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Paper/Poster-Abstract Form

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Title: FTIR spectroscopy of diesel and biofuel particles in off-road engine exhaust

Abstract: (min. 300 – max. 500 words)

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The growing anxieties about environmental impacts of fossil fuel (FF) using and its future availability have resulted in intensive development of alternative energy sources. Vegetable oil based biofuels – oils in their pure, non-esterified form and their methylesters (FAME - fatty acids methylesters, also called biodiesel) – are commonly used as alternative fuels in existing engines. Rapeseed, palm, and other oils can be produced from local renewable resources. However, in spite of spreading of vegetable oil as biofuel environmental impacts of biofuel combustion are poorly understood. Limited information exists concerning the chemical structure of particles produced by burning biodiesel and vegetable oils. This work reviews organic/inorganic composition of diesel and biofuel particles emitted from diesel locomotive and tractor engines at various operation conditions.

Particles produced by burning biodiesel fuel EN 590 and biofuels, namely heated rapeseed oil (HRO), HRO with ethylhexylnitrate, and heated palm oil were sampled from an exhaust of a Zetor 1505 tractor engine at different engine operation conditions (full load, ISO 8178 schedules C-1 and C-2) and from a diesel-electric locomotive (fast idle and full load). The comparative analysis of particle organic chemistry as well as the impact of different engine loads on the surface properties is carried out by Fourier Transform IR (FTIR) spectroscopy. The main characteristic band of biodiesel particles is assigned to aromatic C=C stretching vibrations which can be augmented by adsorbed oxygen. The prominent feature of biofuel-produced particles is significant IR bands of oxygenated functional groups. Vibrations of carbonyl C=O groups are found together with a wide band of hydroxyl O-H groups, they may be assigned to carboxylic acids. Some bands could relate to N-O and N-H nitrogroups in amines and nitrocompounds. Particle inorganic chemistry is revealed by absorption bands associated with nitrates, nitrites, carbonates, sulfates. This interpretation is confirmed by complementary measurements of water-soluble ion species in biodiesel and biofuel exhausts by capillary electrophoresis. The relationship between IR bands of polar oxygen-containing groups to non-polar aliphatic C-H functional groups allows an estimate of the extent of the particle oxidation. Finally, this work allows the decreasing the uncertainties in chemical identity of original combustion particles produced by burning biodiesel and vegetables oils and in quantification of their environmental effects

Short CV:

Mrs. Elena Kireeva
Date of birth, city, state: 01.08.1982, Moscow, Russia. **Education:** 1999-2005: Lomonosov Moscow State University (MSU), Physics Faculty. In 2005 she has received a Master's degree from MSU, Physics Faculty. 2009 – present: Ph.D Student of Lomonosov Moscow State University (MSU), Physics Faculty.

The scientific work of Elena Kireeva is devoted to fundamental studying the properties of combustion aerosols emitted by various sources. The main aim of her research is to establish a link between physical-chemical properties of emitted Black Carbon (BC) and their effects on climate change. The great attention of the work is paid on the fundamental study of combustion particles/water interaction in the humid atmosphere. Elena Kireeva was performing a number of experiments on adsorption and freezing aircraft-generated soot. She was carried out the experimental study of cloud condensation and ice nucleation (CCN/IN) ability of original aviation soots.

Elena Kireeva has a wide experience in characterization of combustion particles by different methods. She was performing the SEM/EDS fractionation analyses of aviation and diesel engine soots with propose to quantify the hydrophobic/hydrophilic/ hydroscopic fractions. It is suggested that elaborated fractionation analyses of particulate emission from combustion sources will allow estimating the potential impacts of hydrophobic/hydrophilic and hygroscopic soots on CCN/IN formation in the atmosphere.

Elena Kireeva takes part in the performance of 5 international and bilateral projects. In 2011 her project "Thermochemistry and oxidation of multicomponent aerosols of ship emission" has received DAAD fellowship of Technical University of Munich. Elena Kireeva is author of 11 paper in peer-reviewed journals and number paper in conference proceeding.

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FTIR Spectroscopy of Diesel and Biofuel Particles in off-road Engine Exhaust

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TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Mechanical Engineering

MEDETOX

Abstract

Vegetable oil based biofuels are commonly used as alternative fuels in existing engines. Rapeseed, palm, and other oils can be produced from local renewable resources. However, environmental impacts of biofuel combustion are poorly understood. Limited information exists concerning the chemical structure of particles produced by burning biodiesel and vegetable oils. This work reviews organic/inorganic composition of diesel and biofuel particles emitted from diesel locomotive and tractor engines at various operation conditions.
Particles produced by burning diesel fuel and heated vegetable oils were sampled from an exhaust of a Zetor 1505 tractor engine at different engine operation conditions and from a diesel-electric locomotive. The relationship between IR bands of polar oxygen-containing groups to non-polar aliphatic C-H functional groups allow an estimate of the extent of the particle oxidation. This work allows the decreasing the uncertainties in chemical identity of original combustion nanoparticles produced by burning diesel fuel and vegetable oils and in quantification of their environmental effects.

Tractor engine - Zetor 1505

Fuels

- ✓ Diesel fuel (EN 590)
- ✓ Palm oil heated (HPO)
- ✓ Rapeseed oil heated (HRO)
- ✓ Rapeseed oil heated (HROe) with ethylhexylnitrate

Loads: full, ISO 8178C-1, ISO 8178C-2

Diesel electric locomotive

Fuel

- ✓ EN 590 diesel fuel (EN 590)

Loads: full, fast idle

All samples were collected at PallFlex T60A20 filters

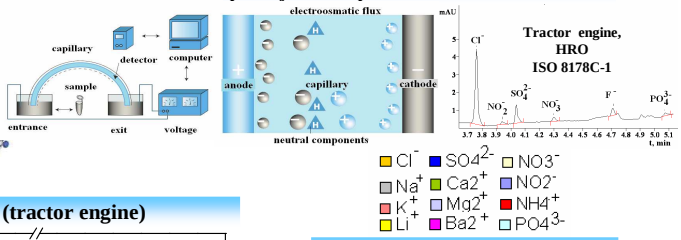
Organic/inorganic content by FTIR spectroscopy

Shimadzu IR Prestige-21

- ✓ Mode: **Transmission**
- ✓ Resolution: 4 cm^{-1}
- ✓ Number of scan: 100
- ✓ Background: Atmosphere

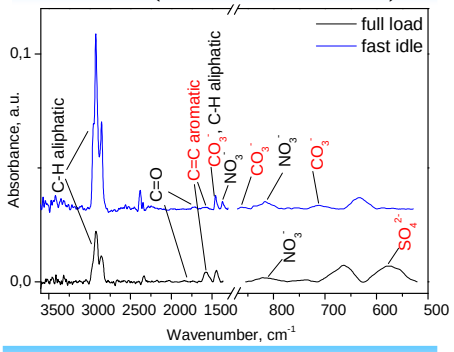
The comparative analysis of particle organic chemistry as well as the impact of different engine loads on the surface properties is carried out by Fourier Transform IR (FTIR) spectroscopy. The interpretation of bands associated with inorganic compounds is confirmed by complementary measurements of water-soluble ion species in diesel and biofuel exhausts by capillary electrophoresis.

Ion content by capillary electrophoresis

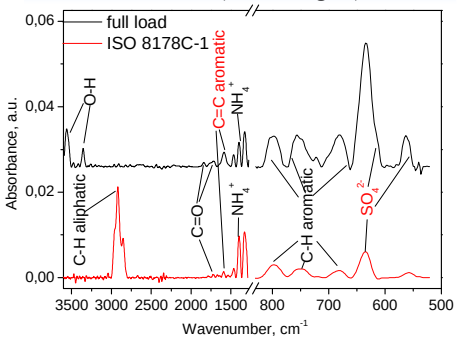


Cl$^-$ SO4^{2-} NO3$^-$
Na$^+$ Ca2$^+$ NO2$^-$
K$^+$ Mg2$^+$ NH4$^+$
Li$^+$ Ba2$^+$ PO4^{3-}

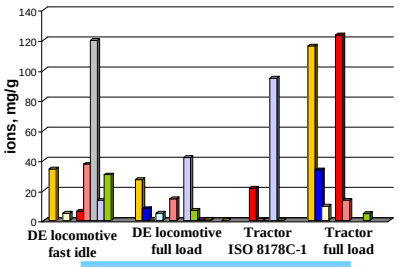
Diesel fuel (diesel-electric locomotive)



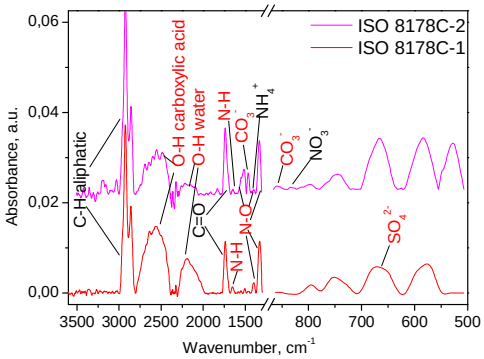
Diesel fuel (tractor engine)



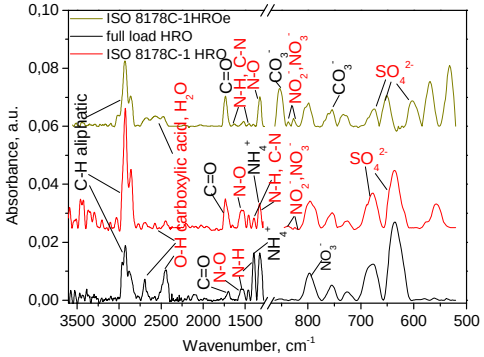
Diesel fuel (EN 590)



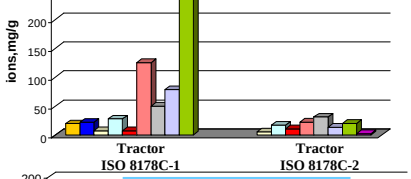
Palm oil heated (tractor engine)



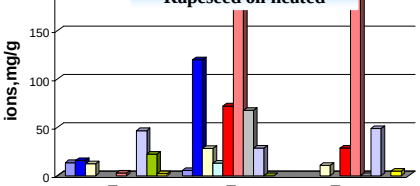
Rapeseed oil heated (tractor engine)

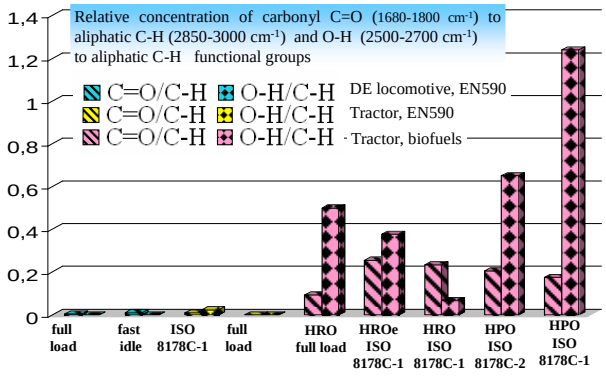


Palm oil heated



Rapeseed oil heated





Conclusions

- ✓ The organic/inorganic content of combustion particles from off-road engines is determined mainly by the type of the fuel used
- ✓ The main characteristic band of biodiesel particles is assigned to aromatic C=C stretching vibrations, which is absent in the spectra of particles from diesel fuel combustion
- ✓ The prominent feature of the spectra of biofuel-produced particles is significant IR bands of oxygenated functional groups - carbonyl C=O and hydroxyl O-H
- ✓ The set of bands in spectra of biofuel-produced particles could relate to N-O and N-H, C-N groups nitrogroups in amines and nitrocompounds
- ✓ Small ratio of peak areas of IR bands C=O/C-H and O-H/C-H for particles produced by locomotive and tractor engines using diesel fuel indicates their hydrophobic nonoxidized surface with low relative concentration of polar oxygen containing functionalities
- ✓ Nanoparticle inorganic chemistry is revealed by absorption bands associated with nitrates, nitrites, carbonates and sulfates

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