Tribology International 61 (2013) 80–87

Contents lists available at SciVerse ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

The nanostructure of soot-in-oil particles and agglomerates from an automotive diesel engine

A. La Rocca [a,*], G. Di Liberto [a], P.J. Shayler [a], M.W. Fay [b]

[a] Department of Mechanical Materials and Manufacturing Engineering, University Park, Nottingham NG7 2RD, UK
[b] Nottingham Nanotechnology and Nanoscience Centre University Park, Nottingham NG7 2RD, UK

ARTICLE INFO

Article history:
Received 30 March 2012
Received in revised form
16 November 2012
Accepted 6 December 2012
Available online 19 December 2012

Keywords:
Diesel soot
Lubrication oil
Particles
Transmission Electron Microscopy

ABSTRACT

The characteristics of soot particles and agglomerates of particles extracted from samples of lubricating oil drawn from the sump of a diesel engine have been investigated. The engine was a high pressure common rail, direct injection diesel designed for light duty automotive applications. Soot from the samples was prepared for imaging by sample dilution with heptane, followed by washing in diethyl ether and in some cases, sample centrifugation. The size and shape of agglomerates were defined from measurements of projected length and width allowing for chain contortion. When used, centrifugation is shown to alter the size and shape of agglomerates, increasing the proportion of chain agglomerates and reducing clusters. Without centrifugation, roughly half of the soot in oil exists in long-chain agglomerates with average length of 130 nm and 50 nm in width. Clusters with modest branching account for the remaining 46%. The average aspect ratio (L/W) was of 2.9. The diameter of spherical primary particles that form the agglomerates ranges between 10 and 35 nm grouped in a Gaussian distribution with a mean value of 20.2 nm. All primary particles exhibit an inner core and an outer shell. The inner core is composed by several nuclei of around 4 nm diameter. Inner core is of around 8–15 nm in diameter and outer shell 4–12 nm thick.

1. Introduction

The particulate matter produced by the combustion process in a diesel engine is mainly carbon soot. Most of the combustion generated soot is expelled from the cylinder with the exhaust gases but a small proportion is transferred from the cylinder to the lubricating oil. The form taken by this soot-in-oil is of interest because of the potential influence on oil properties, for example, and for insights to the history of particle formation and growth. The aim of the investigation reported here has been to examine the form of soot extracted from sump oil of a modern light duty automotive diesel engine and to examine the effect of sample preparation on the distribution of size and shape of particle agglomerates.

The appearance and evolution of soot particles in the cylinder has been the subject of various experimental and computational modelling studies [1–6]. There have also been several investigations of soot aggregation [7–9]; in most cases soot drawn from the exhaust gas stream under conditions far different to those in-cylinder has been used to illustrate soot structures [7,10]. The soot particles are formed in-cylinder on precursors typically 2 nm in size in the vapour-rich zone of the fuel spray close to the injector nozzle holes. The primary particles grow through surface growth and coalescence typically to between 10 and 50 nm in size, and join to form branched agglomerates of various sizes and shapes. Most of the particles and agglomerates of particles are oxidised during the expansion stroke of the engine cycle. Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) are commonly used to investigate the characteristics of individual and agglomerated particles. The examination of the structure and the distribution of the carbon sheets of the primary particles provide information about reactivity and nanostructure morphology [11]. The primary particles have an outer shell composed of planer shaped crystallites orientated perpendicular to the radius of the particle. The crystallites are comprised of several polyaromatic hydrocarbons (PAH) layers. There exist an inner core which is constituted by several fine spherules (3–4 nm in diameter) having a nucleus of 1 nm at the central portion.

Park et al. [12] examined agglomerates of exhaust soot and observed that the primary particles had an average diameter of 31.0 nm. The microstructure of exhaust soot particles from a small DI four cylinders diesel engine was examined by Ishiguro et al. [13] using electron microscopy, leading to the first observation of the inner core and outer shell of soot particles. The microstructure and oxidation behaviour of exhaust soot from a heavy duty (HD) diesel engine were investigated by Su et al. [11].

* Correspondence to: Engine Research Group, Department of Mechanical, Materials and Manufacturing Engineering, University Park, The University of Nottingham NG7 2RD, UK. Tel.: +44 115 95 13815.
E-mail address: antonino.larocca@nottingham.ac.uk (A. La Rocca).

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http://dx.doi.org/10.1016/j.triboint.2012.12.002

Soot from modern HD diesel engines exhibit smaller primary particles. Exhaust and laboratory flame-generated soot is commonly described in terms of fractal dimension due to the complex morphology [14–18]. Smaller fractal dimensions indicate chain-like structures while larger fractal dimensions indicate clusters. The fractal dimension is a statistical index of complexity and Rogak and Flagan [19] noted that agglomerate fractal dimensions measured from two-dimensional image projection of three-dimensional structures may be 10–20% lower than geometric dimensions. Given their irregular branched shape, soot particles are also characterised in terms of maximum projected length (L) and width (W) [7,12,19]; whilst for chainlike structures, Rogak et al. [20] suggested measuring the skeleton length (L_{sk}) of agglomerates.

One important mechanism of soot transfer to the oil film on the cylinder walls is thermophoresis [21,22]. The film is replenished and oil recycled through the influence of the piston and ring pack motion, and the entrained soot will be mixed with the returned oil into the sump reservoir. The soot in oil is similar to exhaust soot and carbon black [23–26] and generally found in irregularly shaped structures with a characteristic length of up to 500 nm. Over time this builds up to levels which modify the performance of the oil and limit the engine service interval. Soot leads to oil thickening [23] which increases the effective viscosity and worsens fuel economy and levels of CO_2 emitted. Various investigators [24,27] have shown that soot build up in oil gives rise to increased engine wear rates; Gautam et al. [28] reported that wear increases with higher soot concentration. Soot reduces the effectiveness of anti-wear additives and its effect on wear depends upon the characteristics of the particles and agglomerates of soot. Abrasive wear occurs and wear scar width closely matches the primary particle size Li [27].

Esangbedo et al. [23] used HRTEM to investigate the reactivity of soot particles which influences the interaction with oil dispersants and affects soot agglomeration. Soot-in-oil high resolution imaging is more challenging; mineral oil is a contaminant for the electron microscope and leads to instability under the electron beam [29]; very limited information is available in the literature on this topic. Cryogenic vitrification and imaging by Cryogenic TEM has also been used by Kawamura et al. [30] and Liu et al. [31] to visualise the soot agglomerates and their distribution in engine oil. However, issues related to viscosity of typical used engine oil leading to localised thick layers might prove to be challenging and constitutes a problem. Li et al. [27] have used solvent extraction technique and ultracentrifugation to prepare the specimen for conventional TEM to analyse soot primary particles from a heavy duty diesel test engine. Clague et al. [25] employed solvent extraction followed by centrifugation to extract soot from used engine oil. Their work suggests that carbon black, exhaust and engine oil soot agglomerates are similar in shape and size, ranging from 150 nm and 500 nm. The images of soot-in-oil agglomerates by Clague are cited in literature as examples of typical engine soot-in-oil agglomerates [24,26]. Similar large agglomerate sizes were recently reported by Esangbedo et al. [23].

A summary of the typical dimension for soot from internal combustion engines is reported in Table 1. In most cases soot agglomerate size is deduced from micrographs reported in literature.

Table 1
Typical dimension for soot from internal combustion engines.

Reference	Soot type	Agglomerate size (nm)	Primary particle size (nm)
Lapuerta et al. [10]	Exhaust	> 500	25 Average
Annele et al [18]	Exhaust	84–270	–
Su et al. [11].	Exhaust	–	13 Average
Esangbedo et al. [23]	Exhaust	> 400	–
Esangbedo et al. [23]	Oil	> 400	–
Clague et al. [25]	Oil	150– > 500	30–50
Kawamura et al. [30]	Oil	–	20–30
Li et al. [27]	Oil	–	15–50

Table 2
Engine specifications.

Fuel injection system	HPCR max. 1800 bar
Injector type	Solenoid injector
Number of orifices	7
Engine type	Single cylinder
Cycle	Four stroke diesel
Valves per cylinder	4
Compression ratio	13.6
Con-rod length (mm)	160.0
Bore × stroke (mm)	86.0 × 94.6
Displacement (cc)	549.5

2. Experimental setup and sample preparation

The oil samples used in the study were drawn from a high pressure common rail (HPCR) direct injection diesel engine which was a single cylinder variant of a multi-cylinder design meeting Euro 4 emissions requirements. The specifications of the engine and fuel injection system are provided in Table 2. The engine was installed on a laboratory 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 predominant two 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%. Although the mix of operating conditions covered was defined for other purposes, this was sufficiently varied to suggest the range of agglomerates formed would be representative of light duty diesel use. At the end of the 10 days, oil samples were drawn from the sump for the investigation of the soot content.

Conventional TEM has been used to assess the size and shape of particle agglomerates extracted from the oil samples and HRTEM has been used to analyse the structure of the primary particles, (i.e. inner core and outer shell). In each case, approximately 200 particles or agglomerates were isolated and examined [14]. The samples for TEM were prepared on a support film of carbon over a copper mesh grid. For optimum resolution, the material needs to be electron transparent, ideally less than 100 nm thick, and stable in high vacuum. 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. Two variants of technique have been used and compared; these are referred to as "solvent extraction" and "centrifugation", and one of the aims of the study was to examine if and how preparation through centrifugation affects the characteristics of the particle agglomerates being investigated, namely the size and shape of these.

The solvent extraction technique minimised the stress on soot agglomerates during preparation for examination and gave sufficient separation of oil and soot to allow conventional TEM (20–50 nm scale) results to be obtained. Oil was simply diluted in heptane (dilution ratio of 1:60) to produce a heptane solution that contained soot with a much lower oil content. When deposited onto a carbon coated TEM grid the solvent evaporated rapidly to leave soot particles of varying sizes and aggregations.