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Characterization of gasoline soot and comparison to diesel soot: Morphology, chemistry, and wear

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ABSTRACT

Soot from gasoline turbocharged direct injection (GTDI) engines and diesel engines, from exhaust and extracted from oil, were characterized by XRF, XPS, Raman spectroscopy, HRTEM, and Soxhlet extraction followed by GC–MS. Laboratory wear tests with drains and supernatants were also conducted. GTDI soot had less carbon content than diesel soot and can have different PAHs associated with it. GTDI soot extracted from oil either showed the turbostratic structure typical of diesel soot, or appeared sludge-like and decomposed under the TEM beam. The different morphology and chemical composition of GTDI soot from diesel soot can lead to changes in the polarity and hardness of the soot particles and affect the wear mechanism in GTDI and diesel engines.

1. Introduction

In the quest to improve fuel economy, automotive manufacturers have increased the production of gasoline engines equipped with turbochargers and direct injection. One unintended byproduct of these GTDI engines (*G*asoline *T*urbo *D*irect *I*njection) can be an increase in soot generation, ~1%, as determined by thermogravimetric analysis (TGA). In conventional port-fuel injection engines, soot levels were much lower [1], and in diesels, soot levels can be several percent. Since diesel soot has been known to cause wear, and has been the subject of numerous wear-related investigations [see [2–4] and references therein], a better understanding of the nature of the carbonaceous species present in the oil and in the exhaust of gasoline DI engines and its impact on engine and engine oil formulations is needed.

The characterization of diesel soot, either extracted from used engine oils or collected from the exhaust, has been the subject of many studies in the past [5–23]. In some cases, the studies have also included different types of carbon black [24–27] which has functioned as a soot surrogate in wear-related investigations. In contrast, relatively few works have been conducted on gasoline DI soot extracted from oil [1,28,29] or collected from exhaust [30–33].

Soot is primarily amorphous elemental carbon with some amount of organic and inorganic compounds attached to it. The soot particles are tens of nanometers in size and form agglomerates. The most commonly used methods to understand the structure and chemical properties of soot have been transmission electron microscopy (TEM) [6,7,9,11–14,16,17,22–24,29,30,33–35], Raman spectroscopy [11,13,18,19,23,35–37], X-ray photoelectron spectroscopy (XPS) [9,11,16,24,26,29,30,38,39], thermogravimetric analysis (TGA) [9,24,39], and infrared spectroscopy (IR) [24,30,37,40]. Some other techniques utilized were electron spin resonance (ESR) [29], differential scanning calorimetry (DSC) [22], electron energy loss spectroscopy (EELS) [15,20,40], X-ray microspectroscopy [20], X-ray diffraction [11,40], X-ray near edge absorption spectroscopy [10,20], inelastic incoherent light scattering [29], secondary ion mass spectrometry [29], and nuclear magnetic resonance (NMR) [24] for chemical characterization, and studies on soot particulate size distributions have also been conducted using the scanning mobility particle sizer [13,14,33]. Aside from general investigations on structure and chemistry, the effects of fuel [13,14,22,39–41], engine operating conditions and parameters [9,13,23,30,33], lubricant formulation effects [9,38], and synthesis conditions [34] on soot characteristics have also been investigated.

In this paper, we compare the nanostructure and chemical characteristics of six GTDI and diesel soot samples, and a carbon black. Soot was either extracted from used engine oils or collected from the exhaust. High resolution transmission electron spectroscopy (HRTEM) is used to determine particle sizes and the nanostructure of the carbonaceous particles. XPS and X-ray fluorescence (XRF) were used to determine the elemental chemical

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composition of the soot on the surface and in the bulk, respectively. XPS, additionally, provided chemical state information of both the carbon and other elements. UV and visible Raman spectroscopy provided additional information on the graphitic nature of the soot, as well as additional compounds attached or integral to the soot particles. Soxhlet extraction followed by gas chromatography and mass spectrometry (GC–MS) was performed on the soot extracted from drain oils in order to remove, identify and quantify polycyclic aromatic hydrocarbons (PAH) with 2–6 rings. Finally, laboratory wear tests were conducted on the drain oil samples, as well as the supernatant oils when the soot was removed by centrifugation. Auger electron spectroscopy (AES) was then used to determine the elemental compositions and the thicknesses of the resulting tribofilms formed on the wear surfaces.

2. Experimental

2.1. Sample collection

2.1.1. Exhaust soot and carbon black

Two samples of diesel exhaust soot and one of GTDI soot were collected for this study. GTDI D and Diesel A exhaust soot samples were collected from the pipes leading into the after-treatment systems of a gasoline turbocharged DI vehicle and a medium-duty diesel truck, respectively. The GTDI vehicle used an SAE 5W-30 GF-4 engine oil. The amount of soot scraped from the pipe was much less than the quantity that was available from the diesel truck.

The diesel truck used an SAE 15W-40 CJ-4 engine oil and was fueled with both ULSD (ultra-low sulfur diesel) and B20 fuel. B20 was used ~7–15% of the mileage at the time the soot was collected from the engine. The truck was part of a fleet that included 80% highway and 20% city driving, and experienced upwards of 10% fuel dilution.

Diesel B was taken from the diesel particulate filter (DPF) of a medium-duty truck running on a dynamometer. It also used an SAE 15W-40 CJ-4 engine oil and ULSD as fuel.

The carbon black used as a soot in this work was Mogul L, which was obtained from Cabot Corporation. Mogul L is a low-structure carbon black possessing an oxidized surface and a primary particle size of 24 nm; we used it as a soot surrogate in our previous wear-related work [2].

The list of samples is summarized in Table 1.

2.1.2. Soot samples extracted from drain oils

Soot was isolated from two GTDI engine drain oils and one heavy duty diesel engine drain oil. Diesel C was from a Mack T11 test; GTDI E was obtained from a batch of drains collected from various GTDI customer vehicles under normal city and highway driving conditions. GTDI F came from a GTDI engine running on a dynamometer with a non-production calibration intended to generate significant amounts of soot.

Drain soot samples were isolated by first diluting the drain with 20% hexanes, then centrifuging the mixture at 59,860*g* RCF (relative centrifugal force) for 20 h at 40 °C. After centrifugation, the supernatant or soot-free bulk oil was decanted and stripped of residual hexane in a vacuum oven, and saved for wear testing. TGA measurements indicate that more than 99% of the soot is removed in this initial centrifugation step. The centrifuged solids were washed with fresh hexanes and centrifuged at 59,860*g* RCF for 1 h. This was repeated four times to remove any occluded oil. The solids were then dried in a vacuum oven to remove the hexanes.

Before isolation, a high resolution thermogravimetric analysis (TGA) was performed on the drains to determine if any carbonaceous material was measurable. TGA is used to measure weight loss (i.e. decomposition) as a function of time and/or temperature. These analyses were performed using a TA Instruments™ model Q5000IR TGA with quartz furnace and infrared heating capability. The drains were loaded onto platinum auto-sampler pans at a target weight range of 10–12 mg. The samples were then exposed to a heating ramp to 650 °C, at a maximum rate of 5 °C per minute, in the presence of nitrogen. Following an isothermal hold at 650 °C for five minutes, the gas through the TGA furnace was switched to air and held at 650 °C for an additional 20 min to allow combustion of any carbonaceous species.

TGA is capable of discerning sludge and fuel dilution from soot and other carbonaceous material. The initial temperature ramp performed in the presence of nitrogen volatilizes the fuel, sludge, and polymeric material (i.e. anything that can be pyrolyzed without the aid of oxygen). The second step (isothermal hold in air) allows for measurement of the weight loss of the carbonaceous species that oxidize in the presence of oxygen. In diesel drains, the carbonaceous species are associated with soot. This is listed in the 6th column of Table 1 as TGA (wt% C).

Along with TGA values, Table 1 lists additional properties of the drains. Fuel dilution for GTDI E and GTDI F capture both gasoline and ethanol (if present) components; for Diesel C, this refers to mineral diesel. TAN is Total Acid Number as determined by ASTM D664 and is a measure of engine oil deterioration.

2.2. Soot characterization

2.2.1. XRF

Concentrations of F and heavier elements were determined by X-ray fluorescence spectroscopy (XRF) using a PANalytical PW2400 WDS XRF Spectrometer equipped with a Cr target X-ray tube as the primary excitation source. X-ray tube power of 60 kV/40 mA was used for wavelengths shorter than 2 Å, and 40 kV/60 mA for wavelengths longer than 2 Å. A 200 μm Al tube filter was used for the portion of the spectrum in the vicinity of the Cr K lines. X-ray intensity data were collected under vacuum for good detection of lighter elements. No X-ray intensity data were collected for elements O and lighter. The weight percent of soot (or carbon for carbon black) was determined by difference based on mass balance (i.e. weight of measured elements subtracted from the total weight).

Table 1
List of samples studied in this work. Characteristics of the drains that were used for extraction of soot are included in columns 6–8.

Sample	Engine type	Engine source	Soot type	Extraction location	TGA (wt% C)	Fuel dilution (wt% fuel)	TAN (mg KOH)
Mogul L	Carbon black						
Diesel A	Diesel	Vehicle test	Exhaust	Scraped from pipe leading into aftertreatment			
Diesel B	Diesel	Engine dynamometer test	Exhaust	DPF			
Diesel C	Diesel (heavy duty)	Engine dynamometer test	Soot-in-oil		7.31	1	4.9
GTDI D	GTDI	Vehicle test	Exhaust	Scraped from pipe leading into aftertreatment			
GTDI E	GTDI	Customer vehicles	Soot-in-oil		0.83	2.1	4.1
GTDI F	GTDI	Engine dynamometer test	Soot-in-oil		1.64	2.2	2.8