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Characterization of particulate matter deposited in diesel particulate filters: Visual and analytical approach in macro-, micro- and nano-scales

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ABSTRACT

Multi-scale analytical investigations of particulate matter (soot and ash) of two loaded diesel particulate filters (DPF) from (a) a truck (DPF1) and (b) a passenger car (DPF2) reveal the following: in DPF1 (without fuel-borne additives), soot aggregates form an approximately 130–270 μm thick, homogeneous porous cake with pronounced orientation. Soot aggregates consist of 15–30 nm large individual particles exhibiting relatively mature internal nanostructures, however, far from being graphite. Ash aggregates largely accumulate at the outlet part of DPF1, while minor amounts are deposited directly on the channel walls all along the filter length. They consist of crystalline phases with individual particles of sizes down to the nanoscale range. Chemically, the ash consists mainly of Mg, S, Ca, Zn and P, elements encountered in lubricating oil additives. In the passenger car DPF2 (with fuel-borne additives), soot aggregates form an approximately 200–500 μm thick, inhomogeneous porous cake consisting of several superposed layers corresponding to different soot generations. The largest part of the soot cake is composed of unburned, oriented soot aggregates left behind despite repeated regenerations, while a small part constitutes a loose layer with randomly oriented aggregates, which was deposited last and has not seen any regeneration. Fe-oxide particles of micro- to nano-scale sizes, originating from the fuel-borne additive, are often dispersed within the part of the soot cake composed of the unburned soot leftovers. The individual soot nanoparticles in DPF2 are approximately 15–40 nm large and generally less mature than in the truck DPF1. The presence of soot leftovers in DPF2 indicates that the addition of fuel-borne material does not fully compensate for the temperatures needed for complete soot removal. Ash in DPF2 is filling up more than half of the filter volume (at the downstream part) and is dominated by Fe-oxide aggregates, due to the Fe-based fuel-borne additive, but otherwise its chemical composition reflects compounds of lubricating oil additives.

1. Introduction

During the combustion process in diesel engines, the sprayed fuel droplets do not mix completely with the abundant oxygen at a molecular level. As a result, complex multi-component particulate matter (PM) consisting mainly of carbonaceous soot particles carrying several other compounds [1] is produced. The mechanisms of the various reactions involved are extremely complex. There is a series of pathways leading to the formation of polycyclic structures, which are the building blocks of soot particles.

The composition of diesel PM is variable, depending on where in the engine they are produced and how they are collected [2]. Already in the cylinder, for instance, as well as along the exhaust path, elemental carbon particles agglomerate and adsorb mainly liquid or solid volatile hydrocarbons as the exhaust gas is cooling down. Whether formation of new particles or adsorption/condensation on existing PM takes place depends on distinctive features of the processes involved. PM of diesel exhaust gas comprises: (a) a solid component including elemental carbon and ash. Ash is defined as the combustion product of lubricating oil and minor amounts of metal compounds in the fuel; (b) a soluble organic component, including organic material from lube oil and fuel and (c) a component dominated by sulfates, i.e., sulfuric acid and water [e.g., 3]. The size of PM in diesel exhaust ranges between micron-, sub-micron- down to nanoparticle-size, i.e., <50 nm in diameter [2].

A variety of ceramic and sintered metal-based diesel particulate filters (DPFs) have been developed for diesel particulate control. Most efficient are the so-called wall flow filters, where the exhaust gas is forced to pass through porous walls of successive channels (see details below) thereby capturing PM. Accumulation of PM leads to increasing pressure-drop across the filter and decreasing engine performance. If no action is taken to remove the accumulating PM, the engine will ultimately cease to function. The optimal way to remove PM trapped in DPFs is to oxidize the carbonaceous

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component to CO_2 and water, following a process commonly referred to as regeneration. However, the temperature needed for oxidation of PM is quite high, commonly exceeding ~500 °C. Since typical diesel exhaust temperatures seldom reach these levels [1], the following main technologies were introduced to promote the regeneration process:

(1) The so-called continuous regenerating trap (CRT) technology, taking advantage of the NO_2 produced by oxidation of engine-out NO over a Pt-catalyst preceding the DPF. NO_2, which is a strong oxidant already at ~250 °C is continuously oxidizing and removing soot PM (so-called passive regeneration). At low temperatures, the degree of soot oxidation by NO_2 is relatively low while at higher temperatures, the production of NO_2 is limited by thermodynamic equilibrium. Some research focusing on the enhancement of passive regeneration efficiency has been carried out, suggesting the use of ceramic foams as oxidation catalyst substrates [4] and/or the use of catalytically coated DPFs to assist re-oxidation of NO to NO_2 and repeated utilization of available NO_x for soot oxidation [5,6].
(2) Incorporation of a catalyst precursor (additive) in the fuel, so that the PM and catalyst are built together and facilitate PM combustion with oxygen at lower temperatures [7].

Despite application of these techniques, passive regeneration is insufficient for soot oxidation. Thus, active regeneration is required, in general triggered by the engine electronic control unit. Based on a model that predicts the soot amount in the filter, combustion is altered during active regeneration to yield high exhaust temperatures, thereby sacrificing on fuel conversion efficiency.

It becomes, therefore, evident that the optimization of diesel exhaust aftertreatment requires detailed information on diesel PM deposition and oxidative behavior. To our knowledge, limited studies have been carried out on these topics. Most investigations focus on the correlation of pressure-drop across the filter [8–11] or the study of PM in DPF by means of computer tomography and gas pycnometry [12]. Moreover, the aforementioned studies include investigation of detailed elemental composition of DPF parts milled after extraction. A thorough visual and analytical study in the sense developed in the present work has been, to our knowledge, inadequately approached.

Within the framework of the present paper, we carried out a detailed investigation of the particulate matter captured in two loaded DPFs, on the macro-, micro-, and nano-scales, with the aim of providing in depth information on: (1) the distribution and interrelationships of PM in the DPF, (2) the morphological and structural characteristics of PM, (3) the chemical composition, as well as the identification of the various PM constituents, (4) determination of the internal micro- to nano-structure of soot PM and (5) the effect of fuel-borne additives on regeneration and PM formation.

2. Experimental

2.1. Diesel particulate filters

DPFs are made of conventional so-called 'honey-comb' structures. They consist of several 'segments' cemented together (Fig. 1A). The first monolithic DPFs have been presented only very recently [13]). Each segment is made of numerous square parallel channels (square tubes) with the opposite ends of adjacent channels being plugged (Fig. 1B). The PM-bearing diesel exhaust gas enters the inflow channels and is forced to flow through the porous walls of the adjacent outflow channels, as the end of the inflow channels is plugged. The exhaust gas is thus filtered and reaches the atmosphere through the outflow channels, practically PM-free. DPFs capture particles with an efficiency of 95–99% in the case of the so-called wall flow filters [e.g., 14 and references therein].

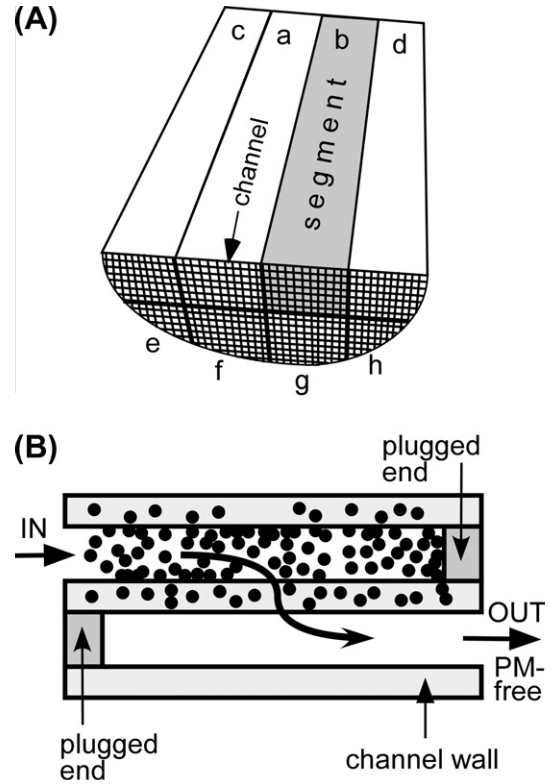

Fig. 1. (A) Schematic of a sectioned DPF exhibiting central segments (a and b) and peripheral segments (c to h); (B) schematic illustration of two neighboring channels plugged at either ends. Black dots in the inflow channel represent PM partly retained in the channel walls.

For our investigations, we selected the most common systems currently in use on the road. The filters examined are made of SiC and do not have any catalytic coating.

DPF1 was taken from an oxidation catalyst-particulate filter assembly of a light truck engine without fuel-borne additive components. The oxidation catalyst-DPF assembly was positioned in the vicinity of the turbine exit. Straight piping lead the exhaust gas to a short entry cone resulting in a nearly symmetric feed of the exhaust gases to the catalyst.

The oxidation catalyst was directly in the upstream of the DPF promoting passive regeneration, i.e., NO_x-assisted soot oxidation. DPF1 operated on an engine test bench for approximately 250 h, during engine development, mostly on high loads. Before dismantling, the filter was actively regenerated and subsequently loaded with engine-out PM reaching a specific load of 7 gr/L. During its use, the filter experienced a limited number of active regenerations.

The dimensions of DPF1 were: 168 mm diameter and 280 mm length, which translates to a total volume of 6.3 L. The total weight of the PM deposition material was approximately 44 g. The channel density was 200 cpsi and each square channel had a 1.5 mm by 1.5 mm opening. The entire filter comprised 25 segments, nine whole segments in the central area and the remaining apportioned 16 in the periphery. Each whole segment had a square cross section of 33 mm by 33 mm and integrated 18 × 18 channels. The average thickness of the walls between the channels was 0.35 mm.

DPF2 was a fuel-borne catalyst system and was used on a passenger car for approximately 120,000 km. DPF2 was a typical