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Full Length Article

Physicochemical property changes during oxidation process for diesel PM sampled at different tailpipe positions

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ABSTRACT

Diesel particulate matter (PM) samples were collected at different tailpipe positions where sampling temperature differed greatly. All the samples were pre-heated in air at high temperature until 40% mass was burnt out. Physicochemical properties of diesel PM both before and after partial oxidation were analyzed, and to further figure out the reasons of oxidation activity changes in the oxidation process. The results showed that ignition temperature of PM whose sampling temperature was higher than 208 °C differed greatly from PM sampled below that temperature. After partial oxidation, sample 3 presented the hugest oxidation activity decreasing with burn out temperature increasing by 14.7 °C. Primary particle size distribution shifted to smaller diameter direction after partial oxidation, and particle stacking degree decreased evidently. Nanostructures of diesel PM transferred from onion like structures with randomly arranged crystallite to core-shell like structures with void inner cores. Oxygen-containing functional groups (carbonyl and hydroxy) decreased evidently after PM partial oxidation that was obtained from Fourier transform infrared spectroscopy (FTIR) spectra, it was consistent with the results of Raman parameter I_{D3}/I_G.

1. Introduction

Soot emitted by diesel engines has brought about huge environmental and health problems [1,2] so that an urgent necessity is needed to decrease diesel PM. Diesel PM is complicated compounds that mainly contain soot, organic compounds, sulphur compounds and metal [3]. Diesel particulate filter (DPF) is considered to be the most successful technology to remove diesel PM while DPF encounters regeneration problem. Diesel PM captured on DPF should be oxidized periodically to keep excellent performance. The oxidation behaviors of diesel PM are closely related to engine operation conditions, fuel properties, cylinder combustion and sampling conditions [4–9]. The factors mentioned above lead to the differences of diesel PM physicochemical properties that are considered to be fundamental factors causing the distinctions of oxidation activity.

PM accumulation consists of many spherical-like particles at the function of organic compounds and bridge forces [10]. The morphology of diesel PM shows chain shape with many particles overlapping [11]. Nanostructures of some diesel PM present onion like structures that are with short and randomly arranged crystallite, and others present void cores with core-shell like structures [12–14]. The effect of fuel on PM oxidation activity and nanostructures was performed [15]. Nanostructures of PM obtained from biodiesel engine are more densely arranged compared with diesel PM. Nanostructures are considered to be vital factors contributing to the differences in PM oxidation activity [10]. However, Song et al. [15] pointed that oxygen functional groups were more important for PM oxidation. This opinion was verified by the fact that biodiesel soot is 5 times more oxidative reactive than diesel soot though biodiesel soot is more orderly arranged. The oxygen-containing functional groups provide active sites that are necessary to form active surface areas conducing to PM oxidation. Biodiesel soot presents higher absorbance intensity at wave number 2928 cm^{-1} and 2856 cm^{-1} in FTIR where aliphatic hydrocarbon is indicated [16]. The nanostructures observed by high resolution transmission electron microscopy (HRTEM) figures are mutually complementary with Raman spectra. Crystallite size calculated using Raman parameters shows consistency with HRTEM results [8]. Raman spectra present information about vibration and rotation of molecules crystal lattice, which is reflected by amorphous carbon and graphitized carbon [17–19] that are closely related to PM oxidation activity, however, the relations of Raman spectra and PM oxidation activity are still in debated [7,8,20,21]. The amorphous carbon is caused by oxygen-containing

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functional groups [22,23].

Meng et al. [24] put forward a PM oxidation model that volatile substance evaporated at the beginning, then the amorphous carbon oxidation, graphitization and combustion. During the oxidation process, physicochemical properties change greatly with nanostructures of diesel PM presenting onion like structures, void core-shell like structures and densely arranged bands [4]. Also, oxygen content decreases greatly due to the volatilization of volatile organic compounds (VOC) and amorphous carbon oxidation. The decrease is evident after 40% mass loss for biodiesel PM while it is 20% for diesel PM, and the content dropped to zero when more than 80% mass was burnt out [25]. In the oxidation process, average primary particle diameter decreases, also the void cores are enlarged. Raman parameter I_D/I_G (intensity ratio of D band to G band) decreases from 1.65 to 1.12 continuously that indicates high graphitization of diesel PM. Markus and Vander [14,26] observed the similar phenomenon that crystallite arranged more orderly and the void cores became huger.

Ref. [27] investigated the particle mode evolution process in diesel tailpipe that particle size distribution and particle number were tested along the tailpipe. The nucleation mode particles and total particle number increase greatly due to the temperature drop along the tailpipe. While the number of accumulation mode particles remains almost the same. The literatures about the differences of diesel PM physicochemical properties along the tailpipe are scarce to date and many questions about PM physicochemical property changes after partial oxidation remain to be addressed. In this paper, diesel PM samples were collected at different tailpipe positions where the temperature differed greatly. The physicochemical property differences were analyzed for samples collected at different tailpipe positions, which was useful for further analyze particle mode evolution in tailpipe. Also physicochemical property changes were investigated after PM partial oxidation, which showed closely related to DPF regeneration.

2. Experimental section

2.1. The test engine

The engine was the power of a diesel generator that the specifications of the diesel engine are listed in Table 1. The load of the diesel engine can be adjusted by the power output of the generator, and the engine load was adjusted as 60% when the samples were collected. The experiment lay-out is shown in Fig. 1. The distances of the exhaust valve and the sampling positions were about 0.5 m, 1.0 m, 1.5 m and 2.0 m in which the temperature was 253 °C, 231 °C, 208 °C and 185 °C, and the samples were designated as sample 1, sample 2, sample 3 and sample 4 respectively. The fundamental properties of diesel fuel used in the experiments are shown in Table 2.

BTDC, before top dead center; ABDC, after bottom dead center; BBDC, before bottom dead center; ATDC, after top dead center.

Table 1
Diesel engine specifications.

Specification	Value
Displacement	0.418 L
Bore	86 mm
Stroke	72 mm
Speed	3000 rpm
Injection type	Direct injection
Injector valve opening pressure	21 MPa
Compression ratio	19
Intake valve opening	16° BTDC
Intake valve closing	44° ABDC
Exhaust valve opening	48° BBDC
Exhaust valve closing	12° ATDC

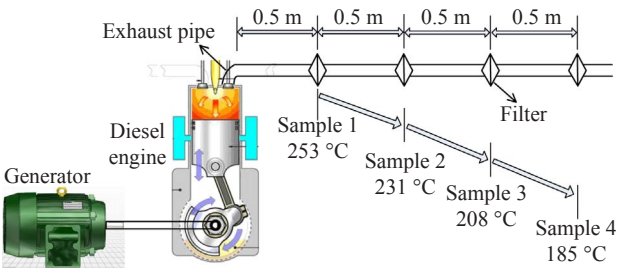

Fig. 1. Experiment lay-out.

Table 2
Fundamental properties of diesel fuel.

Property	Value
Density	850 kg/m^3
H/C ratio	0.156
S content	0.0042 *wt*%
Viscosity (20 °C)	4.1 mm^2/s
Cetane number	52
95% distillation points	340 °C
50% distillation points	290 °C

Table 3
Technical specifications of TGA device.

TGA	Technical specifications
Balance	Horizontal differential type
Weight capacity	200 mg
Signal resolution	0.001 μg
Temperature range	Ambient to 1100 °C
Ramp rate	0.001–100 °C/min
Air flow rate	0–1000 mL/min
Crucible	Alumina

2.2. The instruments used for physicochemical properties testing

Oxidation activity of diesel PM was tested using thermogravimetry analysis (TGA) device (DTG-60) that was made by Shimadzu, and the technical specifications are shown in Table 3. In order to decrease the experimental error, vacant combustion in air was performed to remove the residual. The duplicate tests of TGA experiments are shown in Fig. S1. As can be seen, the repeatability of the TGA experiments is excellent. The flow rate of carry gas and ramp rate of TGA experiments in the paper are 100 mL/min and 5 °C/min respectively. PM samples were collected at different tailpipe positions (raw PM), and all the samples were pre-treated at high temperature in air. Procedure of the pre-treatment using TGA device was as following: samples were heated in air from ambient temperature at ramp rate of 5 °C/min, until 40% mass loss, then, the carry gas was switched as N_2, and temperature dropped to room temperature. Raw PM and pre-treated PM were packaged with silver paper. The oxidation activity of PM both before and after pre-treatment was tested.

The morphology and nanostructures of diesel PM were observed by transmission electron microscope (JEM-2100), the applied magnifications were set as 40,000× and 500,000×. Before the tests, the suspensions were created by ultrasonication of soot within acetone. One drop of the suspension was deposited on a lacey C/Cu transmission electron microscopy (TEM) grid, then, the TEM grid was dried under accent light to remove the acetone. The point-to-point resolution of TEM images was 0.19 nm. Low resolution TEM figures were used to obtain the primary particle diameter distributions. The particle number for diameter statistics was more than 300.

The functional groups of diesel PM were investigated using FTIR device (Shimadzu IRAffinity-1s). The scope of FTIR spectrum was