Research Paper

Oxidation behaviours of particulate matter emitted by a diesel engine equipped with a NTP device

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HIGHLIGHTS

- Final oxidation temperatures increased for PM aggregation compared with raw PM.
- Devolatilized PM aggregation exhibited similar oxidation rate constants.
- DSC-based method is more accurate than TGA-based method.

ARTICLE INFO

ABSTRACT

To resolve the regeneration problem of non-thermal plasma (NTP) reactor, the oxidation behaviours of diesel particulate matter (PM) were investigated. Oxidation kinetic parameters were calculated using Flynn-Wall-Ozawa (FWO) and Friedman-Reich-Levi (FRL) methods based on thermal gravimetric analyzer (TGA) and differential scanning calorimetry (DSC) results. The DSC-based method avoided the disadvantages of TGA-based method, and the oxidation kinetic parameters calculated using the two methods were compared. The results showed that the effect of plasma on the oxidation behaviours differed greatly for PM sampled at engine loads. The TGA profiles of PM aggregation (collected on the collection plate of NTP reactor) sampled at 60% and 100% engine loads were similar although they differed significantly for raw PM. Devolatilization of raw PM led the TGA profiles to shift slightly to lower temperature, however, the TGA curves shifted to higher temperature for PM aggregation and PM treated with plasma (PM escaping from NTP reactor). The oxidation rate constants of devolatilized PM aggregation sampled at different engine loads were almost the same. DSC-based method revealed the oxidation behaviours and kinetic parameters with more accuracy than TGA-based method.

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1. Introduction

Much attention has been paid to diesel engines, due to their lower operating cost, higher thermal efficiency and durability [1]. In Europe, 53% of passenger cars run on diesel [2]. Growing concern has risen in diesel emissions that are harmful to human health and the environment [3]. Many measures have been done to reduce the diesel emissions [4–8]. Fine particulate matter from diesel engines is mainly composed of soot, sulphur compounds, organic compounds, inorganic compounds, trace metals, *etc.* [2]. As a potential alternative technology for PM removal, non-thermal plasma allows simultaneous removal of hydrocarbons (HC), nitrogen oxides (NO_x) and PM [1,9,10]. PM removal using NTP technology involves PM oxidation in the plasma zone and PM capture by the collection

plate of NTP reactor (PM aggregation). The NTP reactor should be periodically regenerated by the oxidation of PM aggregation; otherwise, PM aggregation can cause re-entrainment which deteriorates the performance of NTP reactor [11–14]. There is an urgent need to develop a comprehensive understanding of oxidation behaviours and oxidation kinetics of PM aggregation to fulfil the need for periodic NTP reactor regeneration.

Many factors influence PM oxidation kinetics, including volatile organic compounds (VOC) content, specific surface area, crystallite structure of PM, *etc.* [15–17]. Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM) provide useful information about carbon nanostructures. Studies show that nanostructures of soot particles and their morphology influence the oxidation behaviours of diesel soot [18–20]. Diesel PM exhibits concentric crystallites on the outer layer and fine particles with spherical nuclei [21]. Lapuerta et al. [22] investigated the oxidation behaviours of PM emitted by a diesel engine fuelling with diesel

and biodiesel. The biodiesel PM is easier to oxidize than diesel PM that the initial and final oxidation temperature is lower than diesel PM. Ref. [23] showed that the biodiesel PM contained more oxygen-containing functional groups that were tested using Fourier transform infrared spectroscopy. Oxygen-containing functional groups provide active sites and surfaces for soot oxidation [24]. Ca, Mg and Zn contained in PM ash have high catalytic activities to soot oxidation, while the Na shows good catalytic activity in hydroxide [25]. More PM ash is contained in biodiesel PM [22], that is one of the reasons leading to the high oxidation activity of biodiesel PM. Ruiz et al. [26] showed that the oxidation activity presented positive correlation with active surface area that was obtained through the amount of oxygen chemisorbed on PM. Also, the active surface area increases with VOC content when the diesel engines fuelling with different fuels at stationary engine conditions. Al-Qurashi and Boehman [27] discussed the impact of exhaust gas recirculation (EGR) on the oxidation activity of diesel soot. Slow external oxidation and fast internal oxidation were observed for PM sampled under 20% EGR condition. EGR has a strong influence on the nanostructures of PM that causes the enhanced oxidation rate. Cylinder temperature decreases when EGR is applied to decrease NO_x. Lower temperature leads to more randomly arranged carbon crystallite which increase the PM oxidation activity [28]. Ye et al. [29] investigated the impact of rail pressure and biodiesel fuelling on the PM morphology and nanostructures from a common-rail turbocharged direct injection diesel engine. Similar with other results [23,30], higher biodiesel content leads to higher oxidation activity of PM. For PM generated with higher injection pressure, higher initial oxidation activity is observed.

The usual methods of investigating PM oxidation kinetics are based on TGA results. Samples for TGA testing are commercial carbon black samples, raw PM and pre-treated samples (after devolatilization) [30–35]. The physicochemical characteristics of commercial carbon black samples differ greatly from diesel PM [2,15]. During the oxidation of raw PM, both oxidation and volatilization occur for VOC contained in PM [3]. However, the oxidation kinetics of PM is only involved in the oxidation process, the oxidation of raw PM does not indicate true oxidation behaviours. VOC adhered to PM exerts a significant influence on PM oxidation [3,15,36], while the effect of VOC is neglected if samples are pre-treated at high temperature. Heat-based oxidation kinetic analysis based on DSC results avoids the aforementioned disadvantages. However, few investigations have been undertaken to analyze the oxidation kinetics of PM based on heat-release rate (DSC-based methods).

Recent research into the reduction of PM in engine exhaust using NTP technology is mainly concentrated on novel structures design of NTP reactors and improvements in PM removal performance [9,11,37]. Only several work has been done to investigate the oxidation behaviours and oxidation kinetics of PM collected on the collection plate of NTP reactor that is necessary for periodic NTP regeneration [38]. Ma et al. [38] investigated the oxidation behaviours of PM collected on the collection plate of NTP reactor, however, no comparison of raw PM with PM aggregation was made. The effect of NTP on the oxidation kinetics and crystallite structures of PM remains unclear. Thitipatanapong et al. [39] characterized the PM from a biodiesel engine equipped with NTP device. The ingredients of PM change greatly that the soot decreases and the low volatile VOC increases, however, high volatile VOC is almost with no change.

The aim of this study was to investigate the oxidation behaviours and oxidation kinetic parameters of PM emitted by a diesel engine equipped with a NTP reactor. The effects of NTP and VOC on the oxidation behaviours of PM were researched using temperature-programmed oxidation experiments (TGA). A DSC-based method was put forward to calculate the oxidation kinetic parameters to avoid the disadvantages of TGA methods. The results based on the TGA and DSC methods were also compared.

2. Materials and methods

2.1. Diesel engine and experimental set-up

Fig. 1 shows the PM sampling scheme, and the photograph of the experiment is presented in Fig. S1. The NTP reactor (dotted line, Fig. 1) was designed on the basis of corona discharge. Part of diesel exhaust flowed through the NTP reactor, and a control test was arranged. A vacuum pump was used to extract the exhaust. The voltage applied to the NTP reactor was −7000 V (direct current), and the power input was about 84 W. The distance of the discharge needles and the collection plate was 10 mm. When the high direct voltage was applied to the NTP reactor, electric field was generated between discharge needles and the collection plate (plasma zone). Partial gas in the plasma zone was ionized that some active ions (e^-, O, HO, H and O_3) were generated. When diesel exhaust flowed through the plasma zone, partial diesel PM was oxidized by active ions while some PM was captured on the collection plate of NTP reactor with the action of electric field force. However, some PM was emitted from the NTP reactor to the atmosphere. Due to the strong oxidizing properties of active ions in the plasma zone, that partial oxidation happened for diesel PM when exhaust flowed through the plasma zone. Partial oxidation led to the changes of physicochemical properties, also, the oxidation behaviours. Raw PM (point a), PM treated with NTP (point b), and PM aggregation (collection plate of the NTP reactor) were sampled. The sampling temperature of points a and b was 50 °C, and approximately 150 °C for collection plate. The exhaust flow rate was 150 L/min in the NTP reactor and it was 50 L/min for points a and b. The gas flow rate was adjusted by the valves (Fig. 1). The technical specifications of the diesel engine tested in this work is listed in Table 1. The diesel engine was the power of a generator. The voltage and rated power of the generator were 220 V and 5 kW respectively. The diesel generator had been run for less than 100 h.

The properties of the diesel fuel used in the experiments are as following: density, 850 kg/m³; viscosity (20 °C), 4.1 mm²/s; 50% distillation points, 290 °C; 95% distillation points, 340 °C; S content, 0.0042%; ratio H/C, 0.156; Cetane number, 52; The diesel engine load was controlled by the electrical power output of the generator. The engine speed was 3000 rpm. The engine conditions used for PM sampling are listed in Table 2. Samples 2 and 5 (point b) refer to the PM emitted to the environment after flowing through the plasma zone. Before diesel PM sampling, the diesel engine had run for some time to warm up. Then, the engine load was adjusted by the electrical power output of the diesel generator. When the engine ran steadily, the power supply was performed to work, and the voltage was adjusted to −7000 V. Lastly, the vacuum pump was switched on, and adjusted to make the gas flow rate of points a and b be 50 L/min. When the sampling was ended, the PM was peeled off from the filter (points a and b) and the collection plate. The diesel PM was packed using tinfoil and stored at low temperature (below 4 °C) after sampling.

2.2. TGA and DSC experiments

A TG-DTA 6200 thermogravimetric analyzer was used to perform the TGA experiments. The instrument was computer-controlled and associated software was run which could auto-sample the data during TGA experiments. A DSC 60 differential scanning calorimeter was used to measure the heat flow rate dur-