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Influence of waste cooking oil biodiesel on oxidation reactivity and nanostructure of particulate matter from diesel engine

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HIGHLIGHTS

- Oxidation characteristic of PM fueled with addition of biodiesel was investigated.
- Influences of biodiesel on formation of PM were obtained.
- Effects of biodiesel on structure of carbon functional groups of PM were explored.
- Differences in microstructures of PM with addition of biodiesel were proved.

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ABSTRACT

The objective of this work is to investigate the influence of waste cooking oil biodiesel on oxidation reactivity and nanostructure of particulate matter (PM). The test was carried out in a small agricultural diesel engine. PM samples were collected by MOUDI and subjected to TGA, Raman, NEXAFS and TEM. According to TGA, when waste cooking oil biodiesel quantity increases in the fuel, PM shows a higher volatile organic fraction (VOF). When the blend ratio of biodiesel increases to 50%, lower ignition temperature and burnout temperature are observed, signifying higher oxidation reactivity. Raman spectroscopy shows a higher graphitic-like structure and a lower polyene-like structure for pure biodiesel compared to pure diesel. With the addition of biodiesel, the crystallite dimension of PM increases. C(1s) NEXAFS spectra shows that there are many types of functional groups on the surface of PM. Pure biodiesel PM has lower phenolic, aromatic C—OH and ketone C=O groups than pure diesel and biodiesel/diesel blend PM samples. The analysis of TEM indicates the morphology of PM samples looks like chain shape. The primary particle coheres more closely and the average size of primary particles exhibits a decrease with the increase in biodiesel blend ratios.

1. Introduction

During the past few years, environmental pollution and shortage of fossil fuels have been a hot topic, and research on alternative fuels has received much attention. Biodiesel is considered as a promising alternative to diesel fuel [1]. Biodiesel is defined as long chain fatty acid ester derived from renewable lipids such as vegetable oils and animal fats. Previous studies have shown that addition of biodiesel to diesel can increase the oxygen content of mixture gas and reduce particulate matter (PM) emissions [2–5].

PM emission from diesel engine is main resource of aerosol haze, and it is mainly composed of volatile organic fraction (VOF), dry soot and ash. Polycyclic aromatic hydrocarbons in the VOF have been demonstrated to induce human cancer [6–8]. In recent years, with the increasingly strict emission regulations of PM [9], it is essential to conduct research on oxidation mechanism and nanostructure of PM to further reduce PM emissions.

PM oxidation reactivity and nanostructure are related to the physical and chemical properties of the fuel. Biodiesel derived from different feedstock has various concentrations and different methyl esters, leading to changes in physical and chemical properties [10], which will influence PM oxidation reactivity and nanostructure. Salamanca et al. [11] investigated the influence of palm oil biodiesel on nanostructure of PM emitted from a diesel engine, and it was found that palm oil biodiesel and its blends produced PM with higher graphitic-like structure and lower amorphous carbon material. Agudelo et al. [12] reported that PM from crude vegetable oils possess a higher VOF, a lower fringe length and a lower stacking thickness than those of the diesel PM. Yehliu et al. [13] studied the impacts of fuel formulation on the characteristics

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of diesel soot, and it was observed that pure soybean methyl-ester soot exhibited the fastest oxidation on a mass basis followed by ultra low sulfur diesel fuel soot and Fischer–Tropsch fuel soot. It also suggested that soot nanostructure disorder correlates with a faster oxidation rate.

PM oxidation reactivity is closely related to PM nanostructure. Edge and surface structures in PM may strongly affect oxidation reactivity. When PM is pyrolyzed, carbon atoms at the edges and surface sites firstly contact with O_2. Porosity structure and disorder carbon structure can promote the capacity of oxygen chemisorptions and improve the oxidation reactivity of PM. It has been stated elsewhere that carbon atoms at the edges are much more reactive than those in the basal plane of the grapheme layers [14,15,25,26].

PM oxidation reactivity is affected by the functional groups on the surface of PM due to geometrical structure and available electron. The relative intensity of carboxyl and carbonyl groups is more reactive than carbon element because the energy to form CO or CO_2 is lower than carbon element. Wang et al. [16] reported that aliphatic C—H groups were more important in governing PM oxidation reactivity than oxygenated surface functional groups.

Extensive studies on combustion characteristics and regular emissions of a diesel engine fueled with biodiesel obtained from waste cooking oil have been investigated [10,17,18], however, limited studies on PM physical and chemical characteristics from waste cooking oil biodiesel were conducted. This work investigates the impact of the biodiesel from waste cooking oils on the chemical composition, oxidation reactivity and nanostructure of the PM produced by a small agricultural diesel engine. PM characteristics are related to fuel properties and combustion characteristics. There are a variety of techniques that are used to examine PM parameters. Thermogravimetric analysis (TGA), Raman spectroscopy, X-ray absorption near-edge spectroscopy (NEXAFS) and Transmission Electron Microscope (TEM) were used in this work. TGA was used to characterize PM oxidation reactivity and determine PM composition by proximate analysis. NEXAFS was used to identify surface functional groups of PM samples. Raman spectroscopy was used to determine the graphite-like structure of PM and finally, TEM was used to determine the nanostructure with the average size of primary particles and the morphology of the agglomerates, respectively.

2. Experimental methods

2.1. PM sampling

The main parameters of diesel engine used in this study are shown in Table 1. The waste cooking oil biodiesel was produced by Jiangsu Yueda Kate New Energy Co., Ltd. Pure diesel (B0), biodiesel/diesel blends (B20 equals to 20 vol% waste cooking oil biodiesel + 80 vol% diesel and B50 equals to 50 vol% waste cooking oil biodiesel + 50 vol% diesel) and pure biodiesel (B100) were used respectively. Table 2 lists the main characteristics of the diesel and waste cooking oil biodiesel. The diesel engine was operated at 2000 r/min and 12.27 N m. PM samples from diesel, biodiesel/diesel blends and biodiesel were collected by micro-orifice uniform deposition impactor (MOUDI) produced by MSP company in America. Sampling time is 20 min and sampling flow is 30 L/min.

Table 1
The main characteristics of diesel engine with 186F.

Number of cylinders	Single
Type	Direct-injected, 4 stokes, air-cooled, natural aspiration
Number of cylinders	1
Displacement (L)	0.406
Cylinder bore (mm) × stroke (mm)	86 × 76
Compression ratio	19:1
Rated power (kW)/speed (r/min)	5.7/3000
Maximum torque (N m)/speed (r/min)	20.3/1800

2.2. TGA

A thermogravimetric analyzer (TGA/DSC1, METTLER-TOLEDO) was used to investigate the chemical composition and oxidative reactivity of the PM samples from diesel, diesel/biodiesel blends and biodiesel. The reaction temperature ranges from room temperature (20 °C) to 1600 °C with average accuracy of ±0.3 °C. The controllable range of heating rate was 0.1–150 °C/min. The TGA test was conducted in an O_2 environment at a flow rate of 50 L/min. The mass of PM sample loaded in the alumina crucible was about 2 mg and the PM sample was heated from 25 °C to 700 °C at a heating rate of 20 °C/min.

2.3. Raman spectroscopy

Raman spectra of PM samples were obtained by FILTER Raman microscope system. The wavelength of the laser is 532 nm. The obtained spectrum is in the range of 100–3500 cm^{-1}, and its spectral resolution is less than 2 cm^{-1}. The hardware accumulation number was 20, the exposition time was 20 s and the source electric power used was 10 mW for every PM sample to avoid damaging PM nanostructure [19]. To obtain low signal-to-noise ratio, 10 points were measured and averaged. The first order Raman spectroscopy was fitted instead of the second order Raman spectroscopy due to the second order's doubling frequency. A five-bands fitting curve method presented by Sadezky el al. [20] was used to fit first order Raman spectroscopy. Four Lorenzian functions for G band, D1 band, D2 band, D4 band and one Gaussian function for D3 band were used, respectively located at about $\sim$1580 cm^{-1}, $\sim$1340 cm^{-1}, $\sim$1620 cm^{-1}, $\sim$1200 cm^{-1} and $\sim$1500 cm^{-1}.

2.4. NEXAFS

The NEXAFS spectra were recorded in Shanghai Synchrotron Radiation Facility (SSRF). The SSRF storage ring operates at 3.5 GeV energy and the electron current ranges from 200 mA to 300 mA. The photons of the beamline are in the range of 250–2000 eV and the energy resolution ($E/\triangle E$) is more than 2500. The spatial resolution is less than 50 nm. Oxalic acid was used as the standard reference material. The C(1s) NEXAFS spectra of PM samples were scanned and recorded ranging from 280 eV to 300 eV with steps of 0.3 eV.

Table 2
The main characteristics of diesel and biodiesel.

Fuel	Diesel	Biodiesel
Cetane number	46	51
Density (g cm^{-3} at 20 °C)[a]	0.83	0.88
Kinematic viscosity (mm^2 s^{-1} at 40 °C)[a]	3.4	4.6
Oxygen content (wt%)	0	10.8
Sulfur content (mg/kg)	$\leqslant$350	$\leqslant$10
Condensation point (°C)[a]	0	−1
Calorific value (MJ kg^{-1})	44	39
Ester content (wt%)	–	$\geqslant$96.5
Monoglyceride (wt%)	–	$\leqslant$0.8
Acid value (mg KOH/g)	$\leqslant$0.084	$\leqslant$0.5
Metals content (Na, K, Ga, Mg) (mg/kg)	–	$\leqslant$5

[a] Measured result.