Reactivity and structure of soot generated at varying biofuel content and engine operating parameters

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ABSTRACT

Since the EU demands the use of renewable energy sources, also in the transport sector, the usage of biodiesel fuels increases continuously. As the physicochemical properties of soot are important for the oxidation behavior during the regeneration of diesel particle filters (DPF) and literature provides contradictory information about the reactivity and the structure of biodiesel soot, the aim of this work was to investigate the reactivity of soot produced by a diesel engine operated with fuels of different biodiesel content at varying engine operating parameters.

By temperature-programmed oxidation (TPO) an increasing reactivity with increasing biofuel ratio, except for the conditions with lowest injection pressure was determined. This implies that soot generated with 100% biofuel (consisting of rapeseed oil methyl ester) is more reactive than soot generated with commercial gasoline station fuel containing up to 7% biodiesel, while soot from fossil fuel is even less reactive. In addition, reactivity increases with increasing injection and boost pressure. Raman microspectroscopy (RM) analysis gave very similar spectra for the received soot samples, i.e. all generated soot samples possess a similar graphitic nanostructure. Additionally, a trend in reactivity with the particle size as well as the content of Fe, Zn, and Cu in the soot, which was determined by inductively coupled plasma mass spectrometry (ICP-MS), could be revealed. The soot reactivity is therefore not only determined by one parameter but a product of many soot properties like nanostructure, particle size and/or inorganic components as impurities.

When following the structural change in the DPF during regeneration, a decreased structural order was observed in the beginning. After a certain time (ca. 40 s) a homogeneous oxidation of the soot takes place, which does not change the structure of the soot inside the DPF. This coincides with findings of a constant oxidation rate after a certain time. Overall, it can be ascertained that no graphitization of the soot takes place inside the DPF during regeneration.

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1. Introduction

Aerosols can influence the climate, biosphere and the human health for example by changing the earth radiation, interacting with clouds or causing respiratory diseases [1–4]. Carbonaceous aerosols like soot particles originated by combustion processes are an important fraction of these aerosols present in the urban area with big health effects [3,5–8]. Especially the negative health effects of diesel exhaust have been examined extensively [5,9–13] as diesel engine exhaust is classified to be carcinogenic to humans (Group 1) by the WHO [14]. Therefore, emissions of diesel particulate matter (DPM) from cars and utility vehicles are limited by law in the EU [15–18]. For Euro 6 vehicles, the particle limit is set to 6×10^{11} particles per kilometer while the fixed Euro 6 and Euro VI mass limit is 4.5 mg km^{-1} for cars and 10 mg kWh^{-1} for heavy duty vehicles [15–18]. To reach the particle number limitations an exhaust aftertreatment system is necessary. Thus, diesel particulate filters (DPF) are used to trap the soot from the exhaust [6,8]. However, the filter units have to be regenerated by oxidizing the soot to gaseous products [6,19]. This regeneration step can be performed for example as active regeneration where the soot is oxidized periodically or as passive regeneration where the soot is oxidized continuously by the exhaust compounds O_2 and NO_2 [6,8].The behavior of the soot at this regeneration phase

is strongly dependent on the reactivity of the soot [8,20,21]. Thus, the soot reactivity is of importance and a worldwide research object. Various studies exist on the topic of soot oxidation, including soot oxidation kinetics [19], influences of the soot morphology on the oxidation reactivity [20–23], the influence of catalytic materials in the soot [24–29] or studies addressing the soot particle size dependent oxidation reactivity [30]. Also the influence of the fuel, especially different biodiesel fuels [31–40], or the engine operation conditions like engine speed and load, injection pressure or exhaust gas recirculation [30,38,41–45], to name just a few, are fields of interest concerning the soot oxidation. A soot of high reactivity is preferable because the regeneration of the filter can be performed at lower temperatures and therefore with small energy demand [8]. Stanmore et al. [46] give a comprehensive review of the gasification of diesel soot.

To reduce the greenhouse gas emissions and as a responsible and sustainable act towards nature an increase in the use of renewable energy sources is favored. In the EU, an increase in the usage of energy from renewable sources to 20% until 2020 [47] and to at least 27% until 2030 [48] is set by law. For 2050, the roadmap of the EU aims to reduce CO_2 emissions by 80–95% compared to 1990 levels, e.g. by reduction of greenhouse gases emitted by the transport sector of minimum 60% by 2050 [49,50]. In the transport sector a minimum of 10% of biofuels in transport petrol and diesel consumption up to 2020 is defined in the directive 2009/28/EC [47] and a sustainable alternative fuels strategy shall help to achieve the 2050 goals [50]. As the soot particles generated during the combustion of fossil or biofuels are trapped inside the DPF, the biofuel-originated soot has to be oxidized during the DPF regeneration in the same way the soot originated by the burning of fossil fuel. Thus, the influence of biodiesel on the reactivity of the soot and on the parameters determining the soot reactivity has to be examined. One research group found that biodiesel soot is less reactive than soot from fossil fuels [36], while the predominant results show an increasing reactivity for soot derived by the combustion of biodiesel fuels [32–34,37]. However, in current literature the increased reactivity of biodiesel soot is explained by differences in various properties of the emitted soot.

Soot is mainly composed of carbon (>80 wt.%) [51]. It is generated during combustion of carbon containing materials by nucleation, aggregation and surface growth mechanisms. Soot particles consist of nearly spherical primary particles with diameters of 10–30 nm [6,51] which form chainlike soot agglomerates of sizes up to a micrometer size range [6,8]. The primary particles are composed of more or less ordered and amorphous domains [51]. The ordered structures are small graphite-like crystallites, which consist of 3–4 stacked hexagonal face-centered layers of arrays called platelets with lateral extensions up to 3 nm [6,51,52]. The amorphous domains consist of polycyclic aromatic compounds like graphene precursors in disordered and onion-like orientation as well as other organic and inorganic components [51]. This nanostructure of the soot is dependent on the fuel and the combustion conditions [31,33,38,39,44,53,54] and determines physical and chemical properties of the soot [20,21,23,30,31,39].

Boehman et al. [53] determined a more amorphous structure with folded and bent crystallites with a high content of defects and low orientation for soot derived from biofuels (20 vol% methyl esters in low sulfur diesel fuel and ultra low sulfur diesel fuel) by high resolution transmission electron microscopy (HRTEM) and thereby explained the higher reactivity compared to fossil fuel generated soot. Lapuerta et al. [33] found a more graphitic structure with higher order for soot generated with biofuel (pure biodiesel made from animal fat meeting EN-14214 standard) compared to soot of fossil fuels by using Raman spectroscopy and XRD but could explain the higher reactivity of the biofuel derived soot by its smaller primary particle size visible by TEM, instead. Additional works of Pinzi et al. [35] (using different fatty acid alkyl esters and blends with 40 vol% of rape methyl ester in a single-cylinder engine) and Song et al. [37] (who compared

soot of a six-cylinder turbodiesel engine fueled with ultra low sulfur diesel, a 20% biodiesel blend and pure biodiesel) correlate the reactivity of the biodiesel soot to the higher amount of internal oxygen groups. On the other hand, Yehliu et al. [39] (who fueled their light duty diesel engine with ultra-low sulfur diesel, pure biodiesel and a Fischer–Tropsch fuel) and Zhang et al. [55] (who used a co-flow diffusion flame) negate the influence of oxygen functionalities.

Since a plethora of studies exist using different soot parameters to explain the higher reactivity of biofuel derived soot [31–34, 37–40,53,56], in this project, soot of different biofuel blending quota generated at different engine operating conditions was systematically investigated by diverse analytical methods in order to obtain information about thermochemical, structural and compositional properties of the soot. The thermochemical soot oxidation reactivity is determined by temperature-programmed oxidation (TPO) a method that has been used frequently for this purpose [22,24,25,57,58]. To get information about the nanostructure of the soot, which can influence the soot reactivity [22,57], Raman microspectroscopic (RM) analysis is performed, since Raman spectroscopy is a nondestructive powerful tool for the characterization of the nanostructure of carbonaceous materials [59], inorganic compounds in multicomponent [24,25] and atmospheric aerosols [60]. Because Raman spectra of soot are sensitive to the molecular structures as well as to crystal structures [51], it is possible to make a point on the structural order and the graphitization of a soot by Raman analysis [59]. Additionally, measurements with a scanning mobility particle sizer (SMPS) were performed to get information about the agglomerate particle size distribution, as soot agglomerate size and primary particle size can influence soot reactivity [30,33,43]. Inorganic ash, which may originate from additives, engine wear or lubricating oil [6], can also be found in soot derived from diesel combustion in small quantities. Ash is expected to influence soot reactivity as a catalyst in the soot gasification [24–26], e.g. by supporting the oxidation through a redox mechanism where the framework oxygen of a catalytically active metal oxide oxidizes the soot and the gaseous oxygen is assumed to reoxidize the reduced catalyst [61]. Thus, ash analysis is performed to identify and quantify inorganic elements in the soot samples by inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, the change in the soot structure shall be followed during DPF regeneration by RM. Therefore, successive partial isothermal oxidation of soot inside a DPF structure at exhaust similar conditions [6] is performed, while changes in the nanostructure of the soot are monitored by RM analysis. Thus, it can be examined whether a graphitization takes place inside the DPF, which would be undesirable because graphitized soot is less reactive than non- or less graphitized soot. In addition, a comparison of soot derived from operating the engine with fuels of different biofuel content is possible. Therefore, one can conclude whether different amounts of biofuel in the fuel favor or prevent a graphitization of the soot inside the DPF during regeneration.

2. Experimental methods

2.1. Engine, fuel properties and particulate matter (PM) sampling setup

A four-cylinder production diesel engine from Daimler AG (model OM 651, Mercedes-Benz, Germany) was installed on the engine test bench with an eddy-current brake for the experiments. The turbocharged engine is featured with a common-rail system and direct-acting Delphi-Injectors. The openly accessible engine control unit (ECU) provides the opportunity to adjust engine operating parameters like injection (p_{inj}) and boost pressure (p_{boost}). Communication and management of the ECU occurs via the interface module ES592 and additional modules for temperature, air ratio, pressure and nitrogen oxides, as well as via the Integrated Calibration and Application Tool (INCA) from ETAS Group (Germany). The engine fuel supply takes place via a 1000 l tank for research fuels. The technical data of the engine are shown in Table 1.