Effect of seed oils on the morphology of nanoparticles from diesel engines

Edgardo Coda Zabetta, Clifford Ekholm, Mikko Hupa
Åbo Akademi Process Chemistry Centre – Combustion and Materials Chemistry Group, Turku, Finland

Tommi Paanu, Mika Laurén, and Seppo Niemi
Turku Polytechnic – Mechanical Engineering Department, Turku, Finland

Recent EU directives encourage blending fossil oils with bio-derived oils in order to reduce the CO$_2$ emissions from diesel engines.$^1$ Besides CO$_2$, the bio-oils are also known to reduce the overall mass of emitted particulate. However, recent studies indicate that the mass reduction trades with a severe increase of the smallest portion of particulate (nPM$<1\mu$m).$^{2,3}$ The nPM is considered the most dangerous portion of particulate, and biological studies also warn that the morphology of nPM (structure and composition) might play a role in its damaging properties towards humans (toxicity and carcinogenicity) and machines (corrosivity and poisoning).$^{4,5}$ While the morphology of particulate from diesel fuel is relatively well known,$^6,7$ no such information could be found on the nPM from bio-oils.

The scope of this work was to unveil whether bio-oils lead to nPM whose morphology differs from that of the nPM from diesel fuel, with potential consequences on its properties. For this study nPM was generated in a test cell diesel engine (Tab.1). The engine was operated at different loads and speeds and was fuelled with diesel fuel oil (DFO), untreated mustard seed oil (MSO), untreated rape seed oil (RSO), and their blends (Tab.2). The engine was usually operated without any exhaust treatment, but few tests were performed with a diesel oxidation catalyst (DOC). All tests were performed under similar conditions of pressure, moisture, and temperature. In all tests the global combustion process was maintained as similar as possible by setting the fuel injection timing so as to achieve similar cylinder pressure profiles (Fig.1).

![Figure 1. Cylinder pressure vs. crankshaft angle for 5 of the tested blends at 1500 rpm and 100% load](image-url)

Coda Zabetta et al., 9th ETH-Conference on Combustion Generated Nanoparticles, Zurich, August 15-17th, 2005
The physical properties and the organic composition of the fuel and lubricant oils were measured according to the methods set by the International Organization for Standardization (ISO), the Institute or Petroleum (IP), the American Society for Testing and Materials (ASTM), and the American Oil Chemists’ Society (AOCS). The content of minor and trace elements in the oils were measured by Inductively Coupled Plasma (ICP), X-ray Fluorescence Spectroscopy (XRF), and Atomic Absorption Spectroscopy (AAS).

An electric low pressure impactor (ELPI) was used to record the amount of particles and their size distribution as emitted from the engine during each test. The sampling line of the ELPI was connected to a slip stream from the engine tailpipe through a two-stage diluter designed to avoid homogeneous nucleation and condensation (Fig.2). The ELPI was also used to sample the particles for later analysis of their structure and composition in a LEO Stereoscan 360 scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDS).
The ELPI readings confirmed that seed oils lead to larger amounts of nPM than conventional diesel fuel oil. These readings also proved that such increase of nPM can be limited with an oxidation catalyst (DOC) designed for diesel-operated engines (Fig. 3).

The SEM/EDS investigations revealed structural and compositional differences between the nPM from different oils and blends. All the particles appeared to be clusters of carbon spherules originated in the gas-phase, but the spherules from the seed oils and their blends appeared “transparent”, while the spherules from the diesel fuel oil (DFO) were solid. The transparent spherules appeared also more prone than the solid spherules to undergo alterations when subjected to an electron beam (Fig. 4).

Figure 3. ELPI size distribution of the particles collected from the test engine without any treatment (left) and comparison after a DOC (right). Similar results were obtained under all engine speeds/loads

Figure 4. SEM micrographs of the “transparent” spherules (up) and their “alteration” after intense electron beam (down) observed in the samples from neat seed oils and their blends
Along with the carbonaceous nPM, the seed oils led to localized inorganic bodies (10nm-1µm) while the DFO did not (Fig.5, up). The seed oils led also to minute “anomalies” (~5nm) which were too small for being analyzed, but appeared to be made of elements heavier than carbon (Fig.5, down). The inorganic bodies and the minute “anomalies” were observed in all samples generated from the seed oils and their blends while, in agreement with open literature, neither the bodies nor the “anomalies” were ever observed in any of the samples from the diesel fuel.

Although DFO and seed oils greatly differed in composition, it was calculated that the consumed lubricant oil overwhelmed all compositional differences among fuels, but for the potassium (K) carried with the seed oils. Table 3 shows such calculations, which were based on the elemental analysis of the oils and the estimated consumption of lubricant oil (~5g/kgfuel).
Our findings indicate that the nanoparticles (nPM) from seed oils differ from the diesel nPM in amount, structure, and composition. This suggests that the nPM from seed oils (and their blends) can have different toxic, carcinogenic, corrosive, and poisoning properties than those shown by diesel fuel. Our studies also suggest that all such differences are caused by the potassium (K) contained in the seed oils.

We propose that the “transparent” particles observed in nPM from seed oils might be hollow cenospheres rather than the solid spherules which are usually observed in diesel particulate. We also propose that the observed alterations of these nPM might be the result of structural re-organizations of the carbon layers (graphenes) within the cenospheres, a phenomenon already observed in diesel soot when subjected to intense laser beams.9 Future work will address such speculations by analyzing the nPM in high resolution transmission electron microscopes (HR-TEM) and by investigating a larger variety of bio-derived blends (biodiesel, waste) and oxidation catalysts (OC).

This work was part of the FINE research program funded by the National Technology Agency of Finland (TEKES), and received additional support from the industrial partners Dekati Oy, Ecocat Oy, and Oy Ekolaiho Ab. The work is also supported by TEKES via the research project Chemistry in Biomass Combustion with the industrial partners Andritz Oy, International Paper Inc., Foster Wheeler Energia Oy, Kvaerner Power Oy, Oy Metsä-Botnia Ab, and Vattenfall Utveckling AB.

**Previous publications related to this work**


**References**


Coda Zabetta et al., 9th ETH-Conference on Combustion Generated Nanoparticles, Zurich, August 15-17th, 2005