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Impact of fuel oxygen on morphology and nanostructure of soot particles from a diesel engine

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Abstract

Diesel engines are often preferred over gasoline engines because of their fuel efficiency and reliability; however, there are significant issues around their environmental pollution which is controlled by emission regulations. To meet the ever more stringent regulations, reduction in diesel particle matter emissions can be addressed by minimising particle formation and by optimising particle oxidation in the combustion chamber and in the exhaust and diesel particulate filter systems. Soot formation and oxidation processes are the predecessors to the physicochemical properties of diesel particulate matter and are characterised by morphology and nanostructure. These characteristics principally include primary particle size, fractal dimension, fringe length, fringe tortuosity and fringe separation distance. Thus, understanding of these characteristics is necessary for an efficient reduction of particle emissions from diesel engines. Furthermore, understanding these characteristics is important because they affect the aerodynamic behaviour of the diesel particulate matter in the exhaust system, diesel particulate filter systems, and the environment. This study aims to investigate the impact of butanol on morphology and nanostructure of soot particles from a 5.9 L turbocharged diesel engine at different engine loads. The oxygen content in the fuel was varied from 0% to 4.32% and 6.48% by using diesel, 20 and 30 % of butanol blends with diesel (Bu0, Bu20 and Bu30). The results indicate that the oxygenated fuels made by blending with butanol had a significant impact on the aerodynamic behaviour of soot particles. This could result in different lung deposition patterns and therefore different toxicity, as well as the change in the diesel particle filters' filtration efficiency. As oxygen content increased, the corresponding nano-structural characteristics of fringe length and separation distance increased, whereas fringe tortuosity decreased. The change of the nanostructure properties will further influence the diesel particle filters through the changes in the regeneration processes, and will therefore have a significant influence on implementing these fuels in modern diesel vehicles.

Keywords: Soot; butanol; transmission electron microscopy (TEM); morphology; nanostructure.

Introduction

The use of next generation fuels for their sustainability and lower emission characteristics has been gaining the interest of researchers over the last decade [1]. Biofuels, such as biodiesel and alcohols (ethanol and n-butanol), have emerged as next generation fuels in diesel engines for reduction in fuel consumption of petroleum diesel. Furthermore, literature shows biofuels are useful for the mitigation of hazardous emissions, especially CO_2 and diesel particulate matter (DPM) [2], [3]. The poor volatility, higher viscosity, stability issues and inferior cold flow properties of biodiesel fuels compared to diesel may lead to poor atomisation and clogging of fuel lines [4]. To extend the use of next generation fuels in diesel engines, alcohols have recently been considered as an additive to diesel fuel [5]. Long-chain alcohols such as butanol and pentanol are advantageous over short-chain alcohols (methanol and ethanol) due to their higher heating value and cetane number [6]. The other advantage of butanol is that it can be derived from bio-based resources, making it a fully renewable fuel [7].

It is well known that apart from gaseous emissions, DPM from diesel engines is also a matter of concern due to its health effects on the human respiratory system [8]. Combustion-generated soot often arises from small particles, called soot primary particles, which join together to form soot agglomerates or aggregates [9]. Besides the particle number and particle mass, other important physical properties which must be characterised to understand soot formation include: primary particle diameter, fractal dimension, radius of gyration, fringe length, fringe tortuosity and fringe separation distance [10]. The oxygen present in the fuel blend has been found to be critical in the reduction of particle number and particle mass [11]. To date, few studies have investigated the role of oxygen content in fuels by using blends of biodiesel [12], [13], but there is limited knowledge on the role of oxygen content in fuel with other biofuels, such as alcohol fuels. The primary aim of this paper is to investigate the role of varying oxygen content (0, 4.32 and 6.48%) in the fuel by adding butanol to diesel fuel. This aims to study the effect of the hydroxyl group (-OH) on morphology and nanostructure characteristics of soot particles.

Experimental setup and fuel selection

The engine used in this study was a fully instrumented, six-cylinder turbocharged, after-cooled, common rail compression ignition engine. The engine was coupled to an electronically controlled water brake dynamometer to control the engine load. Details of the exhaust system can be found in references [13], [14]. For this study, three different fuel blends were prepared using commercially available diesel and n-butanol. The oxygen content in the fuel was varied between 0%, 4.32% and 6.48% by using diesel-butanol blends with 0% butanol, 20% butanol and 30% butanol; hereafter these fuels will be referred to as Bu0, Bu20 and Bu100.

Fuel property	**Diesel**	**Bu20**	**Bu30**
Density at 15 °C (g/cm^3)	0.84	0.833	0.83
Lower heating value (MJ/kg)	41.77	40.10	39.20
Kinematic viscosity	2.64	2.56	2.52
O (wt.%)	0	4.32	6.48
C (wt.%)	85.1	81.05	79.03
H (wt.%)	14.8	14.54	14.42

Table 1: Properties of tested fuel blends

Sample collection

Soot samples were collected on 300-mesh holey carbon TEM grids using TSI 3089 Nanometer Aerosol Sampler. The sampling time was optimised to seven minutes in order to avoid overlapping of soot agglomerates and to have enough soot particles for morphology and nanostructure analysis.

Transmission electron microscopy and image post-processing

A JEOL 2100 transmission electron microscope with an LaB_6 filament was used. For determination of the morphology of soot agglomerates, low resolution images with a resolution of 200 – 100 nm were produced. Approximately 50 images per sample were taken from different positions. For analysis of the nanostructure characteristics of soot particles, 20 images were taken at 400,000 times magnification with a resolution of 10 nm.

A MATLAB-based code was developed on the basis of algorithms reported in literature [15] to analyse the TEM images and calculate the morphology characteristics of soot particles. In addition to the morphology of soot particles, an algorithm was developed for nanostructural characterisation (fringe length and fringe tortuosity) by taking guidance of standard procedures [12], [16] as well as calculation of fringe separation distance by the application of a fast Fourier transform.

Results and discussion

Morphological characteristics

Primary particle size is one of the key parameters in the morphological characteristics of soot particles. Figure 1 illustrates the variation in primary particle diameter with engine load for different fuels. In general, primary particle diameter increases with an increase in engine load, and decreases with an increase in butanol percentage in the fuel blend. With an increase in the engine load, the air-fuel ratio decreases and primary particle diameter increases. This is likely due to more burning of fuel mass with less excess oxygen and higher temperatures in the combustion chamber [17].

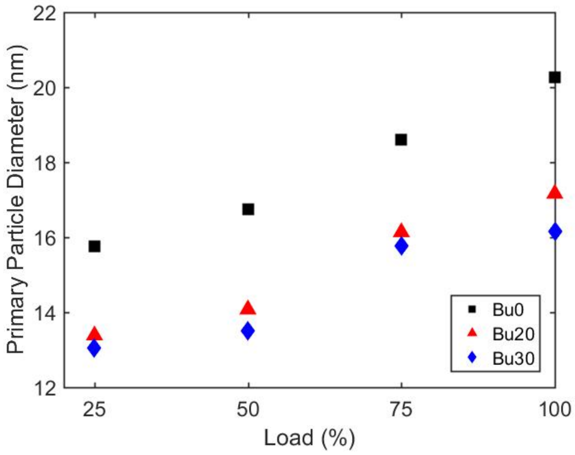

Figure 1: Primary particle diameter for different fuels

Soot is most commonly found in the form of aggregates composed of nearly spherical primary particles which are found in the form of clusters [18]. The higher the value, the more compact particle structure is denoted and vice versa. The fractal dimension cannot exceed the value of three, since objects cannot have more than three dimensions [18]. The variation of fractal dimension of soot agglomerates with engine load for different fuel blends is shown in Figure 2. With increase in butanol percentage in the fuel blend, fractal dimension increased, which means soot aggregates from butanol blended fuel have compact aggregates, whereas, diesel soot aggregates have a longer chain-like structure. The variation in fractal dimension for different fuels was not that much higher at full load than when compared to part load.

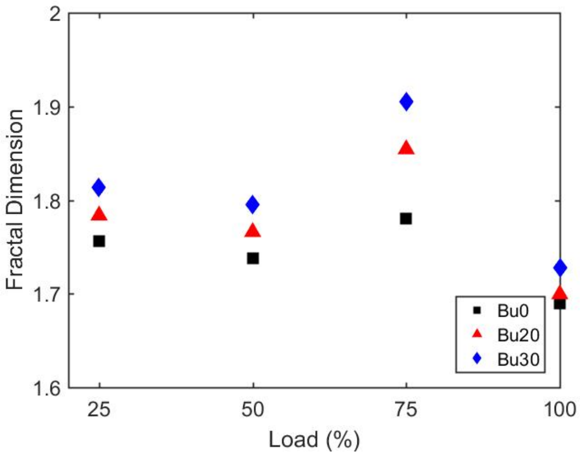

Figure 2: Fractal dimension of soot aggregates

Nanostructure characteristics

The standard high resolution TEM image a diesel soot particle is presented in Figure 1 to explain the nanostructure characteristics. The soot particle consists of shell, core and fringes. The inner core is composed of graphene layers commonly termed as fringes [12].

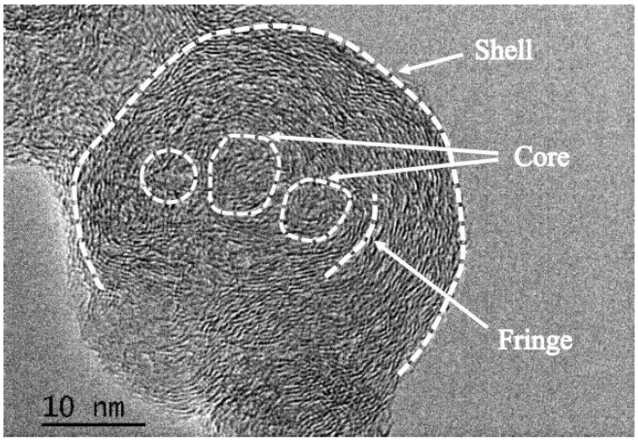

Figure 3: High resolution TEM image of a diesel soot particle

Figures 4 and 5 show the variation of fringe length and fringe tortuosity with engine load for different fuels. An increasing trend was observed in the fringe length, with an increase in the engine load and an increase in the butanol percentage in the fuel blend. The results-related literature, such as Lapuerta et al. [19], reported an increase in the fringe length with an increase in the oxygen content in the fuel blend. This shows lower reactivity of soot particles from butanol blended fuels [20].

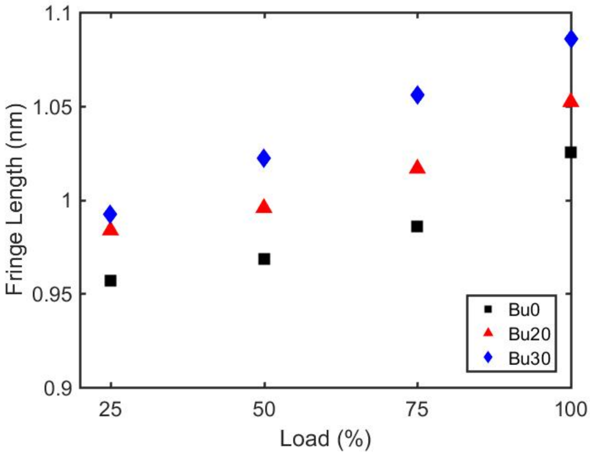

Figure 4: Fringe length

On other hand, fringe tortuosity follows an opposite trend as it decreases with an increase in engine load and butanol percentage in the fuel blend. This shows higher graphitisation for butanol-blended fuels with larger fringes compared to diesel fuel. A similar trend was observed by Zhang et al. [12] as they found larger and more ordered fringes for methyl decanoate fuel when compared to diesel fuel.

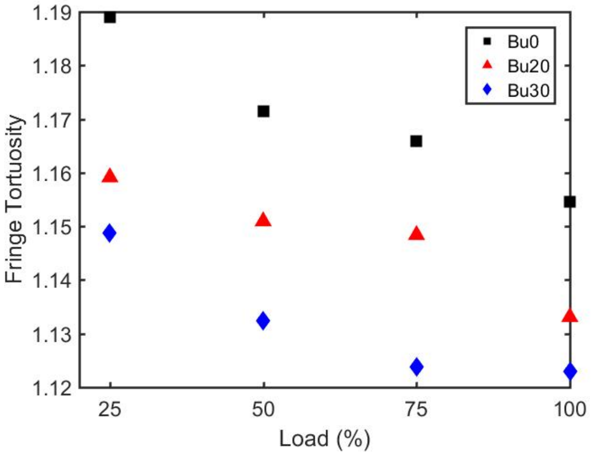

Figure 5: Fringe tortuosity

Figure 6 shows the variation of inter-planer distance (fringe separation distance) for different fuels and engine load. With an increase in butanol percentage in the fuel blend, the fringe separation distance increased. This trend was found in accordance with the literature [13], [21]. On the other hand, with an increase in engine load, fringe separation distance decreased for all fuel blends. Similar trends were observed by Zhou et al. [22] as the fringe separation distance decreased with an increase in the engine load from 30 % to 70 % for different fuels. The authors suggested that an increase in the graphitisation of carbon lamellae relates to a lower fringe separation distance for butanol-blended fuels.

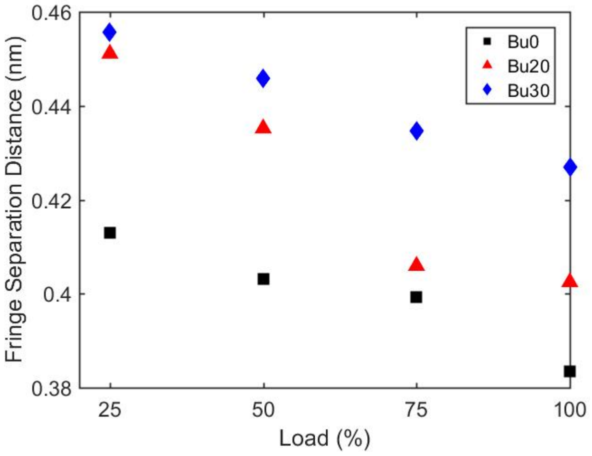

Figure 6: Fringe separation distance

Conclusions

Experimental investigation on a six-cylinder turbocharged, after-cooled, common rail compression ignition engine was conducted using three different fuels of varying oxygen content, namely D100, Bu20 and Bu30, to study the morphology and nanostructure characteristics of soot particles. The following conclusions can be drawn on the basis of this study:

1. The primary particle diameter of soot particles increases with an increase in engine load and decreases with an increase in the oxygen content of the fuel.
2. The fractal dimension of soot aggregates increases with an increase in the fuel oxygen content, and thus shows the compact structure of soot aggregates for butanol blended fuels. There, fractal dimension was found to be independent of engine load.

3. The fringe length increases with an increase in fuel oxygen content and increase in engine load, whereas, fringe tortuosity followed the opposite trend.
4. The fringe separation distance increased with an increase in fuel oxygen content, but decreased with a decrease in engine load.

Under the tested conditions, it was proved that addition of butanol had a significant effect on morphology and nanostructure of soot particles, which may be useful in design of after-treatment devices. Future research is still required to investigate the morphology and nanostructure at different engine speeds and constant load.

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