

A Novel Diagnostics Tool for Measuring Soot Agglomerates Size Distribution in Used Automotive Lubricant Oils

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ABSTRACT

The determination of size distribution of soot particles and agglomerates in oil samples using a Nanosight LM14 to perform Nanoparticle Tracking Analysis (NTA) is described. This is the first application of the technique to sizing soot-in-oil agglomerates and offers the advantages of relatively high rates of sample analysis and low cost compared to Transmission Electron Microscopy (TEM). Lubricating oil samples were drawn from the sump of automotive diesel engines run under a mix of light duty operating conditions. The oil samples were diluted with heptane before analysing. Results from NTA analysis were compared with the outputs of a more conventional analysis based on Dynamic Light Scattering (DLS). This work shows that soot-in-oil exists as agglomerates with average size of 115 nm. This is also in good agreement with TEM analysis carried out in a previous work. NTA can measure soot particles in polydisperse oil solutions and report the size distribution of soot-in-oil aggregates. NTA allows for an estimation of soot mass contained in the soot-laden oil samples. The estimated value was compared with soot mass measured using Thermo-Gravimetric Analysis.

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INTRODUCTION

Most of the particulate matter produced by the combustion process in a diesel engine is expelled with the exhaust gases into the exhaust system, but a small proportion is transferred to the lubricating oil. Soot migrates to the boundary layer, and then into the oil film, early in the expansion stroke. Over time it transfers to the oil sump and builds to levels which modify the performance of the oil and limiting the engine service interval. The morphology, agglomeration and other characteristics of soot-in-oil are quite different to exhaust soot [1]. The form taken by this soot-in-oil is of interest because of the potential influence on oil properties and engine wear. TEM, High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Electron Microscopy (SEM) are commonly used to investigate the characteristics of individual and agglomerated particles to get information about the nanostructure morphology. La Rocca et al. [1] observed the inner core and outer shell of exhaust soot particles using electron microscopy, showing that the primary soot particles have a layered structure and consist of numerous concentric crystallites. A primary soot-in-oil nanoparticle is also formed by an inner core and an outer shell [2]. The inner core is composed of several fine spherules (3 to 4 nm in diameter) which have a nucleus of 1 nm in diameter covered by several carbon layers. However, a TEM image is essentially a projection of the 3D structure of the

soot sample; as such, the information about the ordering of the structure is then lost. Used engine oil is a contaminant for electron microscopes and leads to instabilities under the electron beam; a suitable sample preparation technique has to be employed to effectively remove lubricant from the soot particle [2]. TEM has the drawbacks of high running costs, analysis turnaround time, complex sample preparation procedures and the need for highly skilled operators. Cryogenic vitrification and imaging by Cryogenic TEM have been used by Kawamura et al. [3] and Liu et al. [4] to visualise the soot agglomerates and their distribution in engine oil. Despite a successful demonstration of this approach, the viscosity of typically used engine oils leads to localised thick layers on the TEM grid and requires specialised preparation equipment and expertise, making it unsuitable for routine analysis.

A more conventional and commonly used technique to monitor soot content in oil is the Fourier Transform Infrared Spectroscopy (FTIR). Soot-in-oil levels are determined as function of the reduction of light transmitted at a given wave length. The extent of oil oxidation can also be monitored by FTIR achieving valuable insight on carbonyl functional group and consequently of how well a particle will adsorb dispersant [5]. However, no information is given on morphology of particles and their size distribution. Dynamic Light Scattering

(DLS) is a more conventional scattering technique to measure nanoparticles size distribution in liquid suspensions. It provides an estimate of the hydrodynamic size of agglomerates by analysing the modulation of scattered light intensity as function of time; although concerns upon reliability in detecting particles below 50nm in diameter have been addressed by Liu et al. [4]. Quantitative analysis of soot content by weight can be performed via Thermo-gravimetric Analysis (TGA) as described by ASTM D5967. Soot is heated and completely oxidised recording the percentage loss in weight [6].

Since its development in 2006, Nanoparticle Tracking Analysis (NTA) has been increasingly used for sizing nanoparticles and evaluating particle concentration in liquid samples, with more than 800 papers describing applications to particle sizing in the range from 10nm up to 2 microns in the medical, pharmaceutical, environmental and toxicological fields. This technique has the advantage that data acquisition can be as fast as 10 seconds per acquisition, which allows a high sample throughput at relatively low cost if compared with TEM. Recently La Rocca et al. [7] used, for the first time, the NTA platform to measure the size distribution of soot suspended in heptane showing a good agreement between hydraulic diameter of soot, measured using NTA, and skeleton length measured from TEM images of the soot agglomerates.

One of the purposes of this work is to measure the size distribution of soot-in-oil agglomerates using NTA and compare the results with size distribution predicted by DLS. Soot-in-oil mass is estimated using the NTA soot concentration and the particle size measurements; the results are compared to the soot-in-oil mass measured using TGA.

EXPERIMENTAL SETUP AND SAMPLE PREPARATION

The oil samples used in the study were drawn from High Pressure Common Rail (HPCR) direct injection diesel engines. Two engines, denoted with A and B, were tested.

Engine A was a single cylinder variant of a multi-cylinder design meeting Euro 4 emissions requirements. The engine was installed on a test bed and filled with clean SAE 5W/30 lubricating oil at the start of a 10 day period during which the engine was run daily for typically three hours. The two principal operating conditions were 2000 rpm at a gross IMEP of 11 bar and a fuel rail pressure of 1200 bar, and 1500 rpm at a gross IMEP of 3 bar and a rail pressure 600 bar. The engine ran with EGR levels up to 20%. The second engine, Engine B, was a 2.0 litre direct injection light duty diesel engine which was filled with clean SAE 5W/30 and then run for 8,000 miles under a mix of light duty operating conditions. The combustion chamber and injection system was of a similar design to Engine A. At the end of the test period, oil samples were drawn from the sump for the investigation of the soot content.

Nanoparticle Tracking Analysis

NTA is a novel technique aimed at real-time and direct analysis of nanoparticles in liquid suspensions. A CCD camera examines the Brownian motion of nanoparticles illuminated by a laser. A dedicated particle tracking software tracks every particle simultaneously yet separately. NTA comprises 3 basic stages (i) video capture, (ii) setting of analysis parameters, (iii) tracking analysis. The Nanosight (LM14) was used in the present investigation. A thin laser beam illuminates the particles, from which the scattered light is visualised using an optical microscope. A camera aligned to the beam axis records a video of the movement of the particles at a rate of either 30 or 60 frames per second. Despite having a lower maximum resolution of 10-30nm, the Nanosight offers advantages over other scattering techniques, due to the nature of the analysis it performs, in which it tracks the centre of each identified particle. A typical video is captured at 30 frames per second and the subsequent analysis compares the position of each particle on a frame-by-frame basis and tracks the displacement of each particle until the particle (i) moves out of the capture window, (ii) moves out of the place of focus (particles can sink or float) or (iii) crosses the path of another particle. Brownian particle displacement (D) is measured on a frame-by-frame basis. The hydrodynamic diameter of the particles tracked is calculated by applying the two dimensional Stoke-Einstein equation [8]:

$$d_h = \frac{K_B \cdot T}{3 \cdot \pi \cdot \eta \cdot D} \quad (1)$$

Where D is the mean square displacement, K_B is the Boltzmann's constant, T is the temperature of the sample in Kelvin, η is the sample's viscosity and d_h is the hydrodynamic diameter of the tracked particle.

The data was analysed using the NTA (V2.3) software; attention was paid to achieving a particle concentration of between 10^5 - 10^{10} /ml in the sample, as suggested by Malloy and Carr [9], in order to balance the requirements of long particle track lengths and minimum numbers of particles analysed. Samples were diluted with heptane at a ratio of 5 μ l of oil to 25ml of heptane for sample A and 1 μ l of oil to 50ml of heptane for sample B, giving a dilution of 5000 and 50000 times respectively. The heptane was mixed into the sample by gentle agitation. The reference value of viscosity used in this work is 0.4mPa s at 20°C; at the dilution ratio used, the effect of soot viscosity is low and can be neglected. 1ml of the resultant solution was loaded into a 1 ml glass syringe and this was injected into the sample chamber of the Nanosight (LM14). The laser (404nm) was turned on and the focus of the instrument set on a location where nanoparticles were present. Once particle identification and tracking were optimised, a series of automated batch capture experiments were performed to increase the sample size and reduce statistical errors. Temperature was held constant at 20°C during the experiment, using the temperature control on the LM14.