

Chemical composition of particulate and gas emissions from a 4-stroke marine diesel engine operated with heavy and distillate fuel oils

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Exhaust emissions from ships are known to generate high amounts of particulate and gaseous pollutants which have environmental, health and climate effects. Especially the use of heavy fuel oils may generate high amounts of harmful aerosol emissions into the environment. However, the chemical composition of these emissions it is still relatively poorly known.

Experiments with a 4-stroke single cylinder (80 kW nominal power) research engine with a common rail injection system were conducted in the engine laboratory at the University of Rostock. The structure of the engine represents a typical medium speed ship diesel engine. The engine was operated with distillate fuel (“DF”, EN590) and a heavy fuel oil (“HFO 350”, 2.7 % sulphur) with nominal speed (1500 rpm) and engine loads ranging from “idle” to 100 %. In addition, early and late injection points were used in the engine, representing “low-soot” and “low-NO_x” operations.

The flue gas was analysed for O₂, CO₂, CO, NO_x, SO₂ and THC with single gas analyzers (AVL CEB II). The volatile and semivolatile organic species were measured online with a resonance enhanced multiphoton-ionization time-of-flight mass spectrometer (REMPI-TOF-MS) and a proton transfer reaction mass spectrometer (PTR-MS, Ionicon). Particulate samples from the engine exhaust were collected on quartz fiber filters in steady-state conditions applying a diluting sampling system (AVL Smart Sampler).

The filter samples were analysed for inorganic species (ICP-MS), a number of PAHs, oxy-PAHs, hopanes (Thermal desorption GC-TOF-MS), Azaarenes and 1-nitropyrene (LC-FD) and for organic (OC) and elemental carbon (EC) (thermal-optical analysis, DRI). The carbon analysis was coupled with a time-of-flight mass spectrometer with both single photon ionization (SPI, 118 nm) and resonance enhanced multiphoton ionization (REMPI, 266 nm) in order to analyse molecular compositions of the organic fractions, as described by Grabowsky et al. (2011).

The PM emissions, in the load range of 25-100 %, were between 154-236 mg/kWh with DF and 728-1902 mg/kWh with HFO. The low load conditions generated clearly higher emissions up to several grams per kWh. The particles contained substantial organic material fractions, with OC/EC ratios varying between 2

and 22 depending on the engine operational conditions. The EC and inorganic (metals + sulphate) fractions varied in the ranges 2-29 % and 3-23 %, respectively. The emissions from HFO contained significant amounts of V and Ni, released from the fuel as well as sulphuric acid. Emissions with both fuels contained Ca, originating mainly from the lubrication oil. The thermal desorption GC-MS included quantification of 11 PAHs, 17 oxy-PAHs and 11 hopanes with clearly higher emission from HFO than DF. Furthermore, 9 different Azaarenes were quantified from the HFO samples, while for DF their concentrations were below the quantification limit. The REMPI-TOF-MS showed high amounts of alkylated PAHs in the PM of both fuels, with the most distinct difference the high amounts of alkylated chrysenes in the HFO emissions. A comparison of direct fuel analysis and PM emission analysis by REMPI revealed similar patterns indicating that the aromatic emissions (e.g. PAHs) are mainly present already in the fuel.

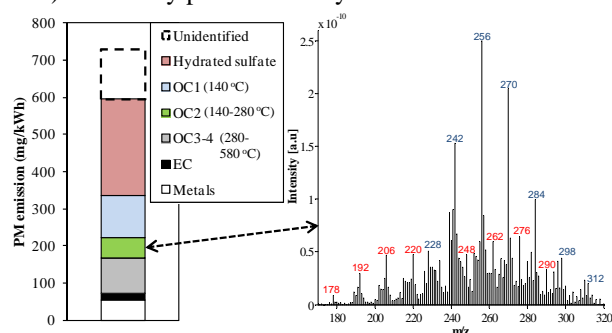


Figure 1. PM chemical composition and REMPI analysis from the OC2 fraction when operated with HFO and 50% load.

The chemical characteristics of emissions in altogether 15 operational conditions with 2 different fuels were analysed. The emissions were generally clearly higher from HFO than from DF, with the exception of EC emissions which were on a similar level with both of the fuels.

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