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Electron microscopic characterization of soot particulate matter emitted by modern direct injection gasoline engines

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ABSTRACT

Modern direct injection gasoline engines (GDI) generate considerably higher soot particulate matter (PM) emissions than conventional, port fuel gasoline, as well as diesel cars with particle filter. Soot PM generated by a typical state-of-the-art GDI (Euro VI) vehicle during two standard international driving cycles (NEDC, WLTC), as well as during a short experimental sub-cycle was investigated by electron microscopy. The study reveals primary particles between ~4–55 nm in diameter, the majority being < 20 nm during all driven cycles; sub-20 nm particles are more abundant in the more dynamic WLTC. Monodisperse agglomerates made of small (<20 nm), medium (~25 nm) and large (~35 nm) primary particles are distinguished; they usually form parts of polydisperse agglomerates but also occur as distinct entities. The particle groups of different sizes are probably derived under diverse operating conditions, the larger ones being likely associated with the cold start phase. This inference is supported by simultaneously ran FMPS measurements, which reveal in addition that the cold start phase seems to account for ~25% of the particle agglomerate emissions of the entire cycle. All particles, especially the medium and large fractions, exhibit low degrees of crystallinity indicating relatively high reactivity. The predominance of sub-20 nm primary particles render GDI soot PM potentially hazardous to human health, especially considering the higher surface and surface/volume ratio compared to larger particles of the same total volume. The engine operating parameters seem to be of prime importance for the resulting morphological features of soot.

1. Introduction

Particulate matter in the exhaust of internal combustion engines is principally soot. It is an undesired component, proven to have detrimental effects on the environment and be carcinogenic to humans [1,2]. Diesel engines are associated with relatively high soot emissions. In diesel combustion technology, the ignition of fuel–air lean mixtures is possible because of the inhomogeneous mixture distribution: local zones with almost stoichiometric mixture ignite first; the heat released enables combustion to propagate in the lean zones, while in fuel-rich zones combustion is diffusion-controlled and slow. The high temperatures in fuel-rich zones are responsible for the particulate matter formation. This combustion principle is opposed to the conventional, port fuel injection, spark ignition (gasoline) engines. Combustion in this engine type is strongly premixed and thus almost homogeneous; the fuel–air mixture is held as close as possible to stoichiometric by the engine control unit and no fuel-rich zones occur in the combustion chamber. As a result, soot formation is negligible.

Based on the global need for abatement measures against climate warming and the international guidelines to reduce CO_2 emissions, the so-called direct injection technology has been developed in recent years for gasoline cars (GDI). This technology aims at high efficiency, as well as reduced fuel consumption and low CO_2 emissions. In GDI engines, fuel is injected directly into the combustion chamber, where it is ignited by a spark plug. GDI-operating cars fulfill the requirement of lower CO_2 emissions but generate significantly higher soot amounts compared to conventional gasoline cars and to diesel vehicles equipped with diesel particulate filters (DPFs) (e.g. [3]). Particulate matter formation in GDI engines is attributed to poor mixing of the fuel with air during fuel injection and the subsequent compression stroke leading to local fuel-rich zones.

As GDI is expected to be the standard gasoline passenger car technology in near future, detailed investigation and in-depth understanding of the related particulate matter emissions is very

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important, especially considering the recent findings that such emissions from GDI cars (Euro V) are hazardous for the respiratory system [4]. Particulate matter in the exhaust of GDI vehicles, especially the ultrafine fraction down to the nano-scale, is poorly researched. Emission studies investigating spark ignition vehicles (port injection, conventional technology) have shown that cold-start, on-road acceleration and high speed cruise conditions produce high particle concentrations (e.g. [3,5]). The corresponding particle emission of GDI vehicles is expected to be worse by at least an order of magnitude [6].

At this point it is important to underline the meaning of the term ‘particle’. In the majority of published papers dealing with particle emissions applying classical measuring tools (e.g. SMPS, ELPI) the term ‘particle’ refers to an entire agglomerate. In the few papers dealing with the in-depth investigation of particulate matter emissions down to the nano-scale, the term ‘particle’ corresponds to the building units of the agglomerates, i.e. their primary, nearly spherical particle constituents. This differentiation is crucial for the present paper, which principally deals with the primary particle constituents of agglomerates studied by electron microscopy.

As emission constraints and regulations continue to evolve, it is still likely that particulate filters may also be required for GDI vehicles. Morphological properties of emitted particles and, in particular, of primary soot particles are critical as they control reactivity and determine soot behavior in the atmosphere and the human body [2,7]. Such morphological soot properties (size, shape, surface area, internal structure) generally depend on engine operating conditions [7,8], as well as on the fuel used (e.g. [9,10]). They are expected to provide key information helpful to establish a link between particle morphology, optical soot properties related to atmospheric behavior, as well as human cell response, which can finally lead to targeted abatement measures. Particle morphology is also important for designing particle filters, should these prove necessary.

Previous researchers [11] dealing with the electron microscopic study of soot investigated the variation in primary particle morphology across a range of engine operating conditions. Electron microscopic studies of particles emitted during driving cycles employed in tests for the certification of light duty vehicle emissions, such as the New European Driving Cycle (NEDC) but also the recently (from 2014 onwards) introduced (but not yet applied as replacement for NEDC) Worldwide harmonized Light duty Test Cycle (WLTC) are missing. It is reminded that the NEDC generally deviates from real-world conditions whereas the WLTC, which was introduced based on the need to measure and certify emissions closest to real-world, approximates better these conditions.

Within the framework of the present study, a detailed analysis and electron microscopic characterization of the particulate matter emitted by a typical state-of-the-art GDI (Euro VI) vehicle during the typical cycles NEDC and WLTC (at normal and low ambient temperatures), as well as during a short (one-minute long) experimental cycle is provided, in terms of detailed morphological features of the primary particle constituents of the agglomerates in the nanometer range. A comparison of morphological features between particles produced during the NEDC and the WLTC is expected to reveal potential differences and similarities in soot morphology and reactivity and provide valuable information on characteristics of soot emitted by non-real-world and nearly real-world driving conditions. Moreover, the influence of ambient temperature during the WLTC on the morphological features of soot is examined. Selected fast mobility particle sizer analysis (FMPS) data of particle number emission measurements that are complementary to the electron microscopic results are also presented. The short experimental cycle, on the other hand, which includes one acceleration and one deceleration phase (repeated 3 and 6 times to investigate the effect of the cold start) is employed to directly correlate morphological characteristics of soot under more controllable conditions.

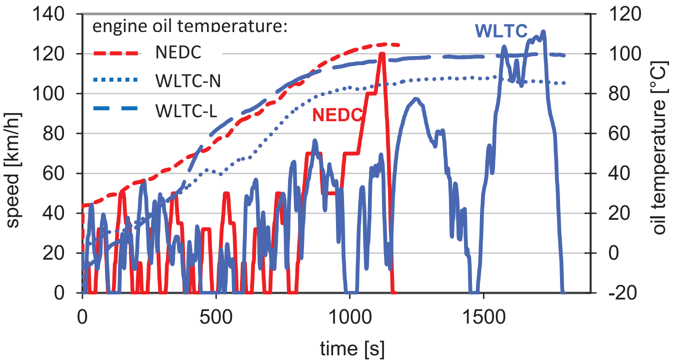

Fig. 1. Driving profiles of the NEDC and WLTC (solid lines) with the associated engine oil temperature time histories (dashed lines).

Both scanning electron microscopic (SEM) and, mainly, transmission electron microscopic (TEM) methods are applied. Morphological characteristics of primary particles are directly related to reactivity (e.g. [9,12]) and bound to the interaction with atmospheric components and human cells. The overall aim is to improve our understanding and enrich our knowledge on GDI-generated PM emissions by highlighting their micro- and nano-scale characteristics. This study is related to atmospheric pollution, on one side but can also help minimizing possible detrimental effects of particulate matter on engine components.

While classically applied particle measuring methods (e.g., SMPS, ELPI) provide rigorous statistics, the electron microscopic methods offer very high magnification and high resolution, and can reveal important morphological details of the primary particles to extremely low sizes, at the cost of a reduced statistical sample. Their importance relies rather on providing information on particle formation conditions and oxidative reactivity, which are of further value to deciphering the interaction with human cells and atmospheric components.

2. Experimental

2.1. Driving conditions and sampling procedure

Particulate matter was collected from a Euro VI, GDI passenger car on a chassis dynamometer. Two different internationally accepted driving cycles were applied, namely the NEDC and the WLTC. The WLTC was driven under normal ambient temperatures of 23 °C (called hereafter WLTC-N), as well as under low ambient temperatures of −7 °C (called hereafter WLTC-L). The duration of the NEDC and the WLTC was 1200 s and 1800 s, respectively. The evolution of the oil temperature with time was very similar for both cycles (Fig. 1); oil temperature was lower at the beginning of the WLTC-L dominated by lower ambient temperatures. Relative to the NEDC, the WLTC has longer duration, higher maximum and average speeds, steeper acceleration / deceleration phases, and less idling time (see Fig. 1 and [13] for details).

During the experiments, the particulate matter-bearing exhaust stream was guided to the measuring site by a conditioning pipe, as shown in Fig. 2a (path 1), heated and diluted by a factor of 13.5. Particulate matter was collected directly on TEM grids at each complete cycle. The collected samples are thus representative of the entire cycle. It is technically very difficult (if not impossible) to apply a proper sampling procedure to collect samples during individual stages of the cycles (e.g. during the short time of the acceleration phases). Even if this were theoretically feasible, it is