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Variation of diesel soot characteristics by different types and blends of biodiesel in a laboratory combustion chamber

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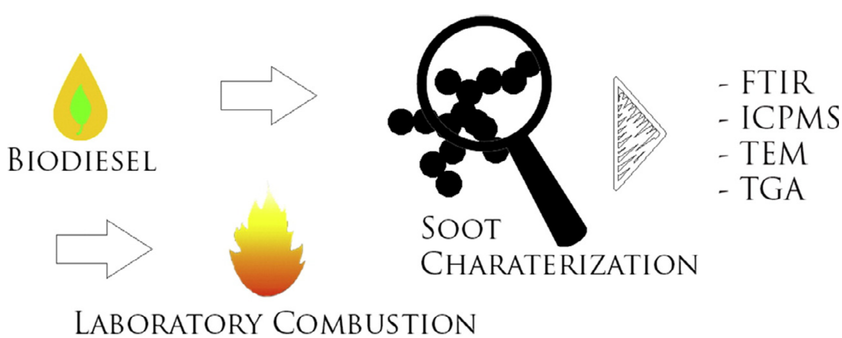
HIGHLIGHTS

- The unsaturation of biodiesel fuel was correlated with soot characteristics.
- Average diameters of biodiesel soot were smaller than that of ULSD.
- Eight elements were detected as the marker metals in biodiesel soot particles.
- As the degree of unsaturation increased, the oxygen content in FAMEs increased.
- Biodiesel soot oxidized faster than ULSD soot.

GRAPHICAL ABSTRACT



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ABSTRACT

Very little information is available on the physical and chemical properties of soot particles produced in the combustion of different types and blends of biodiesel fuels. A variety of feedstock can be used to produce biodiesel, and it is necessary to better understand the effects of feedstock-specific characteristics on soot particle emissions. Characteristics of soot particles, collected from a laboratory combustion chamber, are investigated from the blends of ultra-low sulfur diesel (ULSD) and biodiesel with various proportions. Biodiesel samples were derived from three different feedstocks, soybean methyl ester (SME), tallow oil (TO), and waste cooking oil (WCO). Experimental results showed a significant reduction in soot particle emissions when using biodiesel compared with ULSD. For the pure biodiesel, no soot particles were observed from the combustion regardless of their feedstock origins. The overall morphology of soot particles showed that the average diameter of ULSD soot particles is greater than the average soot particles from the biodiesel blends. Transmission electron microscopy (TEM) images of oxidized soot particles are presented to investigate how the addition of biodiesel fuels may affect structures of soot particles. In addition, inductively coupled plasma mass spectrometry (ICP-MS), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) were conducted for characterization of soot particles. Unsaturated methyl esters and high oxygen content of biodiesel are thought to be the major factors that help reduce the formation of soot particles in a laboratory combustion chamber.

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1. Introduction

In recent years particular attention has been paid to the reduction of soot particles from diesel combustion, because of the rising environmental and health concerns on soot particles that are found to be turned into mutagenic and potentially carcinogenic particulate matters (PMs) (Boehman et al., 2005; Chien et al., 2009; Omidvarborna et al., 2014a; Kumar et al., 2014; Omidvarborna et al., 2015a). A soot particle consists of carbonaceous materials accompanied by various organic and inorganic compounds (Harris and Maricq, 2001; Shandilya and Kumar, 2014). It is widely accepted that the formation of soot particles can be depicted with five sequential steps during diesel combustion (Omidvarborna et al., 2015b): (1) formation of soot precursors such as acetylenes and polycyclic aromatic hydrocarbons (PAHs), (2) nucleation to form heavy molecules that eventually turn into nascent soot particles, (3) mass growth by attracting and interacting with hydrocarbons (HCs), (4) coagulation and agglomeration to form spherical soot particles and large aggregates with chain-like structures respectively, and finally (5) oxidation of soot particles to reduce its mass and size.

One way to reduce emissions of soot particles from diesel combustion is to blend diesel with an oxygenated fuel such as biodiesel (Lapuerta et al., 2008; Benjumea et al., 2011; Macor et al., 2011; Omidvarborna et al., 2015c). In recent years, it is becoming more attractive to utilize biodiesel (fatty acid methyl esters (FAMEs) derived from the transesterification of oils and fats) in diesel engines to meet both emission reduction and energy security objectives. Biodiesel has inherent characteristics that allow its use in modern diesel engines without introducing significant modifications (Kumar et al., 2014). Lower emissions of other pollutions such as CO from biodiesel combustion have been another driving force for more biodiesel uses in the transportation sector (Macor et al., 2011; Kegl, 2011). Biodiesel is commonly blended with diesel in different proportions, commonly 20 vol% of biodiesel and 80 vol% diesel, which is referred to as B20 (Omidvarborna et al., 2014b).

According to the United State environmental protection agency (USEPA) report, emissions from biodiesel are mostly related to the characteristics of biodiesel feedstocks and the chemical composition of regular diesel used to prepare the blends (Salamanca et al., 2012a). Biodiesel lacks sulfur and aromatics, which are considered to be critical for the nucleation step and initial formation of PAHs leading to soot formation (Song et al., 2006; Lapuerta et al., 2008; Vander Wal et al., 2010; Salamanca et al., 2012b; Kumar et al., 2014). Not only the chemical compositions, but also the unsaturation and high oxygen contents in biodiesel are thought to contribute to the reduction of soot particles (Kohse-Höinghaus et al., 2010). The unsaturation degree of biodiesel is an indicator of the number of double bonds present in its FAME chains. A large number of double bonds mean a higher degree of unsaturation. For pure FAMEs, the oxygen content increases slightly with the degree of unsaturation because of the displacement of two hydrogen atoms by saturation of double bonds (Benjumea et al., 2011).

Soot formation process from various biodiesel feedstocks in an engine is very complex and associated with various operational and environmental conditions as well as fuel structure and composition (Neer and Koylu, 2006; Lapuerta et al., 2008; Lin et al., 2008; Cengiz and Sehmus, 2009; Gogoi and Baruah, 2011; Muralidharan and Vasudevan, 2011). In addition, there is a lack of knowledge if the biodiesel from other feedstocks would alter the detailed physical and chemical properties of the soot particles. Therefore, it is reasonable to speculate possible relations between the biodiesel soot particle characteristics and feedstock properties. In the current study, we used a combustion chamber to include only the effects of fuel's unsaturation on soot formation. The detailed morphological, structural and compositional features thus revealed would allow a much improved understanding of the characteristics of soot particles, providing a thorough assessment of the influence of biodiesel fuel structure on soot characteristics. The information will be helpful in selecting the appropriate blends for mobile sources used around the globe and also provide insights into the mechanisms of the fuel formulation in diesel combustion and soot formation processes.

2. Materials and methods

2.1. Experimental setup

Combustion tests were carried out in a laboratory scale combustion chamber (300 mL purchased from Parr Instrument Company). The device included a stainless steel reactor (2.5 in. inside diameter with 4.0 in. inside depth) that was placed in an electrically heated chamber. A J type thermocouple was placed inside the reactor for monitoring the combustion temperature, and a temperature controller was installed to preserve the reaction conditions at the predetermined values. With this arrangement, the reaction temperature was controlled and monitored with a precision of 0.1 °C. A compressed air tank was used to maintain the stoichiometric combustion condition at the beginning. A schematic diagram of the entire experimental setup is shown in Fig. 1.

2.2. Experimental procedure

To measure an estimation of lambda (air–fuel equivalence ratio), the stoichiometric condition was calculated using a mixture of various esters as a representative for a biodiesel fuel. The amounts of fuel and air were determined to keep the equivalence ratio as one. In ambient temperature, the starting pressure of the chamber was set to 200 psi with dried air. Dried air was purchased from Airgas®. Temperature inside the chamber was increased by the heater installed around the chamber. At the ignition point, the chamber temperature rose rapidly, then the heater was turned off. To store soot particles formed in the combustion, the chamber temperature was monitored until the chamber temperature returned to room temperature, and then the soot particles was collected from the inside wall of the combustion chamber. FTIR, ICP-MS, TGA, and TEM were used to analyze the unsaturation of biodiesel fuels and characterization of soot particles. All the instruments were calibrated with the predefined standard operating procedures and tuning solutions prior to any tests.

2.2.1. FTIR analysis of biodiesel fuels and soot particles

FTIR (UMA-600 Microscope, Varian Excalibur Series, Digilab) analysis was conducted on the biodiesel samples with the maximum scan rate with the resolution of 1 cm^{-1} between 650 to 4000 cm^{-1}. For the soot particles collected from the combustion chamber, FTIR

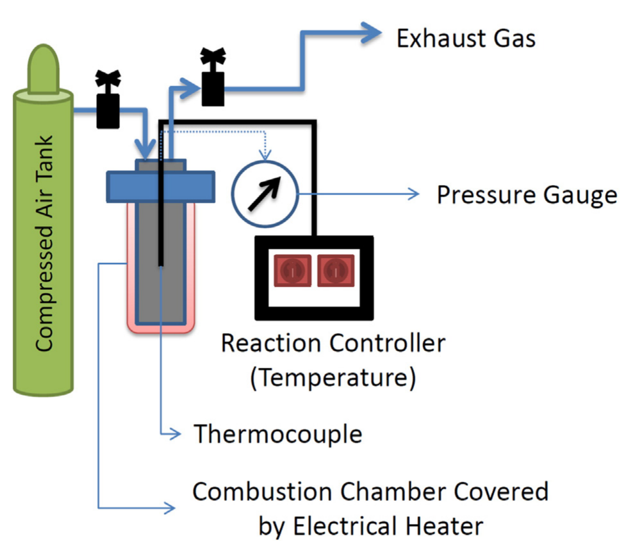

Fig. 1. Schematic diagram of experimental setup.