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Effect of lubricant sulfur on the morphology and elemental composition of diesel exhaust particles

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ABSTRACT

This work investigates the effects of lubricant sulfur contents on the morphology, nanostructure, size distribution and elemental composition of diesel exhaust particle on a light-duty diesel engine. Three kinds of lubricant (LS-oil, MS-oil and HS-oil, all of which have different sulfur contents: 0.182%, 0.583% and 1.06%, respectively) were used in this study. The morphologies and nanostructures of exhaust particles were analyzed using high-resolution transmission electron microscopy (TEM). Size distributions of primary particles were determined through advanced image-processing software. Elemental compositions of exhaust particles were obtained through X-ray energy dispersive spectroscopy (EDS). Results show that as lubricant sulfur contents increase, the macroscopic structure of diesel exhaust particles turn from chain-like to a more complex agglomerate. The inner cores of the core-shell structure belonging to these primary particles change little; the shell thickness decreases, and the spacing of carbon layer gradually descends, and amorphous materials that attached onto outer carbon layer of primary particles increase. Size distributions of primary particles present a unimodal and normal distribution, and higher sulfur contents lead to larger size primary particles. The sulfur content in lubricants directly affects the chemical composition in the particles. The content of C (carbon) decreases as sulfur increases in the lubricants, while the contents of O (oxygen), S (sulfur) and trace elements (including S, Si (silicon), Fe (ferrum), P (phosphorus), Ca (calcium), Zn (zinc), Mg (magnesium), Cl (chlorine) and Ni (nickel)) all increase in particles.

Introduction

Due to their negative impact on health and the environment, diesel engine particle emissions have received more and more attention (Huang et al., 2012; Ris, 2007; Tan et al., 2014). The diesel exhaust particles originate from the combustion of fuels and lubricant entering the combustion chamber (Brandenberger et al., 2005; Kleeman et al., 2008; Fraser et al., 2003). Diesel engine exhaust particles consist dominantly of soot particles as a result of high temperatures and lack of oxygen in the cylinder, soluble organic fraction (SOF) composed of unburned and partially burned fuels and lubricant, sulfates formed by the oxidation of sulfur in fuels and lubricant (Tan et al., 2009; Vaaraslahti et al., 2005), and ash that includes trace metal elements.

The formation and oxidation of particles is a dynamic process in cylinder combustion, cooling of the exhaust and the after-treatment purification in diesel engines (McEnally et al., 2006; Shi and Harrison, 1999). The morphology, nanostructure, size distribution and elemental composition of diesel exhaust particles all directly affect oxidation activity (Vander Wal et al., 2003; Boehman et al., 2005; Vander Wal et al., 2007). Vander Wal et al. (2003) claimed that the increased oxidation reactivity of particles demonstrated to be related with the higher level of tortuosity of carbon lattice layer and they refer it as a

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predominant parameter in determining soot reactivity. Lu et al. (2012) collected exhaust particles from a medium-duty diesel engine and suggested that particles between 100 and 180 nm and 320–560 nm show a more orderly nanostructure; however, those particles less than 56 nm and within 1000–1800 nm have a faster oxidation rate.

Many studies have been performed focusing on the effects of fuel properties, lubricant properties, operating conditions, fuel injection parameters and after-treatment technologies on the characteristics of diesel exhaust particles. Lapuerta et al. (2012) investigated the effects of fuel on soot oxidation reactivity. Results showed that the biodiesel soot displayed higher reactivity due to its smaller primary particles and higher specific active surface, regardless of a higher degree of graphitization. Soewono et al. (2011) studied the morphology and nanostructure of particles in a light-duty diesel engine using ultra-low sulfur fuel and B20 biodiesel. Based on the TEM images, the result shows that the fractal dimensions of the particles measure between 1.70 and 1.85, and fractal dimensions are independent of fuel type. It was also illustrated that the B20 particle exhibited a greater structural disorder through a Raman spectroscopy analysis. Virtanen et al. (2004) evaluated the impact of engine load on soot particle size distributions and morphology. The number distribution follows the lognormal distribution, and the width of the distribution increased with the load. Simultaneously the fractal dimension of soot particles varies from 2.6 to 2.8 in dependence of engine load. Liati et al. (2013a) collected soot from different sites of the engine's exhaust after-treatment system to investigate reactivity in terms of the morphology and structure of primary soot particles. Results showed that primary soot particles that passed through the diesel particle filter (DPF) and entered the atmosphere showed a higher degree of graphitization than those entering the DPF, leading to lower reactivity.

Considering that the exhaust particles from diesel engines originate from combustion of fuels and lubricants entering the combustion chamber, fuel and lubricant properties are critical factors affecting particle emissions. With fuel properties improving (ultra-low sulfur content) and diesel particle emission regulations tightening (Johnson, 2015), lubricant plays an increasingly important role in contributing to the particle emission lubricant (Miller et al., 2007). Many investigations have been performed on the contribution of lubricant on particle emissions. Kyotö et al. (2002) suggested that lubricant can increase the particle number emissions and can provide low particle mass emissions. Storey et al. (2015) showed that the contribution of lube oil to the total mass of the PM is on the order of 1%. Plumley (2005) compared the PM emission form mineral-based motor oils and full synthetic (PAO) base oil on a three-cylinder direct injection engine. Results showed that the specific particulate emissions of synthetic oil were 19–24% smaller than those of the mineral oils. Wang et al. (2014) used neat fuel and blended fuel containing oil pour point depressant (PPD) additive to study the effects of lubricant additives on particle emission. Results show that the layer fringe length decreases from 1.191 nm to 1.064 nm, while both the separation distance and tortuosity increase.

The effects of lubricant properties on diesel particle emissions become more important; this is particularly true of lubricant sulfur content (Ronkkö et al., 2013). Although fuel's sulfur content is as low as 2 ppm, there is a large quantity of sulfur-associated nanoparticles in diesel engine exhaust (Vaaraslahti et al., 2004). Sulfur can be converted into sulfuric acid aerosols that are an important component of particle through combustion (Cornelius et al., 1993). He et al. (2015) showed that sulfuric acid oxidized from SO_2 made a negligible contribution to the growth of >10 nm new particles. Tornehed et al. (2012) summarized that the sulfur-associated particulate emissions increase by a maximum of approximately 0.15 g for every gram of sulfur in the lubricant.

This article will study the effects of lubricant sulfur content on the morphology, nanostructure, size distribution and elemental composition of exhaust particles from diesel engines. Transmission electron microscopy (TEM) was used to observe the morphology and nanostructure of diesel exhaust particles, and advanced image-processing software was applied to analyze the size distributions of the primary particles. Elemental compositions of exhaust particles were obtained through X-ray energy dispersive spectroscopy (EDS). This study can provide useful information regarding the future of lubricant formulation.

1. Materials and methods

1.1. *Test engine, fuel and lubricant*

This study used a light-duty, direct injection and four-stroke diesel engine with a rated power of 24.6 kW at 2400 r/min and a maximum torque of 114 N·m at 1600 r/min. The engine has two cylinders with a compression ratio of 17.1, and a displacement volume of 2.22 L. The engine was manufactured by Fujian Lijia Co., Ltd. in China with a model number of SL2110ABT and met China IV emission standards. To minimize any fuel effects we used an ultra-low sulfur fuel with a sulfur content of less than 10 ppm. The primary specifications of the test fuel are shown in Table 1.

Three kinds of lubricant with different sulfur contents were used in this study. The first lubricant is Castrol oil, which has the lowest sulfur content (0.182%) of the three lubricants, meets the ACEA (European Automobile Manufacturers' Association) C1 grade oil standard (The standard is global strictest lubricant standard for light-duty diesel engines). It is suitable for EURO VI light-duty diesel engines to ensure high DPF performance as a catalyst-compatible and stay-in-grade oil. Now, China has a mandatory regulation for diesel lubricants, which does not limit the sulfur content in lubricants. Therefore, the sulfur content in China's current lubricant is usually far higher than what is found in the ACEA C1 grade oil standard. Based on the preceding ACEA C1 lubricant (called as LS-oil), other two sulfur content lubricants were obtained by adding sulfurous additives (T-323/Amino

Table 1 – Test fuel specifications.

Property	Unit	Method	Parameters
Density @ 20 °C	kg/m^3	ASTM D4052	821.9
Cetane number		ASTM D613	52.3
Sulfur	ppm, m/m	ASTM D5453	<1
Flash point	°C	ASTM D93	92.0
Distillation at 90% volume	°C	ASTM D86	323.1
Kinematic viscosity @ 40°C	mm^2/sec	ASTM D445	4.54
Lower heating value	MJ/kg	ASTM D240	43.96

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