



Full Length Article

The influence of a large methyl ester on in-flame soot particle structures in a small-bore diesel engine



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HIGHLIGHTS

- Methyl decanoate is selected as a biodiesel surrogate fuel for in-flame soot sampling.
- Methyl decanoate soot has smaller primary particles and aggregates than diesel.
- The carbon fringe spacing is lower for methyl decanoate than that of diesel.
- The observed trends indicate more oxidised in-flame soot for methyl decanoate.

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ABSTRACT

Oxygenated biodiesel presents lower sooting propensity than conventional diesel, providing a good opportunity to resolve the high particulate emissions issue. This study reports soot morphology details of methyl decanoate, a selected surrogate fuel for the larger fatty acid methyl esters in biodiesel. The size distribution of soot primary particles and aggregates as well as the fractal dimension of the aggregates are discussed in comparison to those of a conventional diesel fuel. In addition, nanoscale soot parameters such as carbon fringe length, tortuosity, and fringe-to-fringe separation distance are analysed to clarify the internal structure variations depending on the fuel type. Of particular interest are the structures of soot particles within the flame in a running diesel engine. Compared with numerous previous studies reporting exhaust soot particle structures of biodiesel, the present study provides additional and complementary information about soot particles under high formation and oxidation processes during the main combustion event. Thermophoresis-based soot particles collection was conducted in a small-bore optical diesel engine using a sampling probe placed within the combustion chamber for the direct exposure of a transmission electron microscope (TEM) grid to sooting flames. The TEM images were post-processed for statistical analysis of the aforementioned morphology and nanostructure parameters. The results show that methyl decanoate generates smaller soot primary particles and aggregates with lower fractal dimension, which could be explained either by the earlier stage of soot formation or more oxidised soot status. From the fringe separation results showing a smaller gap for methyl decanoate, it is concluded that the sampled in-flame soot particles were more oxidised likely due to the presence of oxidisers in fuel.

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1. Introduction

While the high torque and high efficiency make diesel engines an attractive option for the ground transport, soot particle emissions are problematic due to their negative impact on health and the environment [1,2]. A promising alternative method for reduced soot emissions is fuelling diesel engines with biodiesel. While the

biodiesel production from a wide variety of renewable feed stocks [3–5] is advantageous in reducing fossil fuel consumption and the overall CO₂ level, low engine-out particulate emissions due to the low-sooting propensity of oxygenated biodiesel is also beneficial [6–12]. An immediate need is enhanced understanding of soot formation and oxidation processes of biodiesel combustion occurring inside the cylinder of the engine. In this regard, the analysis of soot particle structures in terms of the physical dimensions of soot aggregates, primary particles, and carbon lamella within the primaries is necessary. The present study aims to provide such information for biodiesel soot particles in comparison to diesel soot particles.

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For the study of soot particle structures, thermophoretic sampling of high-temperature particles on a cold carbon layer of a transmission electron microscope (TEM) grid is widely used [13–21]. In these studies, the sampled soot particles are imaged in a TEM and then post-processed for quantitative and statistical analysis of soot structure parameters such as the diameter of soot primary particles, the soot aggregate radius of gyration, and the fractal dimension. These parameters are useful to understand the variations of soot particles during diesel combustion. For instance, it was found that the flame-wall interaction occurring inside the cylinder of the engine causes the decreased aggregate size and fractal dimension while the size of soot primary particles do not change, suggesting the breakdown of large soot aggregates [13]. Other studies reported that the soot aggregates and primary particles decrease in size due to in-cylinder soot oxidation [13,14,22]. It was also reported that the increased fuel injection pressure leads to not only overall lower soot amounts but also smaller aggregates with lower fractal dimension comprising smaller soot primary particles, which indicates more stretched and less agglomerated soot structures [18]. In addition to the soot morphology parameters, many recent studies reported details of soot internal structures composed of nanoscale carbon fringes [14,16,22–26]. High-resolution TEMs are used to visualise the carbon lamella within the soot primary particles, which are shown as fringes in the TEM images. Those carbon lamella are characterised using nanostructure parameters such as fringe length, tortuosity, and fringe-to-fringe separation distance [14,16,25]. For example, highly graphitised soot particles show higher fringe length, lower fringe tortuosity, and lower fringe spacing, indicating higher oxidation status and lower particle reactivity [27–31].

The soot morphology and nanostructure parameters have been measured for biodiesel in many previous studies by extracting particles from the engine exhaust stream [12,30,32–42]. It was reported that the exhaust soot particles of biodiesel show smaller primary particles and aggregates than petroleum diesel [12,35–38,41] with lower fractal dimension [37,41], suggesting less agglomerated aggregate structures. These trends based on exhaust particle morphology, however, could be caused either due to reduced soot formation or increased soot oxidation occurred inside the cylinder of the engine. The same question is raised from the soot internal structure analysis. For example, some studies [30,36,39] found less graphitic, amorphous soot structures from biodiesel, which was explained by the increased coalescence of heavy polycyclic aromatic hydrocarbon (PAH) species for the soot growth. However, other studies reported a directly opposite trend with more carbonised graphene layers in biodiesel soot particles than those in petroleum diesel because the oxygenates at soot particle surfaces could enhance oxidation [35,38,40].

The mixed conclusion could be simply due to different engine operating conditions. For instance, the particle graphitisation shows a high sensitivity to fuel injection pressure with increased injection pressure causing more graphitised soot structures for the same biodiesel fuel [40]. Other conditions such as ambient gas pressure, flame temperature and the combustion phasing are also known to impact the graphene segments organisation of soot particles [18,43]. Therefore, the engine operating conditions should be closely monitored when soot nanostructure analysis is conducted for biodiesel. Another concern is a conclusion solely based on exhaust soot particles. The evaluation of soot particles in the exhaust stream is very important for their direct environmental impact. However, given that the exhaust soot particles are a product of complex soot formation and oxidation processes within the flame, one could expect the structural variations associated with the fuel type could differ when soot particles within the flame are evaluated. For example, the soot particles sampling directly from a biodiesel flame was conducted in a constant-volume com-

bustion chamber simulating high temperature and pressure ambient gas conditions, from which in-flame soot particles of biodiesel show the same soot primary particle size and larger soot aggregates with lower fractal dimension compared with petroleum diesel [19]. However, these findings made at quiescent ambient gas conditions in a constant-volume combustion chamber might not be directly relevant to diesel engines, particularly small-bore automotive diesel engines, due to the lack of flow and geometry effects (e.g. jet-wall interactions), which makes a significant impact on soot formation/oxidation [44–46]. This motivated the development of in-flame soot sampling technique applicable to a diesel engine, which has been successfully implemented in a single-cylinder light-duty diesel engine for both soot morphology and nanostructure analysis at various engine operating conditions [13,17,18,25]. To the best of our knowledge, the structural analysis of soot particles directly sampled from the biodiesel flame has never been attempted in a working engine.

This study presents in-flame soot particle structures of methyl decanoate ($C_{11}H_{22}O_2$), a selected biodiesel surrogate, and a conventional diesel fuel in a working diesel engine. Methyl decanoate has become of high interest in recent studies [47–50] primarily because the chemical kinetic mechanism is available in the literature [51,52]. The selection of methyl decanoate is justified because its length of the alkyl chain represents fatty acid methyl esters (FAME) and it has also been reported that the ignition delay and negative temperature coefficient (NTC) behaviour are similar with conventional biodiesel fuels [53,54]. The thermophoretic soot sampling was conducted using both a carbon-layer-coated mesh TEM grid and a lacy TEM grid for overall primary particle size and aggregate morphology, and nanoscale carbon fringe analysis, respectively. The sampled soot particles were imaged using a standard and high-resolution TEM and the images were post-processed using an in-house-developed, automated detection code for primary particles and soot aggregates [55] and carbon fringes (except fringe spacing) [24,25]. Key soot morphology parameters such as the primary particle size, aggregate size, and fractal dimension as well as nanostructure parameters such as the fringe length, fringe tortuosity, and fringe-to-fringe separation have been obtained for hundreds of aggregates and thousands of soot primary particles and carbon fringes for statistical analysis.

2. Experiments

2.1. Engine specifications and operating conditions

The in-flame soot sampling experiments were conducted in a small-bore optically-accessible diesel engine as illustrated in Fig. 1. The specifications and operating conditions of the engine are summarised in Table 1. The engine has a displacement volume of 498 cm³ with 80-mm bore and 92-mm stroke. To enable the direct sampling of soot particles from flames, a portion of the piston bowl-rim was removed, which was used to install the sampling probe without a risk of collisions with the fast-moving piston and intake valves. Details of this modification as well as its impact on sampled soot particles are found in our previous study [17]. The geometric compression ratio of the engine including the bowl-rim cut-out is 15.5. The engine was naturally aspirated with a fully opened intake throttle, resulting in a swirl ratio of 1.4. The coolant water was heated with constant temperature of 363 K and pumped through the engine head, engine block and cylinder liner to simulate warmed-up engine operating conditions. Intake air temperature was measured at 303 K throughout the experiment. A common-rail system (Bosch CP3) was used for the direct injection of diesel and methyl decanoate with the timing and duration of injection being controlled by a universal signal controller (Zeno-

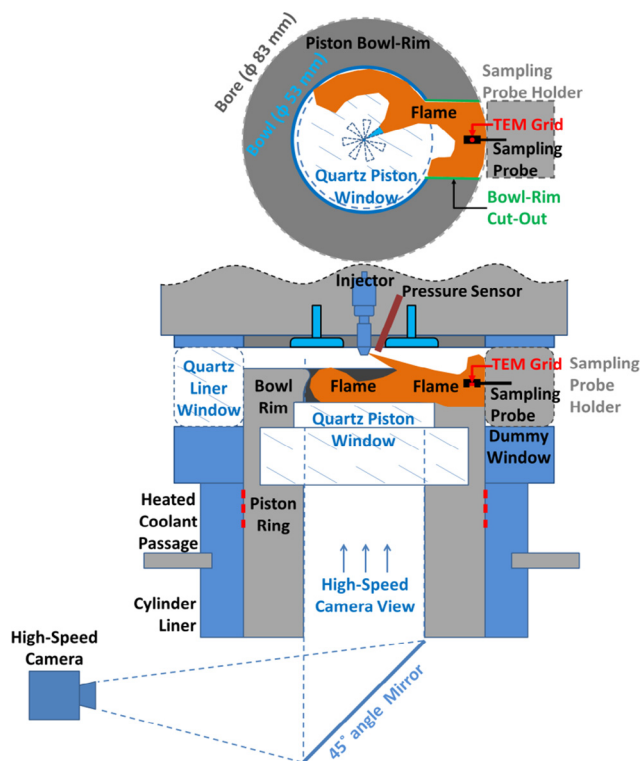


Fig. 1. Illustration of the diesel engine and soot sampling system in the bottom-view (top) and side-view (bottom) orientations.

Table 1
Engine specifications and operating conditions.

Displacement volume	498 cc (single cylinder)
Bore	83 mm
Stroke	92 mm
Compression ratio	15.5 (geometric)
Swirl ratio	1.4
Coolant temperature	363 K
Intake air temperature	303 K
Injector type	Bosch common-rail
Fuel	Ultra-low-sulphur diesel
Nozzle type	Hydro-grounded, K1.5/0.86
Nozzle diameter	134 μm (nominal)
Included angle	150°
Rail pressure	100 MPa
Injection duration	2.24 ms
Injection timing	7°CA bTDC
Engine speed	1200 rpm

balti 9013-P). A solenoid-type injector was originally equipped with a 7-hole nozzle with a nominal hole-diameter of 134 μm and an included angle of 150°. For the soot sampling experiments, only one hole was left open using a laser welding technique. This approach was to isolate the soot processes from complex jet-jet interactions, which are well known to make a significant impact on soot formation [56] and particle structures [25]. The common-rail pressure and injection duration were fixed at 100 MPa and 2.24 ms, respectively, which would correspond to the upper-mid load conditions if the injected mass per hole (about 9 mg) is considered. The injection timing was fixed at 7 crank angle degrees before top dead centre (°CA bTDC) and the engine was run at fixed speed of 1200 rpm.

The in-cylinder conditions were monitored using a piezoelectric pressure transducer (Kistler 6056A) as illustrated in Fig. 1. Simultaneously, a high-speed camera (VisionResearch Phantom v7.3)

was used to image natural combustion luminosity at a high framing rate of 36,000 frames per second. The natural combustion luminosity was dominated by the radiation signals of soot particles at high temperature (i.e. hot soot luminosity), which helped understand the spatial and temporal development of the flames with respect to the soot sampling probe location.

2.2. Fuel selection and properties

In this study, methyl decanoate ($C_{11}H_{22}O_2$, abbreviated to MD) was selected as a surrogate biodiesel due to its long alkyl chain length representing fatty acid methyl esters and its similar ignition delay and negative temperature coefficient (NTC) behaviour to conventional biodiesel fuels [53,54]. Engine tests of MD also reported similar engine-out emissions of smoke, NO_x , CO and unburnt hydrocarbon compared with soybean-derived biodiesel [46]. Moreover, detailed chemical kinetic models are available in the literature [51,57,58]. Therefore, methyl decanoate is an excellent single-component fuel to study structural variations of soot particles associated with a large methyl ester.

Table 2 shows some selected physical properties and chemical composition of MD. For comparison purposes, the in-flame soot particle sampling was also conducted for a conventional diesel fuel. The properties of the used ultra-low-sulphur diesel are also summarised in Table 2. The cetane number of MD varies between 47 and 53 depending on the test methods [11,46] but is similar to that of diesel. This suggests similar ignition delay time and pre-combustion mixing level, which, if the combustion phasing is matched, could effectively isolate the effect of fuel molecular structures on soot particles from other combustion conditions. The viscosity of MD is nearly twice lower than that of diesel and the density is slightly higher, which could cause smaller fuel droplets due to enhanced atomisation [61]. The calorific value of MD is 13% lower than petroleum diesel, which cannot be fully compensated by higher density in terms of the total energy input. However, the increased injection mass to match the total energy would require the increased injection duration and thereby altering the jet development and mixture premixedness, both of which also impact the soot particles significantly. Therefore, the fixed injection duration approach was used in the present study as noted in Table 1. This will be discussed further in the results and discussion section. The oxygen concentration in MD was estimated at 17.2% by mass, which could cause soot suppression and variations in the in-flame soot structures [8,9].

2.3. Soot particle sampling

The soot sampling system and the particle nanostructure analysis technique used in the present study were previously tested for their sensitivity to cyclic variations [17] and the number of samples used for the statistical analysis [25]. As shown in Fig. 1, the soot sampling probe is accessed through a metal dummy piece of the cylinder window so that the TEM grid stored at the probe tip

Table 2
Properties of methyl decanoate (MD) and ultra-low sulphur diesel [8,59,60].

Properties	MD [59,60]	Diesel [8]
Formula	$C_{11}H_{22}O_2$	–
Cetane number	47–53	51
Kinematic viscosity at 313 K (mm^2/s)	1.71	3
Density at 285 K (g/ml)	0.871	0.848
Calorific value (MJ/kg)	37.7	43.3
Carbon (wt.%)	71	86.2
Hydrogen (wt.%)	11.8	13.8
Oxygen (wt.%)	17.2	–

can be placed within the bowl-rim cut-out region where the sooting flames develop. As mentioned previously, this cut-out volume was required to place the sampling probe while avoiding its collision with the fast-moving piston and valves. Our previous studies showed minor variations in the in-cylinder combustion conditions due to the addition of the sampling system [17,21]. The sampling probe tip has a 1.5-mm hole providing a small passage for the direct exposure of the TEM grid to sooting flames. This restricted passage protects the TEM grid from excessive heat and hence remain the low temperature on grid surface. The cool TEM grid was previously proven to induce rapid reaction quenching upon the deposition of soot particles [13]. Detailed discussions on the sampling system design are found in our previous study [21]. The use of single-hole nozzle, optical engine, well-controlled engine conditions, and the bowl-rim cut-out made the tested con-

dition of the present study different from real engines; however, the fixed engine operating and soot sampling conditions ensured the soot particle structures are compared between two different fuels and if variations are found from the test, it was primarily due to the fuel molecular structure difference.

The hot soot particles within the flame could be deposited on a relatively cold carbon layer of the TEM grid due to the high temperature gradient – i.e. thermophoresis. Two different TEM grids were used in this study: one was a 3-mm diameter and 400-mesh copper grid with a 50-nm thick carbon layer coating, noted as a standard TEM grid, and the other was a 3-mm diameter and 300-mesh copper grid with 150- μm -thick lacy carbon layer. These grids were used for the analysis of size and structure of the soot aggregates and primary particles, and nanoscale carbon fringes within soot primary particles, respectively. The usage of the two different

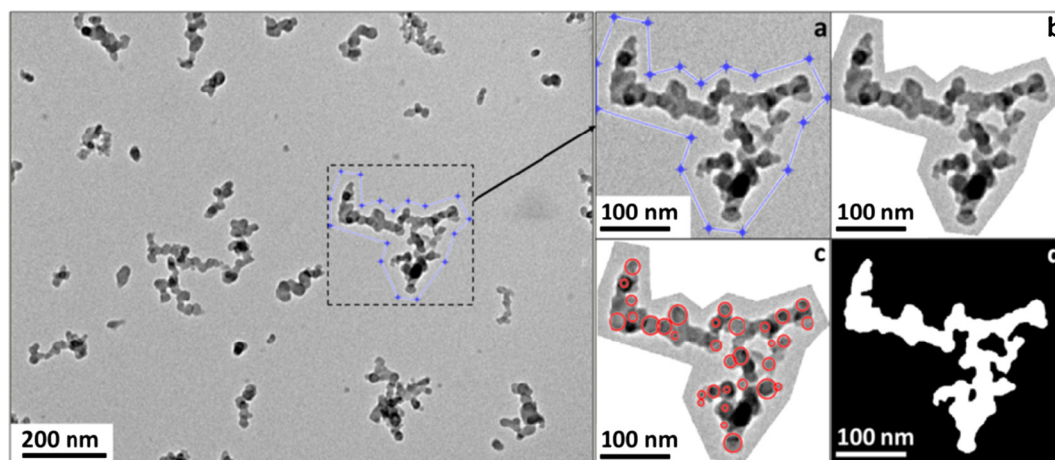


Fig. 2. Post-processing of low-resolution TEM image: (a) identification of soot aggregates on TEM images; (b) selection of the soot aggregate region; (c) automated detection of soot primary particles (Ref. [55]); (d) calculation of the soot aggregate projection area and the radius of gyration based on the binarised image.

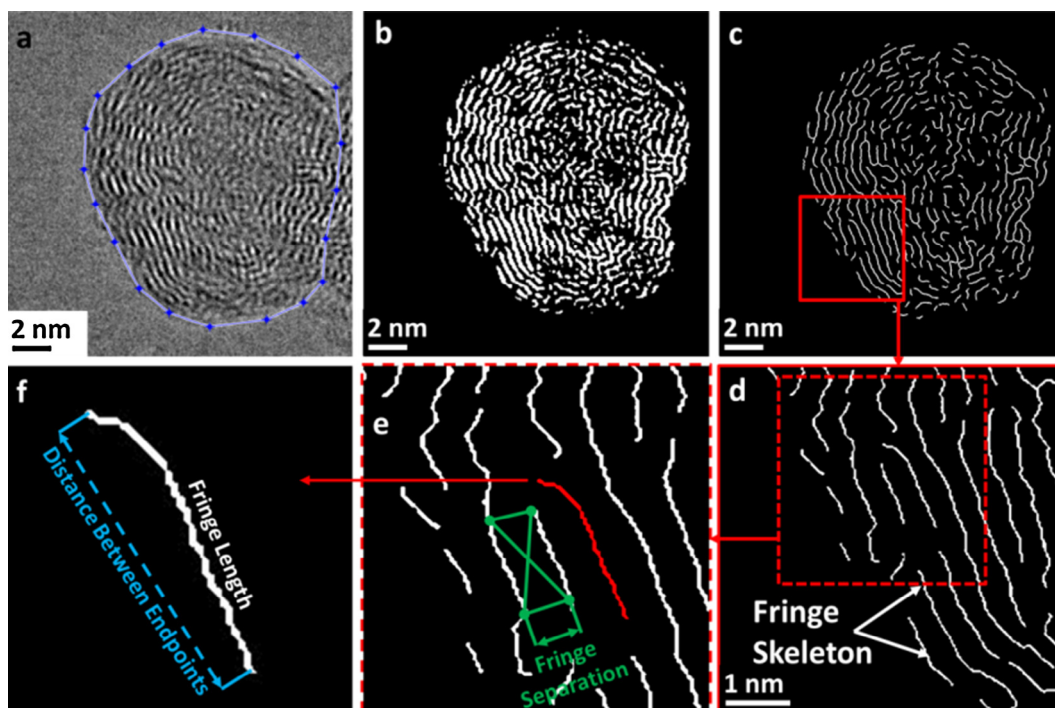


Fig. 3. Post-processing of high resolution TEM images (Ref. [24,25]): (a) identifying soot primary particle of interest; (b) image binarisation for fringe extraction; (c) obtaining a fringe skeleton image; (d) a close-up view of fringe skeletons; (e) fringe separation measurement; (f) fringe length and straight distance between endpoints of the fringe.

TEM grids is required since the standard carbon-film-coated grid gives rise to significant background interference for high-resolution TEM imaging for soot nanostructure analysis, which can be avoided in the lacy grid as the extruded portion of the particles from the grid branches is imaged [17,18,21,25,56]. During the soot sampling experiments, the optical engine was motored for about 90 s to create thermally stable in-cylinder conditions prior to fuel injection. The fuel injection was executed every 10th (i.e. 10 skip-firing) cycle for up to 10 injections (i.e. 10 injections

onto the TEM grid) for each sampling run. The skip-firing method was used to expel the residual gases from the previous firing cycle, minimising cycle-to-cycle variations. The 10-injection approach was a result of extensive optimisation tests conducted previously [17] for high enough soot particles for statistical data analysis but low soot to prevent an overloading issue.

2.4. Low-resolution TEM imaging and post-processing

The soot aggregates/particles deposited onto the standard TEM grid were imaged using a low resolution TEM (JEOL 1400) operating at an accelerating voltage of 120 kV with a point resolution of 0.38 nm. A CCD camera with a pixel resolution of 1350 by 1040 was used to capture soot particle images. The magnification of the TEM was optimised at $\times 100,000$ for image post-processing. Fig. 2 shows an example of low-resolution TEM images in which large soot aggregates appear to comprise several primary particles. Some small aggregates composed of only one or two primary particles (i.e. monomers and dimers) are also noticed. For each fuel, a total of 30 low-resolution TEM images were obtained for the post-processing. A Matlab-based automatic detection code was used for both soot aggregates and primary particle processing [55]. While the aggregate detection was relatively easier due to clear boundaries, it was challenging to develop a method detecting soot primary particles within soot aggregates. The fully automated processing of soot primary particles was achieved by implementing the Canny Edge Detection (CED) and Circular Hough Transform (CHT) on pre-processed TEM images for particle edge enhancement using unsharp filtering as well as image inversion and self-subtraction [55]. The obtained primary particle size and soot aggregate size were also used to calculate the fractal dimension of soot aggregates [13,17,18,21]. An example of these processing of low-resolution TEM images is shown in Fig. 2. For MD and diesel fuels, a total of 862 and 485 soot aggregates were identified, respectively, from 30 different on-grid locations. The processed primary particles for MD and diesel were 2982 and 5689, respectively.

2.5. High-resolution TEM imaging and post-processing

A high-resolution TEM (Philips CM200) with 0.25 nm point resolution and an accelerating voltage of 200 kV was used to observe the nanoscale internal structure of soot primary particles. Soot

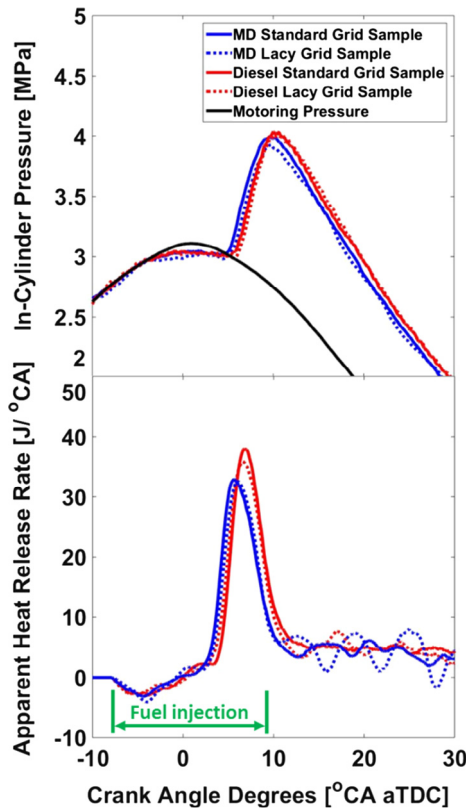


Fig. 4. Ensemble-averaged in-cylinder pressures and corresponding apparent heat release rates during the soot sampling experiments performed for methyl decanoate and diesel.

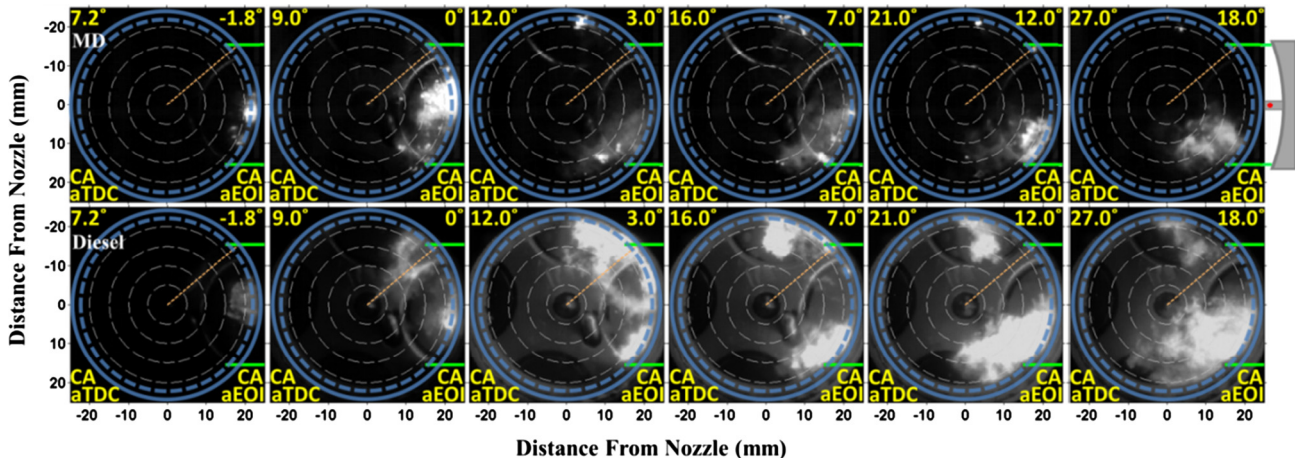


Fig. 5. Hot soot luminosity images of methyl decanoate (top) and diesel (bottom) during the main combustion event. The fuel spray trajectory directing at 2 o'clock is illustrated in each image. The green horizontal bars indicate the bowl-rim cut-out. The soot sampling system is illustrated at the top-right image to show the soot particles sampling location with respect to the flame development (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

nanostructure images were digitised using a CCD camera with pixel resolution of 2688 by 2672 at a magnification setting of 470,000 times. The nanostructure of sampled soot particles, shown in Fig. 3 a as an example, is composed of layered carbon lamellas. In soot nanostructure analysis, those carbon plane segments are referred as “fringes” as they appear on the TEM images. A total of 10 high-resolution TEM images were acquired from 10 different on-grid locations for each sample to minimise the influence of particle-to-particle variations on soot nanostructure analysis [25].

The post-processing of high-resolution TEM images and soot nanostructure analysis were completed using a Matlab-based code developed by Sakai et al. [24] based on the algorithm proposed by Yehliu et al. [23]. Fig. 3 shows an example of the high-resolution TEM image post-processing. The code requires the manual selection of a region of interest in which clear and enough fringe information is available from a soot primary particle protruding from the branch of the lacy TEM grid. This region also requires minimal noise in the background and no significant overlapping of soot primary particles. The region of interest selection is followed by a binarisation to extract the fringes. For the subsequent statistical analysis, the fringes in the binary image

are skeletonised for the evaluation of their structural properties. In the final fringe skeleton image, thin arcs and curves whose length is less than the size of aromatic ring (e.g. 0.24 nm [62]) are regarded as artifacts and hence eliminated [25]. The final result of carbon fringe skeletons is shown in Fig. 3c, and a close-up view of the fringe skeletons is shown in Fig. 3d. While almost all of the image post-processing is automated, the fringe separation measurements required the manual processing. This was because fringe pairs should be selected to mark two points on each fringe skeletons forming a quadrangle, which is very challenging for the automated process. Fig. 3e shows an example of the manual processing for the fringe separation. However, two other nanostructure parameters were processed automatically. Fig. 3f shows an example of the automated measurement for the straight-line distance between two endpoints and physical length of the fringe. The ratio of the endpoint distance to the fringe length is also calculated for tortuosity representing the degree of the curvature of the fringes. In this study, a total of 6574 and 6146 fringes were processed to generate data for the fringe length and tortuosity and a total of 2852 and 3518 fringe pairs were manually selected to measure the fringe separation distance for MD and diesel fuels, respectively.

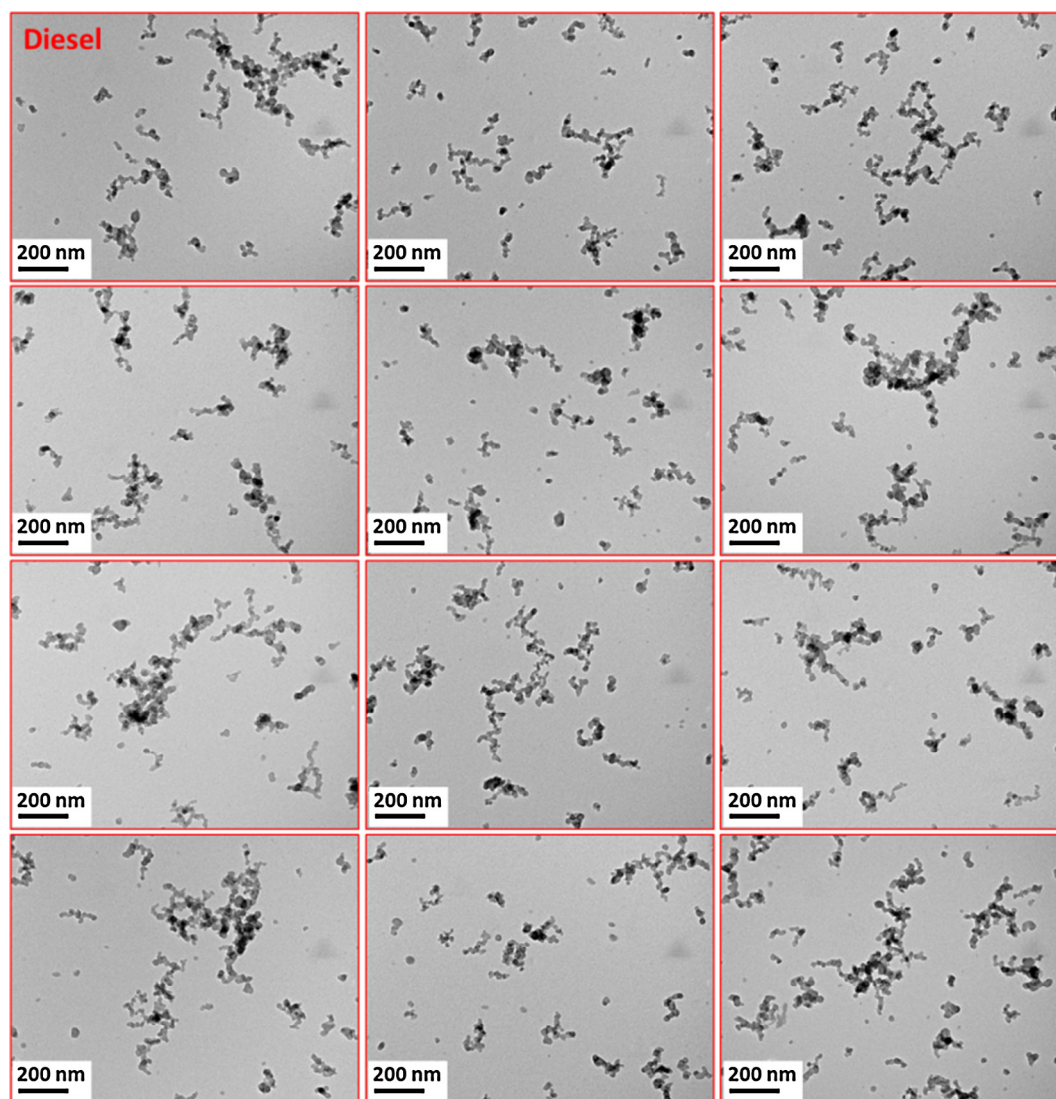


Fig. 6. Example low-resolution TEM images of the sampled diesel soot aggregates. The scale bar of 200 nm is shown on the bottom-left corner of each image.

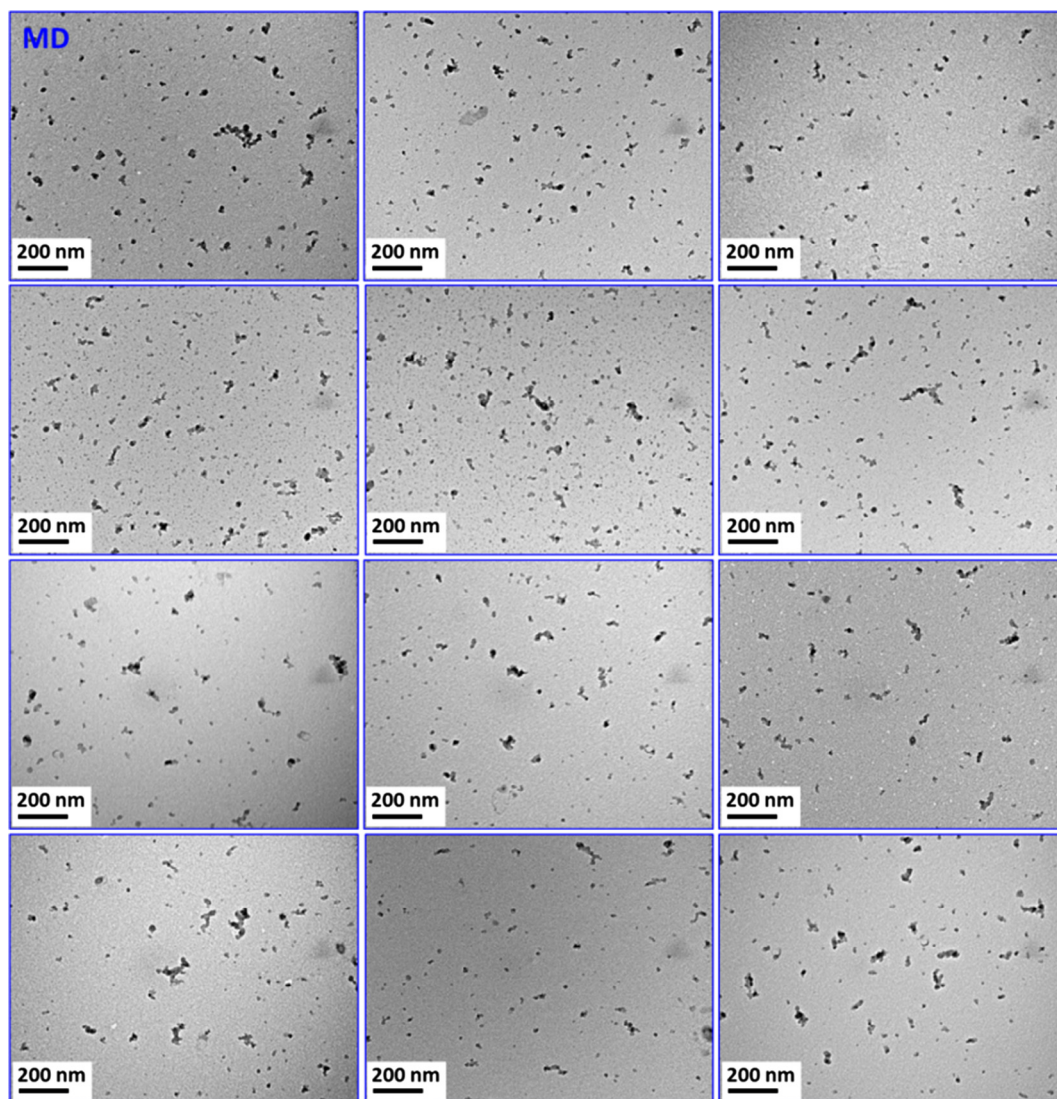


Fig. 7. Example low-resolution TEM images of the sampled methyl decanoate (MD) soot aggregates. The scale bar of 200 nm is shown on the bottom-left corner of each image.

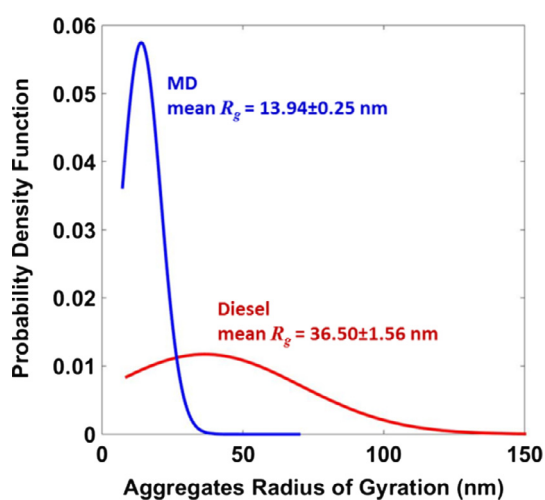


Fig. 8. Probability density functions of aggregates radius of gyration (R_g) for methyl decanoate and diesel.

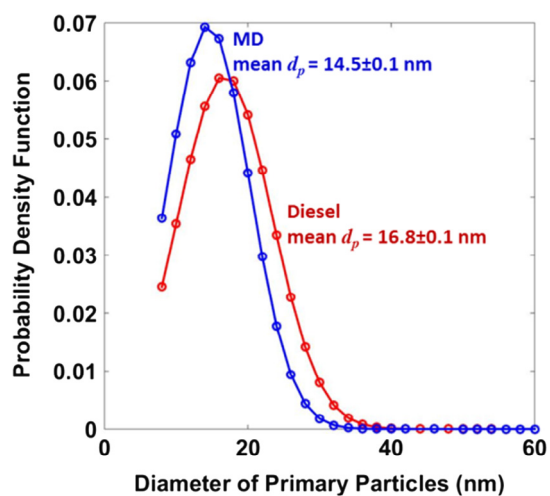


Fig. 9. Probability density functions of diameter (d_p) of soot primary particles for methyl decanoate and diesel.

3. Results and discussion

3.1. In-cylinder pressure and aHRR traces

The ensemble-averaged in-cylinder pressure and corresponding apparent heat release rate (aHRR) traces for MD and diesel soot sampling experiments are plotted for various crank angle locations in Fig. 4. The in-cylinder pressure trace of motored cycle is also shown in the figure using a black solid line. It is expected for both fuels that aHRR becomes negative due to the evaporative cooling right after the start of fuel injection at 7°CA bTDC when the in-cylinder pressure of the fired cycles is lower than that of the motored cycle. For both fuels, the combustion starts to occur at around 4°CA after TDC (aTDC), indicating similar ignition delay time as predicted from their comparable cetane number. The main combustion event was represented by a high peak in the aHRR traces and a steep increase in the in-cylinder pressure traces observed at 8–9°CA aTDC. The overall combustion phasing of the two fuels is well matched, which effectively isolated the fuel molecular structure effects from the influence of thermodynamic conditions on soot particles. Given the ambient gas density and temperature makes a significant impact on soot formation and oxidation [18,43], the similar in-cylinder pressure conditions also helped isolate the soot structure variations due to ambient gas conditions. One concern was the higher peak aHRR measured for diesel than that of MD, as its higher calorific value allows more energy input. Since the higher peak aHRR could mean higher flame temperature to promote soot oxidation [63], the soot particles sampled from diesel flames could be in a more mature stage than those of MD. This difference in the peak aHRR was likely due to the lower calorific value of MD than diesel [8,49], and one idea to compensate this lower heat release rate is to extend the injection duration for MD. However, the increased injection duration would also alter the premixing conditions and the jet dynamics. The higher peak aHRR and its possible impact on the soot particle structures will be closely monitored in the following sections.

3.2. Hot soot luminosity images

The hot soot luminosity images for MD and diesel fuels captured through the piston window are shown for 7.2–27.0°CA aTDC in the top and bottom row of Fig. 5, respectively. In each image, the corresponding crank angle (°CA aTDC) and time after the end of injection (°CA aEOI) are noted. The bowl boundary (solid circle), the piston window boundary (dashed-line circle), and the jet axis targeting in the 2 o'clock direction (dot line) are illustrated in each image. Also shown in each image is the bowl-rim cut-out line (green horizontal bars). On the top-right corner of the image, the sampling probe position is also illustrated.

Soon after the start of injection, the liquid and vapour-phase fuel impinged on the edge of bowl-rim cut-out to form a wall-interacting jet [49,59]. As was illustrated before in Fig. 1, the fuel jet was split into two wall-jet heads travelling along the bowl wall or cylinder liner wall with the latter passing through the soot sampling probe tip. Although the limited field of view does not show the direct interaction of the sooting flame and the TEM grid stored at the probe tip, Fig. 5 suggests that the overall flame development will induce the direct exposure of the TEM grid to soot particles within the flame for both fuels. For MD fuel, the sooting flame was initially visible at 7.2°CA aTDC from the bowl-rim cut-out region. It was likely that the sooting flame developed within the cut-out region in earlier crank angles before a volume of soot clouds move out of the cut-out region between 7.2 and 27°CA aTDC. The sooting flame of diesel fuel develops in the same manner as MD but the overall luminosity signal is much stronger, which

could be due to higher soot formation associated with higher aromatics contents, as was reported in Ref. [50]. In other words, since the particle incandescence is the dominate source of natural combustion luminosity [64], the lower soot luminosity signal for MD fuel in Fig. 5 indicates lower soot concentration in the tested conditions.

3.3. Low-resolution TEM images

Indeed, the sampled soot particles were much less for MD fuel than that of petroleum diesel. The low-resolution TEM images of the collected soot particles for diesel and MD are shown in Figs. 6 and 7, respectively. Similar to previous studies [13,16–19], the majority of in-flame soot particles in the diesel sample are soot aggregates larger than 200 nm (see the scale bar), composed of many soot primary particles forming chain-like or ring-shaped structures. The same trend is found from all twelve TEM images taken at various on-grid locations. Fig. 7, however, shows overall much less soot particles for MD with much smaller aggregates than those of diesel. Large soot aggregates are hardly found in the TEM images for MD but many single-primary particles (i.e. monomers) and small soot aggregates consisted of only several soot primary particles are predominantly found from the MD sample. The soot aggregates also present clear differences in the level of agglomeration depending on the fuel type. For example, the majority of MD soot aggregates exhibit stretched chain-like structures whereas the diesel soot aggregates appear to be ring-shaped or clustered particles. These observations based on the visual inspection of TEM images were further analysed by performing statistical analysis of soot primary particles, aggregates, and their fractal dimensions in the following sections.

3.4. Size distribution of soot aggregates and primary particles and the aggregate fractal dimension

For diesel and MD fuels, the probability density functions (pdfs) of aggregates radius of gyration (R_g) and soot particles diameter (d_p) are plotted in Figs. 8 and 9, respectively. In each plot, the mean values and error ranges of 95% confidence are shown. Fig. 8 shows that the mean R_g of MD is significantly lower by about 50% than that of diesel, which is supported by the pdf profile skewed towards lower R_g range. For instance, the likelihood of soot aggre-

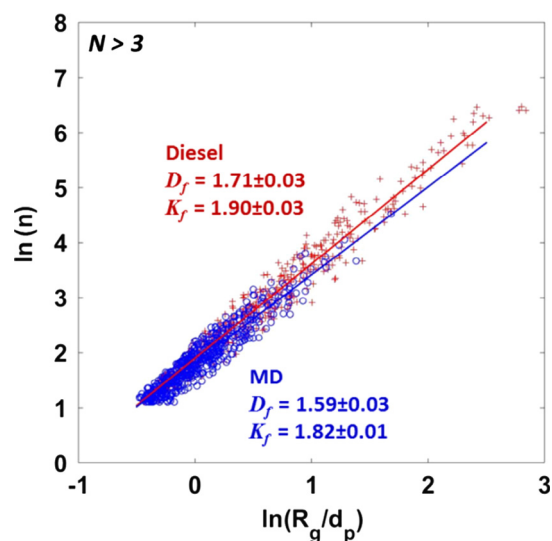


Fig. 10. Log-log plot of the aggregate fractal dimension (D_f) and prefactor (k_f) for methyl decanoate and diesel soot.

gates with R_g less than 25 nm increases significantly while large aggregates (e.g. $R_g > 40$ nm) are rarely found. By contrast, the wider pdf distribution of the diesel sample is stretched to the 100-nm range, which is consistent with the images shown in Fig. 6. The R_g trend observed from Fig. 8 is also consistent with previous studies reporting the decreased soot particle size in the exhaust stream when oxygenated biodiesel fuels are tested [12,32,33,35].

It is not only the soot aggregates becoming smaller but also the soot primary particles for methyl decanoate. Fig. 9 shows the mean d_p is lower by 2.3 nm (13.7%) for the MD sample than that of the diesel sample. Specifically, it is seen that the pdf of having small primaries (e.g. $d_p < 20$ nm) is apparently higher for MD while its

pdf for d_p of 20 nm (or higher) is much lower. The lower d_p for MD could be explained using the suppressed soot formation due to the fuel-bound oxygen. That is, the oxygen molecules in MD would suppress the formation of soot precursor, nucleation, and subsequent surface growth as was reported in other biodiesel studies [51,65–67], which would cause smaller soot primary particles as well as less primaries to agglomerate and form large soot aggregates. The lower viscosity and thus lower fuel droplet size might also contribute to lower soot formation and smaller particle sizes. Furthermore, it should be noted that MD has no aromatics compared to over 20% aromatics in the tested diesel, which would help reduce the size of soot primary particles and aggregates [16,26]. On

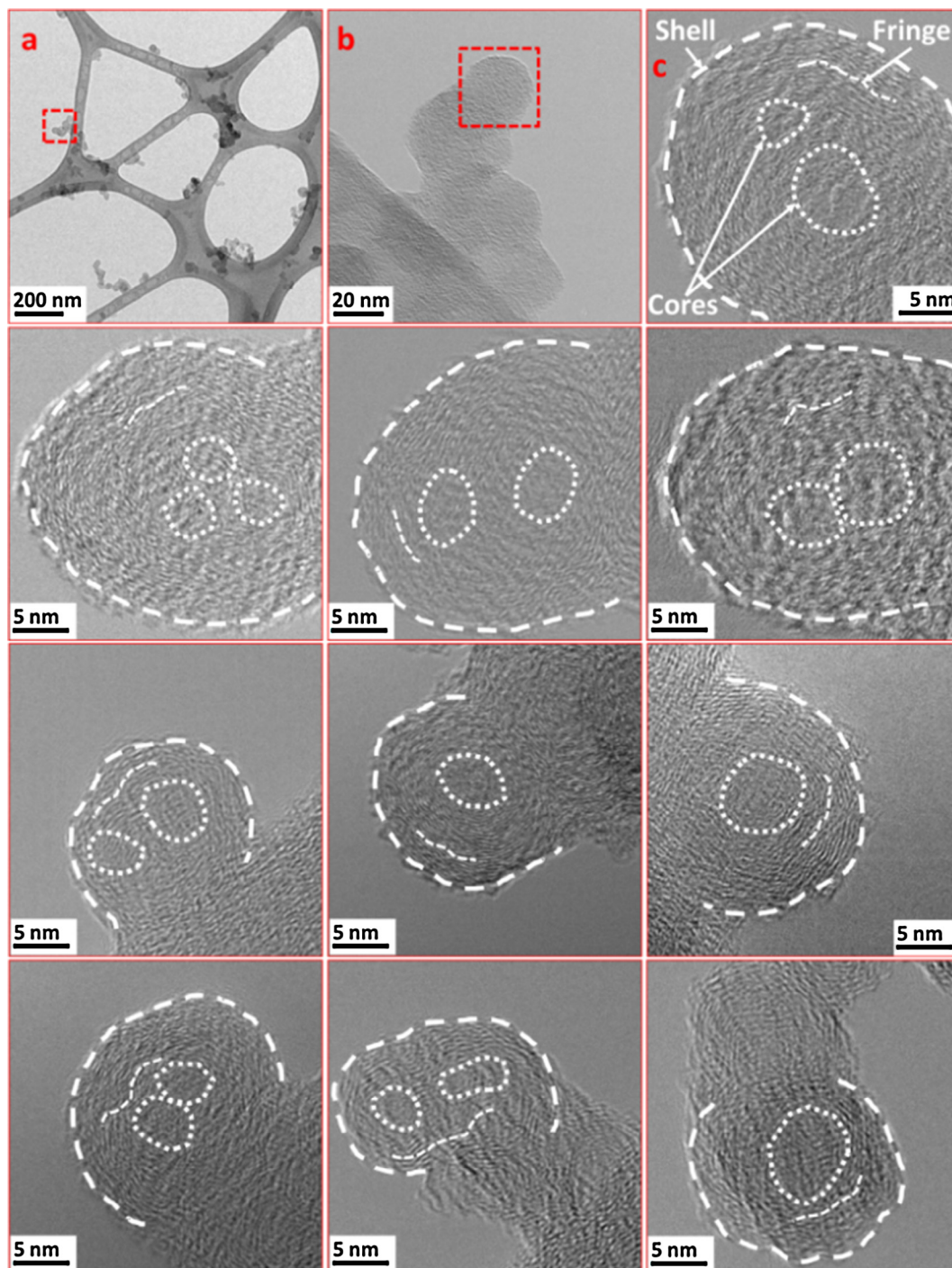


Fig. 11. Example high-resolution TEM images of the sampled diesel soot primary particles.

the other hand, the effect of oxygen in fuel on soot oxidation should not be underestimated. It was reported that oxygenated fuels cause the removal of carbon atoms from soot during the oxidation process, leading to smaller soot primary particles [35,38,40]. In addition, the soot primary particles with smaller size have higher relative surface area that could cause more reactive soot primary particles and thereby increasing the oxidation rate [40,42,68,69], which accelerates the particle size reduction. The enhanced oxidation of soot primary particles could also cause the fragmentation of soot aggregates [70,71], leading to lower R_g as seen in Fig. 8. Simply based on the R_g and d_p data, it is unclear whether it was solely decreased soot formation or increased soot

oxidation to cause significantly smaller soot aggregates and soot primary particles for the MD sample.

While both the soot aggregates and primary particles become smaller for MD, the aggregates become less agglomerated and more stretched. This was found from the fractal dimension analysis shown in Fig. 10. The fractal dimension, D_f , represents the structural compactness of fractal aggregate, and was calculated using the measured R_g and d_p and the estimated number of primary particles within the aggregates, n , and the fractal prefactor, K_f , for the optical and transport properties of soot particles [13,18,72]. For instance, more compacted soot aggregate has higher fractal dimension. Fig. 10 shows the log-log plot of D_f and K_f noted with the

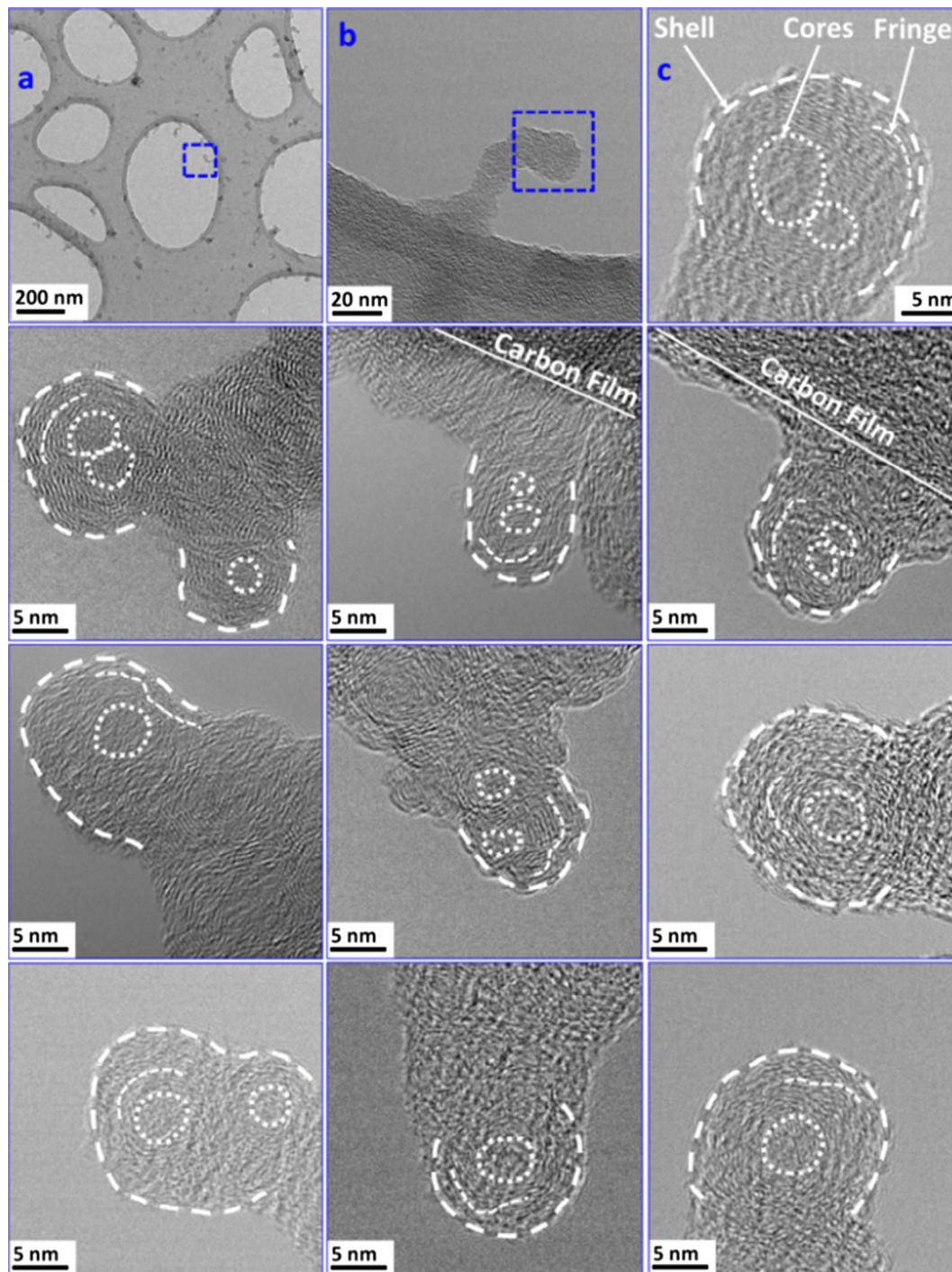


Fig. 12. Example high-resolution TEM images of the sampled methyl decanoate soot primary particles.

mean values and error range of 95% confidence for MD and diesel soot aggregates. The mean D_f of MD is evidently lower than that of diesel, which confirms less agglomerated and more stretched structures seen from the TEM images (Fig. 7). Similar to the earlier discussion on R_g and d_p , it is not entirely clear whether the smaller soot primary particles for MD formed aggregates with simpler structures or the soot oxidation was extensive to cause fragmentation of large aggregates.

3.5. High-resolution TEM images

In Figs. 11 and 12, the examples of soot aggregates deposited onto the branches of lacy carbon film (a), selected soot aggregates protruding from the carbon film (b) and soot primary particle in the selected aggregate (c) are shown in the top row from left to right for MD and diesel fuel, respectively. The corresponding scale bars of 200, 20, and 5 nm are annotated on the bottom-left corner of each image. A total of 10 high-resolution images of soot primary particles were obtained for each fuel, which were post processed for 6146 and 6574 carbon fringes for diesel and MD fuel, respectively. Figs. 11 and 12 show overall similar internal soot structures with stacked graphene layers, commonly termed as fringes, forming the inner core region and outer shell as illustrated by white dashed lines. Previous studies [25,73–75] explained that the inner core region is composed of short graphene segments with no clear orientation. As shown in Figs. 11 and 12, there could be more than one inner core region due to the nucleation occurring in multiple locations prior to the surface growth [74]. These amorphous inner core regions are surrounded by a concentrically oriented outer shell, which is consisted of more extended graphitic carbon layers.

3.6. Soot nanostructure parameters

The high-resolution TEM images shown in Figs. 11 and 12 suggested overall similar internal structures of soot primary particles between MD and diesel fuels. However, the visual inspection of raw TEM images provides limited information and cannot unveil details about carbon fringes. Therefore, the TEM images were post-processed to extract individual fringes, which were then used to calculate three key nanostructure parameters including fringe length (L), fringe tortuosity (T) and fringe separation distance (d). The results are plotted in Figs. 13–15, respectively. The figures show that the sampled in-flame soot particles comprise about 1-nm-long carbon fringes with approximately 1.2 tortuosity and 0.4 nm fringe-to-fringe gaps. Compared to diesel fuel, the MD sample shows higher fringe length, lower fringe tortuosity and narrower fringe separation with the differences in the mean values all exceeding the error margin, which means the observed trends are statistically meaningful. This suggests a higher graphitisation level for MD fuel than that of diesel. However, it is also true that the differences in the fringe length and tortuosity are minor and more importantly, the overall pdf profiles appear to be very similar between the two fuels. For ease of interpretation, the insert plot is added to each pdf figure showing the pdf difference (i.e. MD pdf subtracted by diesel pdf), which indicates less than 0.05 pdf gap. By contrast, the pdf difference of the fringe separation exceeds 2 and the pdf profile of MD fringe separation shows much higher peak in the lower fringe separation range of 0.33 and 0.47 nm while it is much lower in the 0.5–0.6 nm range. The relatively higher sensitivity of the fringe separation to the soot oxidation was also reported in previous studies. For instance, the structural changes within the carbon layer governed by the removal of 5 or 7 membered rings as a result of soot oxidation showed minimal variations in the tortuosity pdf of about 0.1 while the pdf difference of fringe separation was measured very high at 5 [76]. Also, from the soot sampling conducted in a high soot formation region and

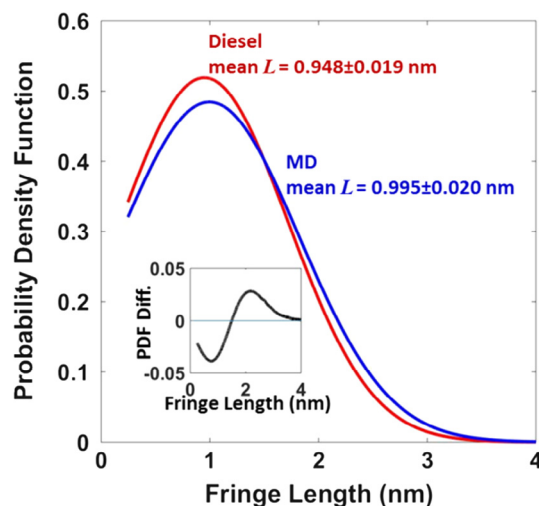


Fig. 13. Probability density functions of fringe length (L) of soot primary particles for methyl decanoate and diesel.

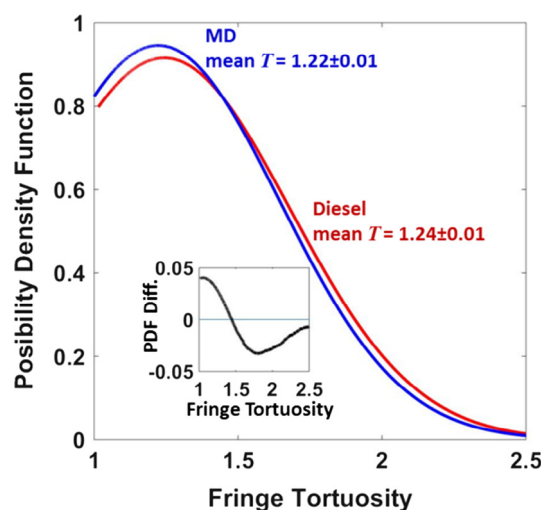


Fig. 14. Probability density functions of tortuosity (T) of soot primary particles for methyl decanoate and diesel.

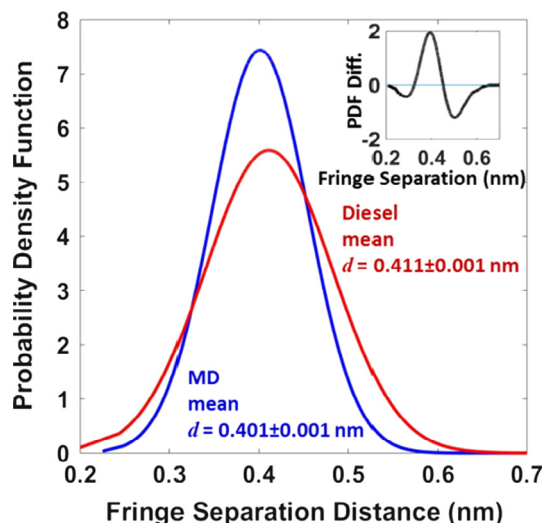


Fig. 15. Probability density functions of fringe separation distance (d) of soot primary particles for methyl decanoate and diesel.

high oxidation region of the flame, it was reported that the fringe separation decreases significantly while the fringe length and tortuosity are unchanged [16]. It was noted that slightly lower aHRR for MD shown in Fig. 4 does not influence the results because the lower aHRR and thus lower reaction temperature should have increased the fringe separation (i.e. less oxidation and less mature soot structures). Therefore, the sampled MD soot particles directly from the flame, which showed much lower sizes in both the soot aggregates and primary particles with a lower fractal dimension, are thought to be in a more oxidised stage with more graphitic carbon layer structures than that of diesel soot particles.

4. Conclusion

The influence of large methyl esters on the in-flame soot structures has been investigated in a single-cylinder small-bore diesel engine. Methyl decanoate and diesel soot particles were collected using a thermophoretic sampling technique for subsequent structure examinations through low and high-resolution TEM imaging. The TEM images were post-processed to obtain size distribution of soot aggregates and primary particles, fractal dimension, fringe length, tortuosity and separation distance between fringes. The results show much less soot particles in the TEM images of methyl decanoate with apparently smaller sizes for soot primary particles and aggregates than those of petroleum diesel. The methyl decanoate soot aggregates also show less agglomerated and more stretched structures, which is supported by lower fractal dimension. The overall soot nanostructures are similar between methyl decanoate and diesel with multiple amorphous inner cores surrounded by a concentrically oriented outer shell. However, the detailed analysis of carbon fringes show lower fringe-to-fringe separation distance for methyl decanoate, indicating more graphitised and hence more oxidised soot particles than petroleum diesel.

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