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Characterisation of soot agglomerates from engine oil and exhaust system for modern compression ignition engines

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Abstract

The characteristics of soot in oil samples extracted from lubricating oil and exhaust system of a modern common rail compression ignition engine were studied. The morphological parameters of the soot agglomerates were calculated from micrographs obtained by a High-Resolution Transmission Electron Microscopy (HR-TEM). The morphological analysis indicated that the soot in oil agglomerates have a larger average primary particle size and overall larger agglomerate size (determined by the radius of gyration) compared to the agglomerates sampled in the exhaust system. This can be a consequence of the dehydrogenation of hydrocarbon (HC) chains from the oil around the soot agglomerates. The shape of the agglomerates is quantified by fractal dimension. The soot in oil agglomerates presented a slightly larger fractal dimension than those studied in the exhaust system. Therefore, it seems that soot in oil agglomerates were more compact than those found in the exhaust system. The impact on lubricating oil properties should be further investigated.

Keywords

diesel engine, soot, fractal dimension, engine oil, HR-TEM

Introduction

Compression ignition engines produce high levels of particulate matter (PM) from incomplete combustion[1,2]. PM is majorly composed of soot carbonaceous particles which can be moved to the lubricating oil via the engine cylinder[3,4]. In addition, the type and size of soot particles that transferred inside the engine oil depends on the operation conditions and type of the engine used. Literature reports that more than 5% of unburned fuel could be enter the oil[5]. While, most of the soot emission is expelled from combustion chamber with unburned hydrocarbons to the engine crankcase and exhaust system. Exhaust PM emitted from diesel engines cause concerns linked to health impact and environmental issues.

The engine oil properties (viscosity, film thickness, and friction coefficient) are degraded with time because of the soot nanoparticles accumulated into the lubricating oil film[6–8]. Gautam et al.[9] stated that anti-wear properties of engine oil are deteriorated due to the contamination of oil with soot particles. Mainwaring[10] found that the intensity of the wear mechanisms depends on the soot concentration, oil film thickness and size of soot particle. Clague et al.[11] observed that the composition of soot particle in the exhaust is different in comparison with the soot from engine oil. They found that the soot in the exhaust consists of 90% carbon, 4% oxygen and 6% other, while the soot in the engine oil consists of 50% carbon, 30% oxygen and 20% other. A high concentration of soot agglomerates in the lubricating oil increases the dynamic viscosity of the oil lubricants which in turn leads to undesirable impact on CO2 emissions and fuel economy[6,12].

Transmission electron microscopy (TEM) and high-resolution (HR) TEM has been used to investigate physical soot characteristics (morphology and structure)[13,14]. The development of further methodologies enables to quantify soot characteristics such as of shape and size for primary particles and soot agglomerates from HR-TEM micrographs[15–20].

Primary particle size composing the agglomerates has been studied. Generally, the average size of soot primary particles generated from the diesel fuel combustion is around 25-30 nm[21,22]. The soot agglomerates are also characterized, generally by size and morphological properties such as n_{po} (number of primary particles), D_f (fractal dimension) and R_g (radius of gyration)[23]. The majority of studies[17,23,24] characterise soot agglomerates extracted from the exhaust gas, while the information of soot agglomerates extracted from engine oil is limited in the literature[14,25,26]. Novel methods have been also studied regarding the sample and conditioning of the sample PM. For instance, cryogenic vitrification and imaging by cryogenic TEM was utilised to

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observe the fitted size distribution of soot agglomerates in engine oil[27,28].

It is pointed out that the wear mechanisms can be affected by the characteristics of agglomerates and soot primary particles in the engine oil[14]. Analysis of size distributions of soot particles in lubricating oil contributed to understand the possibility effects on the properties of engine oil. The work by Green et al.[7] found that the wear scar width and abrasive wear occurs depending on both soot primary particle and size of soot agglomerates. La Rocca et al.[14] and Li et al.[29] employed experimental method to prepare the specimen for HR-TEM by using solvent extraction and ultracentrifugation for take out soot particles from engine oil. Also, similar method was used in previous studies by Clague et al.[11] and Esangbedo et al.[6] extracting the soot particle from lubricant oil and prepare a suitable sample for analysis by HR-TEM. Green et al.[7] and Clague et al.[11] suggest that the soot agglomerates in the exhaust, carbon black and agglomerates of soot emission in the engine oil have the similar shape and size (150-500 nm). Moreover, the size of soot primary particles and soot agglomerates produced from combustion process in diesel engine are listed in Table 1.

Table 1. Summary of soot agglomerate and primary particle size from IC engines.

Type of soot specimen	Size of soot agglomerate (nm)	Size of primary particle (nm)
Soot in exhaust[16]	>500	26
Soot in exhaust[6]	>400	–
Soot in exhaust[30]	48–270	–
Soot in engine oil[14]	45–132	10–35
Soot in engine oil[11]	150–500	35–45
Soot in engine oil[29]	–	15–50
Soot in engine oil[6]	>400	–
Soot inside cylinder[31]	273 to 897	11.65
Soot inside cylinder[32]	–	15

Consequently, the physical properties of soot agglomerate in lubricating oil have become significant subject to understand the interactions between the soot morphology characteristics and lubricating oil properties. Studies of soot agglomerates characteristics in lubricating oil in the sector of automotive industry are of growing interest and a new challenge for researchers to increase the engine oil life, maintenance, engine durability. This work investigates the size of primary particles and the morphological parameters (n_{po}, R_g, and D_f) and size of soot agglomerates in the engine oil and compared with those from soot agglomerates in the exhaust system.

Materials and methods

Engine test cell

The experimental work was carried out using a common rail fuel injection, single cylinder diesel engine. Table 2 listed the technical specifications of diesel engine. The samples of soot agglomerates used in this work were drawn from this engine (exhaust system and oil sump). The clean lubricating oil (SAE 5W/30) was used to fill the engine sump. An electric dynamometer was coupled with the engine to measure and adjust the engine torque and speed. The fuel consumption was measured during the engine test. The engine values such as temperature of exhaust, engine torque, IMEP (including COV), oil temperature and air flow were recorded during the experiments. For all the experiments, the engine was run during 20 hours at 1800 rpm and 3 bar IMEP (indicated mean effective pressure). The injection system is a common rail equipped with a 6-hole solenoid injector with a nozzle diameter of 160 μm and with an angle 144°. The injection pressure and timing are determined using our bespoke injection control system based on the common rail injector test bench STPiW2 manufactured by Autoelektronika. The fuel injection condition was split in two injection events with injection timing of 15 and 3 degrees before top dead centre (bTDC) for pre and main injection, respectively. The injection volume percentage was calculated from the injection timing percentage of each of the injections with respect to the total opening injection timing. The fuel injection pressure was kept at 650 bar for all tests. The diesel engine was fuelled by conventional diesel fuel (Ultra Low Sulphur Diesel) which supplied by Shell Global Solutions UK.

Table 2. Research engine specifications.

Engine parameters	Specifications
Engine type	Diesel 1-cylinder
Fuel injection system	High pressure common-rail
Injection type	Solenoid injector
Stroke type	Four-stroke
Cylinder bore x stroke (mm)	84 x 90
Connecting rod length (mm)	160
Compression ratio	16:1
Displacement (cm^3)	499
Engine speed range (rpm)	900–2000
Fuel pressure range (bar)	500–1500
Number of injections	3 injection events

Sample preparation

The engine was flushed twice with clean oil at the beginning of the testing period, followed by SAE 5W/30 type of clean lubricating oil when start the real test. At the end of test, the collected samples of soot particles from oil used (engine sump) were post-treated according to the procedure reported by La Rocca et al.[14] using a solvent extraction process. The sample of engine oil is diluted in heptane at 1:60 (dilution ratio). The heptane solution produced from this process contained soot with much lower oil content and low viscosity to allow the soot particles deposition onto HR-TEM grids. Afterward, both soot particles and soot agglomerates left the solvent by evaporating quickly and this soot was then subjected to close-to-vacuum conditions to guarantee the solvent evaporation. Furthermore, two stages of diethyl ether bathing were used to improve image quality and reduce the contamination. In addition, ultrasonic bathing device was used for five minutes to break up the agglomerates pile into individual agglomerates via several stages. The heptane used in this work was supplied from Sigma-Aldrich.

Characterisation techniques

The imaging for soot in engine oil with high resolution is more challenging compared to the exhaust soot to study the characteristics of soot agglomerates. Samples of soot particles were collected on copper grids from exhaust system and engine oil. A Philips CM-200 HR-TEM was used with a resolution 0.2Å to analyse both soot in oil and exhaust soot particles. Soot characterisation by HR-TEM has been previously demonstrated to provide accurate measurements of soot size, morphology and structure[17,33]. Matlab software was designed to measure the characteristics of soot agglomerates such as R_g, n_{po}, and D_f[33–35]. R_g is the radius of a ring with the same centre of mass and moment of inertia as the agglomerate[36,37]. R_g and A_p (projected area) were calculated from the position of each pixel in the binarised image of the agglomerate[36]. n_{po} was determined by taking into account the overlap between the primary particles by calculating the overlap exponent which relates the area projected by the agglomerate and the area that would be projected by all the primary particles if they were in the same plane[38].

The primary particle diameters (d_{po}) were measured directly on each enlarged image[39]. For each condition, more than 33 photographs were taken to determine the morphological characteristics of soot agglomerates. Besides, at least 200 particles of soot emission were selected from soot agglomerates to find the average particles size of soot emission as well as the size distribution of collected soot particles.

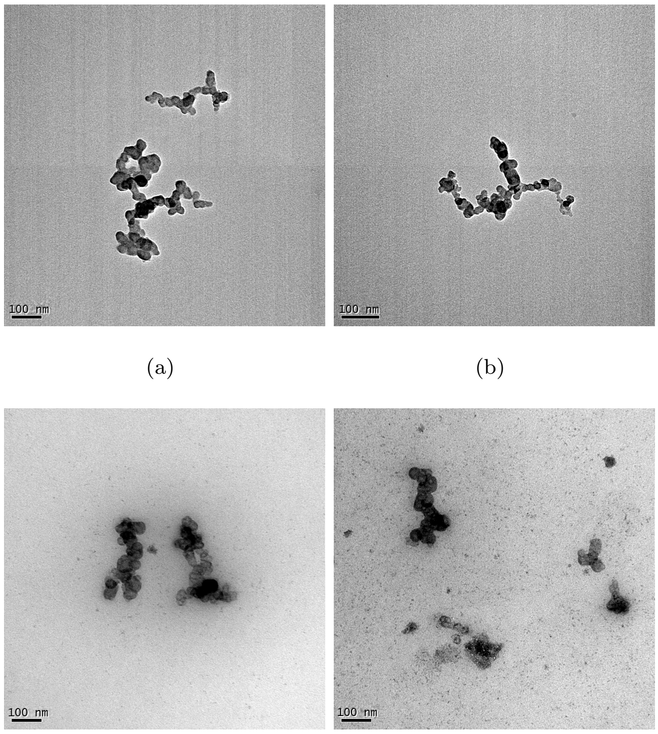
Fourier Transform InfraRed (FTIR) spectrometer was used to measure the level of soot contamination in the engine oil (liquid sample). It is used to measure the soot level in lubricating oil as a function of the reduction of light transmitted at a given wave length. The light emitted from the source splits into two equal parts by a beam typically made of ZnSe which allows the measurement of spectra in the range of 1.5-18 μm. Spectral range was from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} at room temperature.

Results and discussions

Physical properties of soot agglomerates

Figure 1 illustrates typical HR-TEM image of soot agglomerates from exhaust soot and from oil sample. In the current experimental work, the soot agglomerates (Figure 1) that comprised of primary particles ranging from 20-28 nm forming chain-like and clusters of spherules for both exhaust soot and soot from engine oil. The TEM images (Figure 1) requires more development to remove the remnant oil on particles to allow further analysis for nanostructure of primary particle. The particles produced from diesel fuel combustion forms irregular clusters in different shapes and sizes[40,41].

The morphological parameters are calculated from the obtained images (Figure 1) for both cases (soot in oil and soot in exhaust). Furthermore, the number of primary particles in the exhaust is slightly higher in comparison with case of soot particles produced from used oil (Figure 2). This could be due to the higher level of randomly collisions between soot agglomerates in the exhaust process, as a result of higher level of turbulence in the exhaust gas in comparison with case of engine oil which caused by lower viscosity of the exhaust gas which compared to that of the oil. In addition, the soot particles can enter to the cylinder wall and then to the crankcase to accumulate in the lubricating oil are not very high.



(a) (b)
(c) (d)

Figure 1. HR-TEM micrograph (100 nm scale) of soot agglomerates collected from diesel fuel combustion for (a-b) exhaust gas, and (c-d) engine oil.

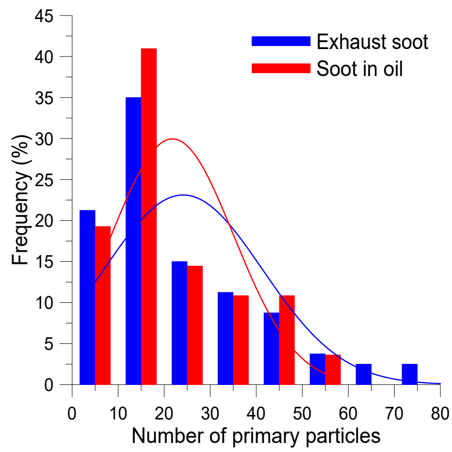


Figure 2. Number of primary particles of soot agglomerates from combustion of diesel fuel for exhaust soot and soot in oil.

According to these results, the radius of gyration is slightly higher in the case of soot in oil agglomerates with respect to the exhaust soot agglomerates (Figure 3). This could be due to the growth of primary soot particles when they are in the oil result in more branched soot particles that expand further towards outward from the centre of mass. Furthermore, the mean projected area within aggregate is higher in case of soot extracted from the engine oil in comparison with the exhaust soot (Figure 4). As a result of that, the projected area produced from soot agglomerate in engine oil is higher therefore probably tends to increase the radius of gyration.

It means that the results of radius of gyration are closely followed by the projected area. Meanwhile, the work by Orhan et al.[42] reported that the radius of gyration is not mostly related directly to the that of A_p. The larger R_g and A_p from soot agglomerates in engine oil indicates that the mass clustered far to the centre of mass.

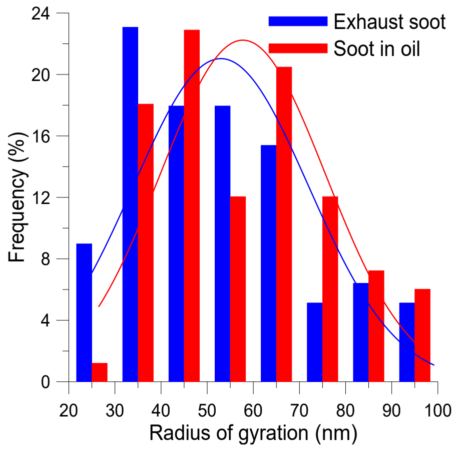


Figure 3. Radius of gyration of soot agglomerates from combustion of diesel fuel for exhaust soot and soot in oil.

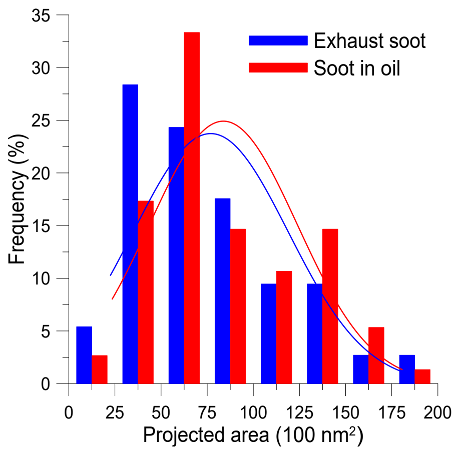


Figure 4. Projected area of soot agglomerates from combustion of diesel fuel for exhaust soot and soot in oil.

The fractal dimension of soot agglomerates produced in the exhaust and engine oil from diesel fuel combustion is shown in Figure 5. D_f is a measure of the irregularity of the agglomerates and its value indicates what kind of collisions generated it. In the present study, the average D_f results obtained varied in the range 1.6-1.7 for both cases of soot agglomerates and this in typical range of diesel particulate[43]. The D_f measured of soot agglomerates in engine oil was 1.7 and this agreement with Li et al[29]. Slightly larger fractal dimension of soot particle aggregates in engine oil than that produced from exhaust soot (Figure 5) could be due to lower primary particles concentration resulting reduced the possibility of collisions between soot agglomerates. Furthermore, slightly branched chain-like particles (i.e agglomerates mass clustered far to the centre to form cluster structure) of soot in oil agglomerates leading to smaller D_f values[42]. In contrast, the combination between individual particles of soot emission and soot agglomerates in the exhaust will decrease the agglomerate size and reduces the value of fractal dimension (higher rate of particle formation). La Rocca et al.[14] described that the larger values of fractal dimensions indicate clusters structure of soot agglomerates while smaller fractal dimensions indicate chain-like structure. Therefore, the relationship between mass branching and fractal dimension is opposite. According to the results, the soot agglomerate in oil have a slightly more compact shape than to the soot agglomerate in the exhaust system[17,33].

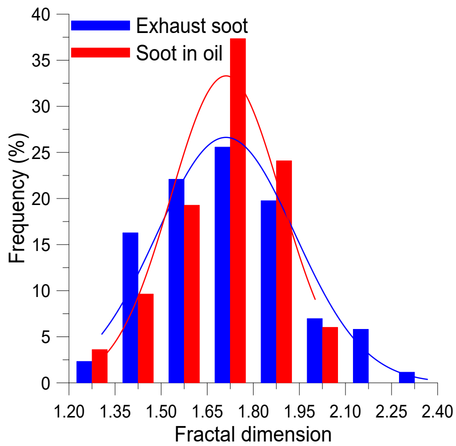


Figure 5. Fractal dimension of soot agglomerates from combustion of diesel fuel for exhaust soot and soot in oil.

The primary particle size distribution for diesel exhaust soot and soot in oil is presented in Figure 6. For each case, around 300 primary particles have been randomly selected to measure and produce the fitted normal distribution (Figure 6). The primary particle size is different from the two sources of soot particle produced (soot in engine oil and exhaust soot) as measured from HR-TEM images. The average size of primary particulates of soot agglomerate in engine oil was larger (in range 27 nm) than to the average size of primary particulates of soot agglomerate in the exhaust system (in range 22.5 nm). This is due to the higher soot formation inside cylinder as a result of pressure and temperature values[44,45]. In addition, could be due to the fact that part of the HC chains of the oil are dehydrogenated around the soot participating on primary and soot agglomerate surface growth and therefore increase the soot agglomerates size that collected from lubricating oil. This behaviour is consistent with the fact that the fractal dimension of soot in engine oil is larger compared to the exhaust soot. This is due to smaller n_{po} and larger primary particles size which compose the soot agglomerates. The variable size of soot agglomerate is associated with the engine operation conditions (fuel type, engine features, injection strategy)[16].

Soot level in the lubricating oil

During the warm-up of the engine, incomplete combustion can lead to a series of by-product (soot particles, unburned fuels dissolved in the lube oil, etc.). The soot samples were collected from the lubricating oil in crankcase as mentioned in previous section. The soot particles contamination in the engine oil doesn't exhibit a specific IR absorption therefore its treated differently. The two typical spectra of in-service oil highlighting various different signals correlating

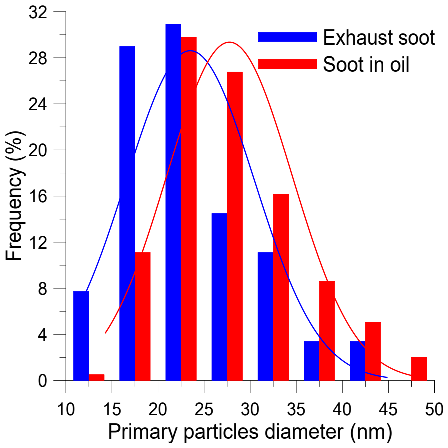


Figure 6. Primary particle size distribution of soot agglomerates from combustion of diesel fuel for exhaust soot and soot in oil.

were shown in Figure 7 with changes exhibited by the oil during operation. The ASTM E2412 method was depends in this test to analysis the used oil. Figure 7 shows modern analytical technique of soot level in engine oil by FTIR for used oil and fresh oil. The fresh oil was analysed by FTIR spectrum to obtain a baseline FTIR trace. It is clear that the soot contamination level of used oil was slightly higher than fresh oil. This is indicated by subtracting the fresh oil spectrum form used oil spectrum (called difference spectrum). According to Figure 7, it can be noticed that the soot in used oil causes a vertical shift in the bassline of the spectrum (affected by amount of soot present and size of soot particle size). This is due to absorption and scattering of light in the region around 2000 cm^{-1} (this region is used to assess the level of soot in oil sample). It can be observed from Figure 7 that two peaks in rang 1600 cm^{-1} and 1300 cm^{-1} due to aromatic C=C stretching and symmetric and symmetric modes respectively. Clearly, there are small differences in the peak positions of the band due to a little soot contamination with lubricating oil.

However, it is difficult to distinguish the degradation of oil properties for short time of engine operation because the soot particles take long time to dissolves in lubricating oil. In contrast, the solid soot particles can affect engine parts wear mechanisms due to the increase of friction and reduce the anti-ware mechanism for engine parts.

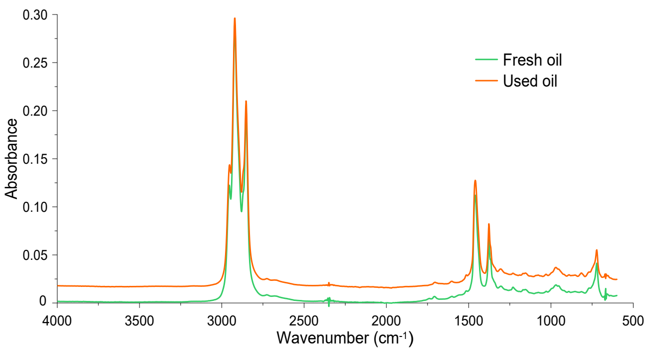


Figure 7. FTIR spectrum from fresh and used lubricant oil.

Conclusions

The soot characteristics sampled from engine oil and exhaust gas have been characterised for modern compression ignition engines. The size and number of the primary particles composing the agglomerates, the size of the agglomerates (Radius of gyration) and the shape of the agglomerates quantified by fractal dimension are determined.

The average primary particle size of the soot in oil agglomerates are larger than those from the exhaust agglomerates. This could be due to the fact that some of the HC chains from the oil in contact to the soot agglomerates within the combustion chamber could be thermally dehydrogenated, which in turn leads to new particle layers contribution to particle surface growth resulting in larger primary particles. The size of the soot in oil agglomerates are also larger than those of the soot particles found in the exhaust system.

The fractal dimension of the agglomerates in engine oil was slightly larger than in the case of exhaust soot agglomerates. This indicates that soot in oil particles have a more compact (spherical-like) shape, lower surface area and it is thought a lower effect on engine components' wear than if exhaust particles are present in the engine oil. Further research, studying the impact of actual soot in oil agglomerates on lubricating oil properties, their potential degradation and engine wear is proposed.

Nomenclature

A_p	projected area
IC	internal combustion
d_{po}	primary particle diameter
D_f	fractal dimension
FTIR	Fourier transform infrared
HC	hydrocarbon
HR-TEM	high-resolution transmission electron microscopy
PM	particulate matter
n_{po}	number of primary particles
R_g	radius of gyration

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CRediT author statement

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Declaration of conflicting interests

The authors declare no conflict of interest.

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