Fuel 194 (2017) 423–435

Contents lists available at ScienceDirect

Fuel

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

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.

ARTICLE INFO

Article history:
Received 5 November 2016
Received in revised form 7 January 2017
Accepted 10 January 2017
Available online 17 January 2017

Keywords:
Biodiesel surrogate
Methyl decanoate
Diesel engine
Thermophoretic sampling
TEM
Soot particles

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.

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 CO_2 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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http://dx.doi.org/10.1016/j.fuel.2017.01.044

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 combustion 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 cm^3 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-