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

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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< 1μm).[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 carcinogenity) 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).

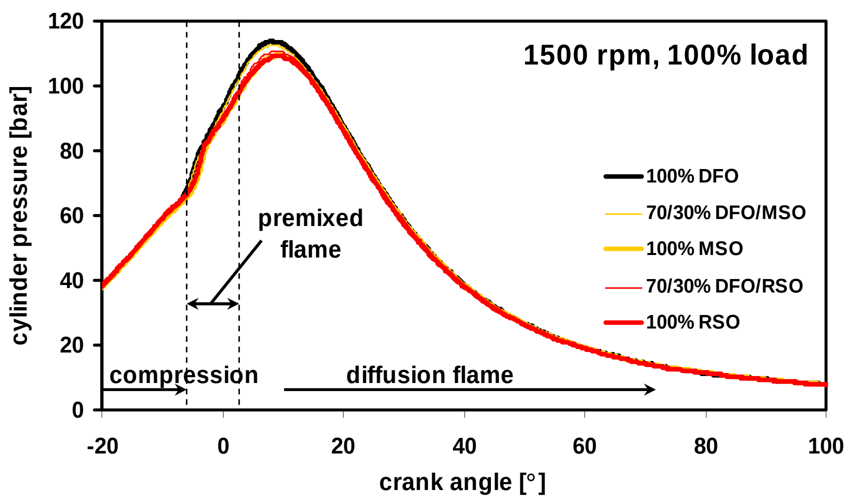


Figure 1. Cylinder pressure vs. crankshaft angle for 5 of the tested blends at 1500 rpm and 100% load

Table 1. Test engine specifications

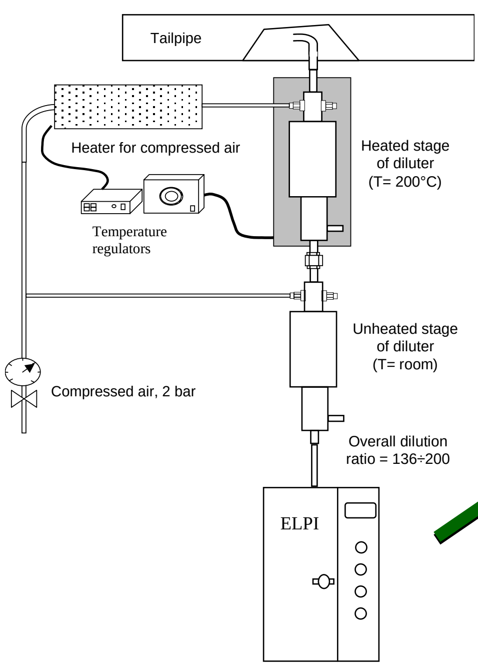
Type	Valmet 420 DSJ
Bore	108 mm
Stroke	120 mm
Swept volume	4.4 litres
Compression ratio	16.5
Injection pump	Bosch A
Injector tips	5-holes, bore 0.275 mm
Turbocharger	Schwitzer S1 B
Intercooler	air-to-water, Valmet

Table 2. Test engine operation

Load	100% & 50%
Speed	2400 & 1500 rpm
Fuels	Diesel Fuel Oil (DFO) Mustard Seed Oil (MSO) Rape Seed Oil (RSO)
Blends	70/30% & 50/50% DFO/xSO
Post-treatment	with and w/o diesel oxi-cat. (DOC)
Settings	fuel injection timing (other boundary conditions constant)

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)[8] 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).



ELPI sieving

foil #	D 50% [μm]
1	0.029
2	0.058
3	0.101
4	0.161
5	0.246
6	0.380
7	0.619
8	0.97
9	1.57
10	2.39
11	3.87
(12)	(6.52)
13	9.89

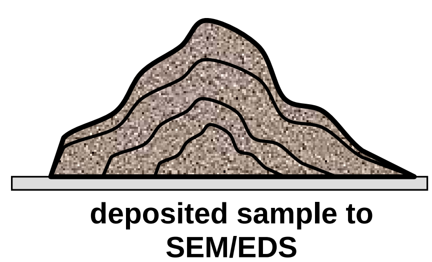


Figure 2. Schematic representation of the sampling setup with the engine tailpipe, diluter, and ELPI

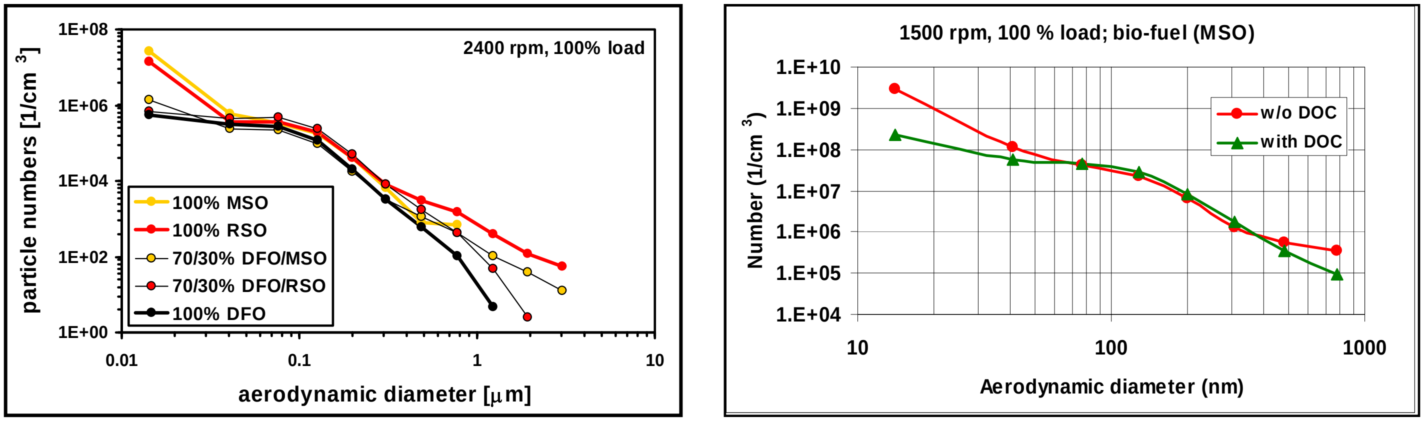


Figure 3. ELPI size distribution of the particles collected from the test engine without any treatment (left) and comparison after a DOC (right). Similar results were obtained under all engine speeds/loads

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).

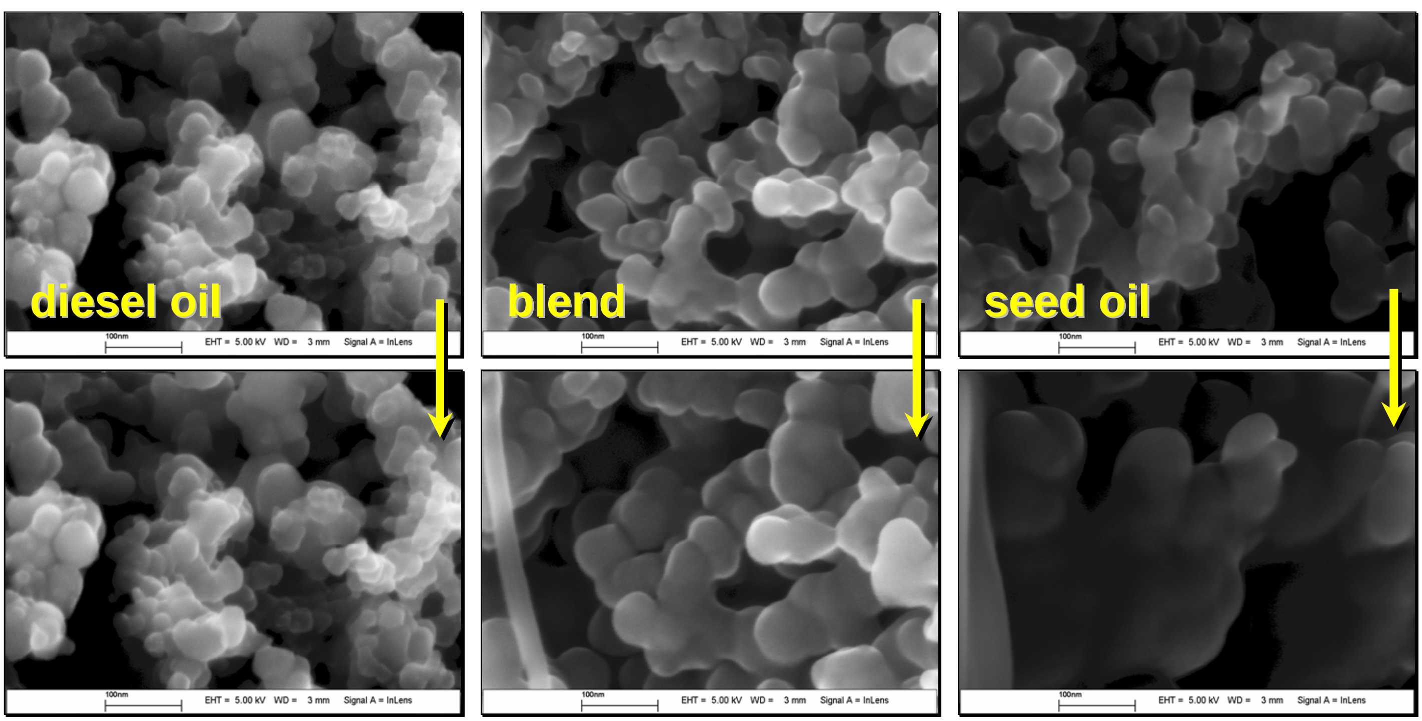


Figure 4. SEM micrographs of the “transparent” spherules (up) and their “alteration” after intense electron beam (down) observed in the samples from neat seed oils and their blends

Table 3. Calculated mass of minor and trace elements from fuel and lube oils per kg of fuel

Fuel blend	Minor and trace elements released from fuel and lubricant [mg/kg]												
	Ca	**Mg**	**Na**	**K**	**Mn**	**Al**	**Fe**	**Si**	**Cl**	**P**	**S**	**Zn**	**Mo**
DFO	10.77	4.35	0.59	<0.01	0.34	<0.01	0.12	0.72	0.48	4.38	102.25	5.51	0.07
MSO	34.84	5.69	1.77	1.34	0.38	<0.01	2.52	0.90	0.48	18.78	74.25	11.46	0.61
RSO	15.77	5.81	0.82	1.45	0.37	0.10	0.53	0.23	0.48	21.58	47.25	5.55	0.23
70/30% DFO/MSO	17.99	4.75	0.94	0.41	0.36	<0.01	0.84	0.78	0.48	8.70	93.85	7.30	0.23
70/30% DFO/RSO	12.27	4.78	0.66	0.44	0.35	0.03	0.24	0.58	0.48	9.54	85.75	5.52	0.11
50/50% DFO/MSO	22.81	5.02	1.18	0.67	0.36	<0.01	1.32	0.81	0.48	11.58	88.25	8.49	0.34
50/50% DFO/RSO	13.27	5.08	0.70	0.73	0.36	0.05	0.33	0.48	0.48	12.98	74.75	5.53	0.15
		As	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Ni**	**Pb**	**Sb**	**Tl**	**V**
DFO		<0.01	0.09	<0.01	0.01	0.60	<0.01	0.34	<0.01	<0.01	<0.01	<0.01	0.27
MSO		<0.01	0.05	<0.01	0.03	0.19	<0.01	0.38	<0.01	<0.01	<0.01	<0.01	0.25
RSO		<0.01	0.06	<0.01	0.00	0.19	<0.01	0.37	<0.01	<0.01	0.32	<0.01	0.24
70/30% DFO/MSO		<0.01	0.08	<0.01	0.02	0.48	<0.01	0.36	<0.01	<0.01	<0.01	<0.01	0.26
70/30% DFO/RSO		<0.01	0.08	<0.01	0.01	0.48	<0.01	0.35	<0.01	<0.01	0.10	<0.01	0.26
50/50% DFO/MSO		<0.01	0.07	<0.01	0.02	0.40	<0.01	0.36	<0.01	<0.01	<0.01	<0.01	0.26
50/50% DFO/RSO		<0.01	0.08	<0.01	0.01	0.40	<0.01	0.36	<0.01	<0.01	0.16	<0.01	0.26

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/kg$_{fuel}$).

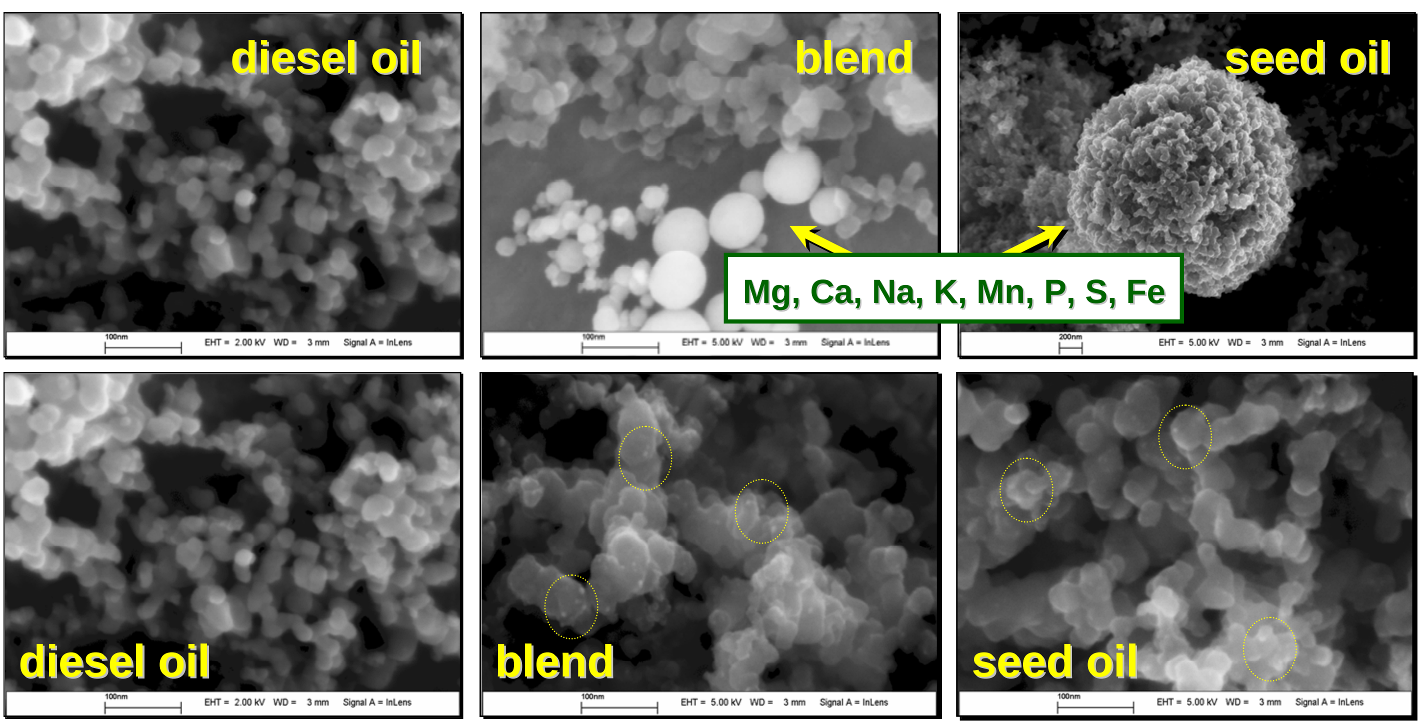


Figure 5. SEM micrographs of the localized inorganic bodies (up) and the "anomalies" (down) observed in the samples from neat seed oils and their blends

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).

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Previous publications related to this work

Coda Zabetta E., Ekholm C., Hupa M., Paanu T., Laurén M., Niemi S., TEKES FINE-BioPM "Dieselmoottorin nanohiukkaspäästöt biopohjasia öljyjä poltettaessa" (Nanoparticles from diesel engines operated with bio-derived oils), Report, Åbo Akademi Process Chemistry Centre, ISSN 1459-8205, No. 05-03, ISBN 952-12-1559-3, PCC, Turku, Finland, April, 2005 (available online at http://www.abo.fi/fak/ktf/cmc/publications/index.html)

Coda Zabetta E., Hupa M., Gas-born carbon particles generated by combustion: a review on the formation and relevance, Report, Åbo Akademi Process Chemistry Centre, ISSN 1459-8205, No. 05-01, ISBN 952-12-1511-9, PCC, Turku, Finland, February, 2005 (available online at http://www.abo.fi/fak/ktf/cmc/publications/index.html)

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