Fuel 157 (2015) 232–239

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Diesel/biofuel exhaust particles from modern internal combustion engines: Microstructure, composition, and hygroscopicity

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HIGHLIGHTS

- Diesel/biofuel combustion emissions from modern internal combustion engines are analyzed.
- Particulate microstructure is revealed in soot and fly ash groups as well as their hygroscopicity.
- Most polluting conditions with respect to fouling of the exhaust system are indicated.
- Multicomponent composition is impacted by both fuel and operation conditions.

ARTICLE INFO

Article history:
Received 26 December 2014
Received in revised form 15 March 2015
Accepted 28 April 2015
Available online 8 May 2015

Keywords:
Diesel/biodiesel emissions
Chemical and physical characterization
Exhaust microstructure
Multi-component aerosol

ABSTRACT

Changes in fuel characteristics and design of diesel engines have been applied in the last decades to reduce pollutant emissions in the transportation sector. Characteristics of exhaust particles and their environmental impacts need to be brought up to date. In this study, diesel and rapeseed oil were used in modern internal combustion engines (BMW and John Deere) in order to simulate stationary and transient non-road driving conditions, with attention on fouling processes in the exhaust system and contributions to atmospheric pollution. Engine particulate exhaust samples were subjected to individual particle analysis and bulk physico-chemical characterization with respect to polycyclic aromatics, water-soluble organic carbon and inorganic ions. Functionalities of alkanes and oxygen-containing compounds were determined in the exhaust particles. The emitted particles with similar morphology and composition were separated in specific groups, revealing the exhaust microstructure. In-depth characterization of individual particle composition provided insights into the relationship of chemical composition and hygroscopicity, based on fractionation analysis. With improved characterization of diesel/biofuel combustion emissions we demonstrate that the multicomponent composition of modern internal combustion engine exhaust is impacted by both fuel properties and operation conditions.

1. Introduction

Transport activities contribute around 25% of total anthropogenic emissions of carbonaceous aerosols [1]. Particulate exhaust of transport systems is currently acknowledged to be the largest source of uncertainties in understanding traffic impacts on the regional environment, while combustion emissions are increasingly recognized as a globally important source of aerosols impacting air quality, visibility, and radiative balance of the atmosphere [2]. Soot particles have significant effects especially in humid environments [3], acting as cloud condensation nuclei (CCN) and thus exerting indirect effects on haze formation and wet deposition, by instigating longer cloud lifetimes and higher cloudiness. In urban areas diesel engine-emitted particles are considered as a dangerous pollutant with respect to human health because of their high number density, small respirable size, large

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http://dx.doi.org/10.1016/j.fuel.2015.04.073
0016-2361/

surface area, and potential toxicity. These particles may cause and enhance respiratory, cardiovascular, and allergic diseases [4]. Based on inflammatory responses, hazardous substances were found in diesel-emitted particles [5], while risks associated with specific chemical particle constituents remain uncertain. Most previous studies have aimed to obtain information on average chemical characteristics of diesel exhaust particles by bulk analytical techniques. It was found that unburned organic components are condensed on soot particles in various chemical forms dominated by alkanes and polycyclic aromatic hydrocarbons (PAHs), representing from 5% to 90% of particulate matter (PM) mass in dependence of operation conditions [6]. PAH emissions presented irregular results, leading to the hypothesis that the influence of biodiesel source material was particularly strong on the formation of these pollutants. Some increase in light PAHs with biodiesel was observed, becoming the dominant compounds in the exhaust, while nitro-PAHs and oxy-PAHs were reduced with biodiesel blends [7]. Fly ash contains mostly transition and alkali earth metals, as well as water-soluble ionic compounds produced by inorganic contaminants in the fuel, lubricating oil, and engine wear [8–10].

Electron microscopy was developed as a powerful tool for analyses of morphology and composition of individual particles in combustion emissions [11]. Characterization of diesel exhaust was previously done in accordance with morphological specification, such as soot, char, and mineral particles [12]. Soot was found to consist of chain agglomerates of primary particles with a microstructure of graphite microcrystallites [13,14]. Advanced cluster analyses, applied in the on-going studies on modern engine emissions, allows for the grouping of particles, revealing soot and fly ash in the microstructure of diesel engine exhaust [15,16].

The general assumption that diesel exhaust soot is insoluble and therefore poor CCN [17] was based on elemental carbon (EC) and hydrophobic alkanes dominating the composition of traffic-emitted particles, while the contribution from hydrophilic oxidized organics and sulfuric acid was found to be small [10]. Analysis of water interaction with soot of various composition, from EC to complex mixtures with water-soluble compounds, significantly improved the association between soot physico-chemistry and CCN formation, indicating that C—H and oxygen-containing functionalities are related to hydrophobic and hydrophilic surfaces, respectively, while the presence of water-soluble compounds leads to soot hygroscopicity [18,19].

A number of approaches were proposed to differentiate combustion particles at the microscopic level with respect to their ability to take up water. Okada and Hitzenberger [20] separated combustion-derived PM into water-insoluble and hygroscopic particles with and without water-soluble inclusions. The fractionation into C—O, C—O—S, and Me—C—O components of chain soot agglomerates, irregular internally mixed soot, and particles of mineral morphology, respectively, has allowed categorizing particles as hydrophobic, hydrophilic, and hygroscopic [21]. On average, for road traffic emissions, 41% of carbonaceous particles were found to be hydrophobic and 54% of them were separated into hydrophilic and hygroscopic particles.

Important changes in the design of diesel engines have been applied in the last few decades in order to reduce transport pollutant emissions. The effects of engine type and model were emphasized, with major concern on environmental protection by using alternative fuels [22,23]. Biodiesel has been recognized as effective in reducing the exhaust particle mass as compared to conventional diesel fuel [24,25], specifically during various transient/driving cycles [22]. However, improved characterization of diesel/biofuel combustion emissions is needed, specifically for newly designed internal combustion engines and biofuel utilization as alternative fuel to conventional diesel.

This study is devoted to comprehensive physico-chemical and hygroscopic characterization of diesel/biofuel particle exhaust from modern internal combustion engines. First, we differentiate the role of diesel engine operation in regards to the effect of pollutant emissions on fouling in the exhaust system and environmental concern. Furthermore, we highlight the impact of diesel vs biofuel on the particle properties at given operating conditions. Chemical characteristics are inferred from analysis of functionalities, ions, and water-soluble organic carbon. The particles with similar composition and morphology are grouped by cluster analysis to reveal the exhaust microstructure, while the group identification is performed with respect to physico-chemical relevance. Cluster analysis is combined with fractionation analysis here for the first time for categorizing the individual particles with respect to their ability to interact with water in the humid atmosphere.

2. Experimental

2.1. Engine operation and sampling

Two different internal combustion engines were utilized at the Verbrennungkraftmaschinen test bench of the Technical University Munich (TUM). First, a 2 Liter BMW M47D20 4-cylinder engine with a displacement of 1950 cm^3 and nominal power of 100 kW was used. Conventional diesel fuel DIN EN 590 with 7% biofuel (Version 2010) was used, with sulfur (S) content of 10 ppm and ash content of 0.01 wt%. The exhaust was diluted with air depending on the operation point of the combustion engine. At the nominal power point of the engine the dilution ratio was 5. The exhaust pipe was isolated and its wall temperature was kept above 180 °C by the usage of heating coils, in order to avoid hydrocarbon condensation. The operation conditions of the exhaust gas heat exchanger were changed by variation of exhaust gas and coolant temperature, as well as the exhaust mass flow. Different adjustments of the engine provided a variation of exhaust composition, especially with respect to total hydrocarbons, PM, and soot which had a major influence upon the fouling behavior. An exhaust-throttle in the exhaust-pipe (i.e., long pipe) was used in order to operate the engine with increased exhaust-backpressure. PM measurements were performed at 1.5 m after the turbocharger of the engine by the CVS (constant volume sampling) method. For particle sampling Pallflex membrane filters EMFAB TX40HI20-WW were used.

The BMW engine met the European emission stage III standard and was suitable to conduct the experiments with the goal to analyze the deposition build-up (fouling) in the tube exhaust gas heat exchanger in dependence on operating conditions of both the engine and heat exchanger. We did not use exhaust gas recirculation (EGR), catalyst or diesel particulate filter (DPF) to analyze the soot deposition and fouling of raw emissions without any exhaust gas after-treatment. Soot concentration was derived from an AVL photoacoustic Micro Soot Sensor. It was found that if the soot concentration in the exhaust was high, the fouling of the exhaust cooler surface by a soot layer build up was extremely fast. Therefore, such conditions are regarded as polluting ones from here on throughout the manuscript. Parameters of the BMW engine stationary operation, such as number of revolutions, break mean effective pressure, fuel mass consumption, and combustion air ratio were varied from 830 to 4000 L/min, 0 to 18.68 bar, 0.6 to 26.28 kg/h, and 1.31 to 3.46, respectively. More than fifty samples were analyzed; a list of diesel stationary (DSB) samples with detailed characterization of the operating conditions is presented in Table 1.

In addition, a John Deere CD6068HL4812 6-cylinder engine was operated. Conventional diesel fuel DIN EN 590 and refined