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Nanostructure characterization of soot particles from biodiesel and diesel spray flame in a constant volume combustion chamber

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ABSTRACT

This study investigates the effect of biodiesel fuels on morphological characteristics of soot particles from spray flame in a constant volume combustion chamber. The experiments were carried out under simulated diesel engine condition. The auto-ignition of injected fuel was carried out at an ambient pressure of 5 MPa and ambient temperature of 978.15 K. The soot particles were captured with a transmission electron microscope (TEM) grid inside the flame by thermophoretic effect. They were characterized as primary particle diameter, graphene layer (fringe) length, fringe tortuosity, and fringe spacing based on the image processing from original TEM image. Three different kinds of biodiesel fuels, waste cooking oil biodiesel, Jatropha biodiesel and Karanja biodiesel were used in the test. Conventional diesel fuel was utilized as a baseline fuel for the comparison. The tested fuels were injected with injection pressures of 40, 80, and 120 MPa by means of common-rail injection system. The experimental result showed that all of the biodiesel fuels had smaller primary particle diameter than that of conventional diesel regardless of injection pressures. The soot particles from biodiesel fuels were also distinguished showing characteristically shorter fringe length and lower tortuosity. These experiments unveiled a correlation between the nano-structural parameters for the early stage of oxidation inside the flame.

1. Introduction

Even though there have been many improvements in diesel engine technology, issues regarding emission of harmful gases from diesel engines are still remaining. The current focus in the improvement of diesel engine emissions is on the reduction of soot and nitrogen oxide (NO_x) emissions. Moreover, there is an increasing concern about depletion of petroleum resources. In this situation, biodiesel fuels are gaining importance as alternative fuels for conventional diesel engines. As they are produced from renewable feedstock, the emission of greenhouse gases can be significantly reduced. A well-to-wheel analysis investigating the greenhouse gas emissions (CO_2, CH_4, and N_2O – weighted by their global warming potentials) showed a reduction of those emissions by 66%–94% for soybean-derived biodiesel fuel [1]. Other advantages of biodiesel compared to standard diesel fuel are its lower sulfur and aromatic content, higher flash point which makes handling safer and its biodegradability [2]. However, besides that, biofuels are often criticized due to the use of edible feedstocks. Thus, researchers are trying to utilize non-edible plants such as Karanja, Jatropha, and algae which can offer a way out of the food vs. fuel debates [2]. Furthermore, wasted sources such as used cooking oil also can be used as a raw material for the biodiesel production. Using waste sources for biodiesel production can reduce not only disposal expenses but fuel production costs.

The study of soot morphology was started in early 1960, due to more stringent emission regulations the focus was drawn to the influence of the soot nanostructure and its connection to the soot oxidative reactivity. Vander Wal and Tomasek [3] pointed out the effects of morphology and soot oxidation at first. They analyzed nanographene layer length, tortuosity, and spacing by using soot particles generated by benzene, ethanol, and acetylene. They found out, that those soot particles exhibit a different nano-structural order and oxidative

Abbreviations: aTDC, after top dead center; CAD, Crank angle degree; CVCC, Constant volume combustion chamber; fps, frame per second; HR, High resolution; NO_x, Nitrogen oxides; PCV, Pressure control valve; ROI, region of interest; TEM, Transmission electron microscopy; WCO, Waste cooking oil; XRD, X-ray diffraction

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Nomenclature

C_2H_2	Acetylene
CH_4	Methane
CO_2	Carbon dioxide
D	Inter-laminar spacing [nm]
H_2	Hydrogen
N_2O	Nitrous oxide
O_2	Oxygen
P	Pressure [MPa]
T	Temperature [K]

reactivity. Benzene-derived soot is found to have a more amorphous structure and is more reactive than acetylene-derived soot. Song et al. [4] also studied the oxidation characteristics of diesel soot. They found a higher reactivity for soot from soybean-derived biodiesel in comparison with soot from Fischer-Tropsch diesel fuel. They suggested that the relative surface oxygen content is an important factor influencing the oxidation rate. The authors also report a unique oxidation process leading to capsule-type oxidation and eventual formation of graphene ribbon structures in case of the biodiesel soot.

A methodology to investigate prospective fuels for their potential as an alternative energy source using a constant volume combustion chamber (CVCC) has been presented. It can provide much better optical access to perform high speed optical imaging which can facilitate analysis of spray and flame characteristics. Hwang et al. [5] investigated the spray characteristics of biodiesel fuels, namely WCO biodiesel, Jatropha biodiesel and Karanja biodiesel in a CVCC. The experiments were carried out under simulated engine condition. They reported that Karanja biodiesel and Jatropha biodiesel showed a longer liquid tip penetration length, narrower spray cone angle and smaller spray area due to a higher viscosity, density, and lower volatility. They also showed, that due to the inherent oxygen content of the biodiesel fuels, they appeared to have a ~10% leaner air-fuel mixture. Many previous researches have reported the increased reactivity of soot particles from biodiesel fuels compared to standard diesel fuel [6–11]. Possible explanations are that soot particles from biodiesel fuels have more amorphous nanostructure than the one from standard diesel fuel [7,9,10,12,13] shown as higher tortuosity of the fringes and in general a less ordered structure of the carbon fringes. Vander Wal et al. [3] investigated the influence of the particle nanostructure on the soot oxidation. They showed a correlation between higher tortuosity and shorter fringe length to a higher soot reactivity.

It is known that the soot reactivity increases with a higher number of accessible edge sites [6,7,10,12,14,15]. This explains that with a higher disordered carbon structure the reactivity increases, as the higher amorphous structure leads to a larger number of accessible carbon atoms on the edge sites. Moreover, oxygen functional groups bounded to edge sites can induce more micro-pore structures during the attack by air, which results in much faster oxidation process of biodiesel soot [9]. Higher soot reactivity is favorable as it speeds up the regeneration process of the diesel particulate filter and therefore leads to less fuel consumption. It was reported that regarding the soot macrostructure the agglomerate size of palm-oil biodiesel soot is slightly smaller as the one from fossil feedstock [16]. Both studies, the one of Hwang et al. [6] investigating pure WCO and the one of Savic et al. [12] investigating blends of WCO, microalgae, cottonseed oil biodiesel with standard diesel reported a smaller primary particle size in comparison to diesel soot. However, it should be emphasized that not all researchers coincide with the above points. For example, Ma et al. [8] reported a higher-ordered structure for biodiesel in comparison with standard diesel.

Despite these efforts, soot formation and differences in soot morphology of biodiesel fuels and standard diesel fuel are not fully understood. Most of the previous studies are concentrated on engine out soot particles, not on spray flame soot particles. This study has own uniqueness in terms of fuel injection parameters which have not been yet investigated in spray flame. The effects of fuel injection parameters on soot morphology must be understood to reduce soot emission from diesel engine. A brief summary of previous soot study in flame is shown in Table 1. Related previous researches were only concentrated to show experimental results with conventional fuels with limited experimental parameters. Meanwhile, this study can provide comprehensive experimental data of soot morphology by in-depth understanding in effects of biodiesel fuels and injection parameters on soot particle generated in spray flame. The ignition of fuel spray was accomplished under simulated diesel engine operating condition in CVCC. Fuel injection pressure was changed from 40 MPa over 80 MPa to 120 MPa using a common-rail direct injection system. Soot particles were collected during the experiment directly in the flame by thermo-phoretic effect.

Table 1
Summary of spray flame soot morphology studies.

Work	Setup	Changed parameters in setup	Tested fuels	Investigated soot parameters
Zhang et al. [17]	One-cylinder engine	Injection timing, Injection pressure	ultralow-sulfur diesel fuel	Primary diameter, Radius of gyration, Fractal dimension
Kondo et al. [18]	Constant volume combustion chamber	Two sampling locations in flame	JIS#2 Japanese diesel	Diameter of particles, radius of gyration, projected area ratio
Aizawa et al. [19]	Constant volume combustion chamber	none	US#2 diesel, soy-ethyl ester	Density of soot particles, diameter of particles, gyration radius, fractal dimension
Lemaire et al. [20]	spray burner	none	Gasoline/ethanol, gasoline-surrogate/ ethanol blends	Soot volume fraction, soot precursors concentration
Eduardo et al. [21]	Burner	none	Gasoline and blends with ethanol, …	Smoke point
Khosousi et al. [22]	Laminar coflow diffusion flame burner	none	Gasoline/Ethanol blends	Soot volume fraction distribution
This work	Constant volume combustion chamber	Fuel type, injection pressure	Conventional diesel, Karanja, Jatropha, WCO	Primary particle size, Tortuosity, fringe length, interlaminar spacing