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Regular Article

Impact of oil aging and composition on the morphology and structure of diesel soot

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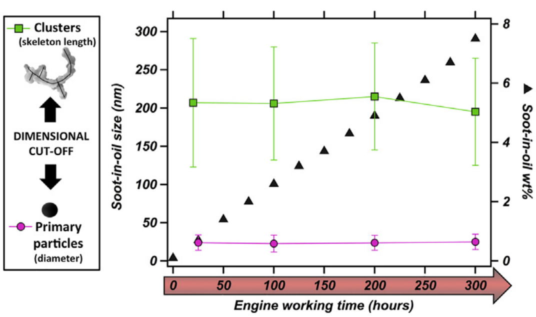
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Soot is a black powder-like substance consisting of carbonaceous amorphous particles, formed by incomplete combustion of hydrocarbons. In the last decades, industrial research on lubricant oils has grown to develop more efficient formulations, mainly to reduce the formation of soot in oil so to increase engine lifetime. The comprehension of the mechanism of soot formation and particles growth/aggregation in times during real applications is of fundamental importance for the design of better performing lubricants.
Experiments: In this work, we report on a multi-technique investigation of soot-in-oil samples, drawn from the oil sump of a direct-injected heavy-duty diesel engine at increasing working times in a standard engine test. Scanning Electron Microscopy, Small Angle X-ray Scattering and Dynamic Light Scattering are employed to study the evolution in term of soot size, morphology and fractal dimensions.
Findings: Our results evidence that, in a complete lubricant formulation, exhaust oil viscosity evolution correlates well with the increase of soot amount inside the oil. Moreover, the growth of both primary soot particles and aggregates during the engine test is limited to about 24 and 200 nm, respectively, because of the active role of the dispersant present in the investigated oil.

1. Introduction

In the last decades, the industrial research has grown to develop more efficient engines and reduce their maintenance costs. One of the main factors affecting engine performances is the formation of carbonaceous particles (i.e. soot in diesel engine) during the normal operation of the engine, which is mainly responsible for the

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Nomenclature

SAXS	small angle X-ray scattering	TGA	thermogravimetric analysis
SEM	scanning electron microscopy	GDI	gasoline direct injection
DLS	dynamic light scattering	EOT	end-of-test

change in the lubricant oil viscosity, eventually leading to engine failure [1,2]. It is well known that soot formation results from the incomplete combustion of fuel and/or form the partial decomposition of the lubricant oil [3]. Since diesel fuels contain a large amount of high-boiling components that are less prone to be completely combusted, soot formation is a chronic problem particularly in the case of diesel engines.

To reduce the formation and growth of soot particles, commercial lubricants contain many chemical additives [4]. Among them, oil-soluble dispersants, particularly succinimides functionalized with alkyl groups [5,6], are used to inhibit the growth and aggregation of carbonaceous deposits. Obviously, the comprehension of the main characteristics of soot [3,7] and the mechanism of its formation and growth [8] is of fundamental importance to design better performing lubricant additives.

Previous works reported the use of computer simulations to describe the formation of soot inside the engine [9,10]. These methods are useful to predict the engine region where soot is likely to be produced and an average particle dimension. However, the comprehension of how the particulate grows and aggregates inside the oil is still missing. Other works focused on the characterization of soot-in-oil samples for a gasoline direct injection (GDI) [11] or a light-duty diesel [7] engine in terms of shape, size and polydispersity of both primary units and clusters. It was found that the size and the shape of soot change depending on engine and fuel types, service period of the oil, and engine features, such as the fuel injector type. In particular, it is reported that soot agglomerates in the light-duty diesel engine are mainly composed of primary particles with diameters in the range 10–30 nm while the average agglomerate length is around 130 nm [7]. Differently, in the case of the GDI engine, it was found that the mean length of clusters is around 153 nm with a characteristic diameter of primary particles around 40 nm [11]. In addition, primary particles formed in GDI engines present more irregularities than in the case of typical diesel soot particulates, both being globular in shape. The main limitation of these studies is that the particulate characterization is reported only at certain times and a direct correlation with the oil viscosity increase is missing. Other articles [12,13] reported the tribological behaviour of diesel soot dispersed in oil matrix. However, these model systems are not fully representative for the real behaviour of soot-in-oil due to differences in the chemical composition (i.e. more oxygenated exhaust soot was used) and in the aggregation of the particulate (i.e. dried carbonaceous substrates redisperse differently in pure oil phases).

In this work, we report on the investigation of soot-in-oil samples drawn from the oil sump in the case of a heavy-duty diesel engine, focusing our attention on how primary particles and aggregates change in size, shape and polydispersity as a function of engine working time. At the sub-micron scale, the combined use of scanning electron microscopy (SEM) and dynamic light scattering (DLS) allows to monitor how carbonaceous particulate evolves in terms of morphology and size distribution of both primary particles and clusters, while Small Angle X-ray Scattering (SAXS) is used to evaluate the structure of the particulate at the nanoscale. In parallel, the different aliquots of exhaust oil were analysed in terms of oil viscosity and amount of soot produced to assess if there is a correlation between macroscopic and microscopic properties during oil aging. The combination of the information obtained at different length scales can give a better understanding of soot evolution as a function of engine working time.

2. Materials and methods

2.1. Exhaust oil production: Mack T8 motor test

Engine tests are carried out using a diesel heavy duty engine (Mack T-8) to evaluate the soot handling/viscosity properties of engine crankcase oils in turbocharged and intercooled four-cycle diesel engine. This engine test simulates field service during heavy-duty, stop-and-go operation, and high-soot loading. The test was run for a total duration of 300 h (+10 h run-in phase), alternating medium-high load/speed to fast idling to accumulate enough soot (4.8% min) for pass/fail limit. Kinematic viscosity at 100 °C and soot content were evaluated at 25-h intervals. Different aliquots of exhaust oil were drained from the sump to detect the changes occurring in the viscosity of the fluid. In this way, the behaviour of the lubricant under defined conditions of the test can accurately be followed and reproduced.

The test engine is a Mack E7-350 [14], fixed time, in-line six cylinder configuration 11GBA77623, direct injection, four-stroke, turbocharged, intercooled, compression ignition engine. The bore and stroke are 12.4 × 16.5 cm. The engine is rated at 261 kW@1800 rpm.

2.2. Exhaust oils

Three kinds of exhaust oils were investigated: one was specifically developed for heavy-duty diesel engines (containing standard additives) and it was produced with the above-mentioned engine test, while other two exhaust oils produced in a light-duty diesel engine (one containing the dispersant and one not) are included in this study for comparison to show the effect of the dispersant on the mean diameter of primary units. All lubricant oils used in the tests were provided by Eni S.p.A. and, due to the proprietary nature of this information, no details on oil composition and additives can be disclosed.

2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is carried out with a SDT Q600 Instrument (TA) following the ASTM procedure D7156–05 [15] used for the quantification of soot-in-oil content.

2.4. Viscosity measurements

The evaluation of oil viscosity at different run times is assessed by means of the ASTM procedure D5967 [15].

2.5. Small angle X-ray scattering (SAXS)

SAXS measurements were carried out with a HECUS S3-Micro (Kratky camera) equipped with two position-sensitive detectors (PSD-50M) containing 1024 channels of 54-μm width. Cu K_α radiation of wavelength 1.542 Å was provided by the GeniX system