



Variations in diesel soot reactivity along the exhaust after-treatment system, based on the morphology and nanostructure of primary soot particles

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ABSTRACT

The reactivity of soot at different sites of the exhaust after-treatment system of a diesel engine (upstream and downstream of the diesel oxidation catalyst (DOC), downstream of the diesel particulate filter (DPF), as well as inside the DPF) was investigated on the basis of morphology and structure of primary soot particles by high resolution transmission electron microscopy (HRTEM). The results indicate that combustion-formed soot particles are susceptible to further transformations of their morphology within the exhaust system. The same primary soot particles can possess both oxidation-promoting and oxidation-inhibiting morphological features, the particle cores being highly reactive. Most reactivity-promoting features are encountered in pre-DOC and post-DOC primary particles, suggesting that soot can be more easily oxidised before it enters the DPF. The residence time of soot in the DPF contributes to modification of its reactivity by affecting size distribution and nanostructure of primary particles. Partial NO₂ oxidation and high temperatures during active regeneration modify the morphology of outer particle shells, thus rendering post-DOC and post-DPF primary soot particles less reactive in this respect. Primary soot particles that pass through the DPF and reach the atmosphere are characterised by the highest graphitisation degree and sizes larger than those entering the DPF. Complementary Near-Edge X-ray Absorption Fine Structure (NEXAFS) analyses proved not as relevant regarding soot reactivity but indicate higher chemical inhomogeneity of pre-DOC than of post-DOC and post-DPF soot and high contents of carboxyl carbon in post-DPF particles.

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1. Introduction

Removal of soot from the diesel combustion products is a very important long-standing issue influencing engine efficiency on one side and environmental pollution on the other. The introduction of diesel particulate filters (DPF) in diesel cars and trucks for capturing emitted particulate matter (PM) proved very successful. During engine operation, soot PM accumulates in the DPF and is to a great extent (usually >99%) removed by oxidation during a series of processes dominated by the so-called passive and active regeneration. Passive regeneration (at temperatures of 200–400 °C upstream of the DPF) contributes only to partial soot removal, despite application of several assisting techniques (e.g. ‘continuous regenerating trap’ technology; incorporation of a catalyst precursor in the fuel; e.g., [1]). Thus, active regeneration is required, which is generally triggered by the engine electronic control unit. Based on a model, which predicts the soot amount in the filter, combustion

is altered in order to yield high exhaust temperatures (550–650 °C upstream of the DPF) thus initiating the process of active regeneration. In the course of active regeneration, fuel conversion efficiency is diminished.

A key factor for soot elimination is its oxidative behaviour, which is strongly related to its morphology. The morphology of primary soot particles encompasses their size and shape, as well as their internal structure (in terms of carbon atoms arrangement) and surface functionality. Advances in analytical techniques and instrumentation, especially within the last decade, have added increasingly detailed knowledge in our understanding on the morphology and reactivity of soot (e.g., [2–4]). Although primary soot particles are commonly considered, in a simplified way, as ‘mono-disperse’, i.e. uniform in size (e.g., [5]), they display a small but clear size variation in the soot agglomerates (e.g., [6,7]). As for their internal structure, a series of HRTEM studies (e.g., [3,4,8,9]) reveal that primary soot particles are characterised by the presence of graphene layers (one atom thick sheets of carbon arranged ideally in connected hexagons) and, to some extent, polyaromatic hydrocarbons (PAH) and heteroatoms (atoms other than carbon), most

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commonly hydrogen. Surface functional groups, which are likely to be bonded to edge sites in the primary soot particles may induce structural changes and influence oxidation. Variations in the internal structure have been described as a result of the composition of the initial fuel, the engine operating conditions, the nature of gases in the exhaust stream, and the ambient temperature (e.g., [4,10,11]). Primary soot particles can modify their morphological and internal structural characteristics during post-formation thermal treatment and oxidation [12]. Finally, after initial oxidation of the soluble organic fraction of soot within the DPF (usually about 15–20% of the total soot mass) the morphology of its primary particles is the main factor influencing its oxidative reactivity [13].

It goes without saying that an in-depth comprehension of the internal structure of primary soot particles produced by combustion of diesel fuel is a prerequisite for additional progress in technical improvement of PM emission control systems. While some research has been carried out on the dependence of combustion-produced soot nanostructure upon its source and upon engine operating conditions, studies dealing with variations of soot morphology and nanostructure versus susceptibility to oxidation within the entire exhaust path of diesel engines, i.e. from engine-out through the diesel oxidation catalyst (DOC) and DPF to the ambient air are, to our knowledge, limited [14,15].

Within the framework of the present paper, the capacity of soot for oxidation is investigated in different parts of the after-treatment assembly of a diesel engine, on the basis of the morphological features of the primary soot particles by means of High Resolution Transmission Electron Microscopy (HRTEM). For this purpose, a series of experiments were undertaken using a small truck on a chassis dynamometer. Complementary to the HRTEM investigation, Near Edge X-ray Absorption Fine Structure (NEXAFS) analyses were carried out for part of the samples, in order to obtain additional information about possible soot reactivity variations along the exhaust stream. The aim of this work is to contribute to the optimisation of soot elimination during better targeted exhaust gas after-treatment procedures.

2. Experimental

2.1. Soot sampling from the exhaust gas after-treatment system

In the present investigation, the exhaust gas after-treatment system used for the experiments consists of a DOC–DPF assembly, the DOC placed upstream of the DPF (Fig. 1). Note that the DOC promotes passive regeneration in the DPF by NO₂-assisted soot oxidation. The assembly of serial production components was posi-

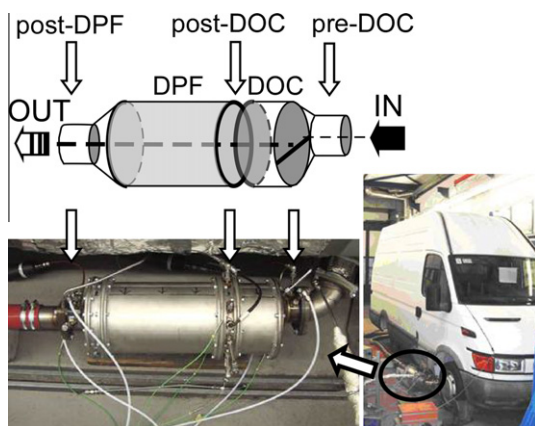


Fig. 1. Sketch and photographs of the after-treatment assembly used for soot sampling; the sampling sites are marked by vertical arrows.

tioned following the turbine exit, approximately 0.5 m further downstream, in order to allow easy accessibility.

The vehicle used for the experiments is an Iveco Daily equipped with a 2.3-litre 4-cylinder (F1A) common rail diesel with turbo-charger. Sampling was performed during steady state operation at 2000 rpm, 18 kW engine speed and output, respectively. EGR during operation was at 15%. Commercial fuel (S content <10 ppm) and commercial lubricating oil were used. During normal operation conditions, the exhaust gas temperature upstream of the DOC, downstream of the DOC and downstream of the DPF was approximately 275 °C, 355 °C and 255 °C, respectively. During active regeneration conditions, the temperature downstream of the DPF was initially around 600 °C, reached a maximum of ≈750 °C and returned to ≈600 °C before the end of active regeneration.

The DPF is cylindrical and measures 168 mm in diameter and 280 mm in length, which translates to a total volume of 6.3 L. It is made of SiC, has no catalytic coating and consists of a total of 25 segments cemented together. Each segment has a square cross section of 33 mm by 33 mm (except for the peripheral segments which are round on their external side) and integrates 18 × 18 square channels with a 1.5 mm by 1.5 mm opening. The square adjacent channels are separated by a ca. 0.35 mm thick porous wall and the opposite ends of each channel are alternately plugged (e.g., [16]). As a result of the alternately closed ends, the PM-bearing exhaust stream entering the DPF from the inlet channels (open at the inlet side and closed at the outlet side) is forced to flow through the porous walls between inlet and outlet channels and exit the DPF via the outlet channels, practically PM-free. The PM filtering efficiency of such DPFs reaches 99% (e.g., [17] and references therein). The DOC is cylindrical, made of cordierite and measures approximately 170 mm in diameter and 101 mm in length, has a channel density of 400 cpsi and a total volume of 2306 cm³. The specific surface of this structure lies at 2.740 m²/lt.

For the experiments carried out in this study, soot was collected from the exhaust stream directly on TEM grids, as well as from the soot cake deposited inside the DPF. For sampling directly from the exhaust stream, an electrostatic particle sampler connected with a short sampling line at different sites of the exhaust pipe was used. Soot sampling was performed as follows: (a) immediately upstream of the DOC, (b) immediately downstream of the DOC, (c) immediately downstream of the DPF (Fig. 1). Sampling downstream of the DPF was performed both under normal operating conditions, as well as under active regeneration conditions. The ambient temperature at the sampling sites around the TEM-grids was ≈150 °C upstream and downstream of the DOC (with 1:10 diluted exhaust gas), ≈25 °C downstream of the DPF during normal operating conditions (with undiluted exhaust gas, due to the low number of soot agglomerates after the DPF) and ≈150 °C downstream of the DPF during active regeneration conditions (with 1:10 diluted exhaust gas). The sampling parameters are summarised in Table 1.

For the TEM studies, direct loading of an appropriate amount of soot was done on round (3 mm in diameter) copper-supported carbon-coated TEM grids. For NEXAFS studies, samples were collected under exactly the same parameters, on 3 mm by 3 mm rectangular TEM grids with a 0.5 by 0.5 mm SiN-supported sampling window, directly from the exhaust stream upstream and downstream of the DOC and downstream of the DPF. We repeatedly failed to collect sufficient amounts of soot on the SiN grids for NEXAFS investigations downstream of the DPF until soot-loading time reached almost 2 h.

For the samples taken from the soot cake deposited in the DPF, soot was brought into suspension with ethanol and put into ultrasonic bath for ca. one minute. This way, the soot aggregates are mechanically broken and the individual particles can be better

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