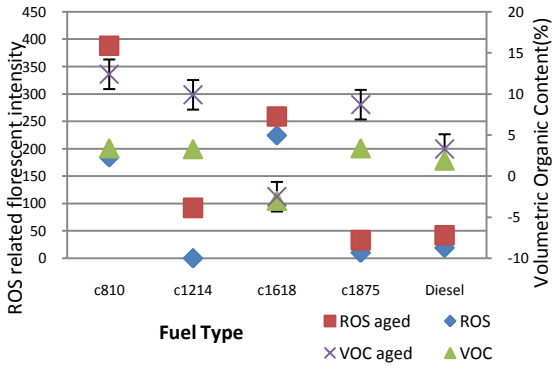

Figure 1. The change in volatile content of particles and ROS of particles before after ageing process

References:

1."The influence of oxygenated organic aerosols (OOA) on the oxidative potential of diesel and biodiesel particulate matter" Authors: Stevanovic, S.; Miljevic, B.; Surawski, N.; Fairfull-Smith, K.; Bottle, S.; Brown, R.; Ristovski, Z. Manuscript ID: es-2013-007433, Submitted to ES&T.