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Carbonaceous composition changes of heavy-duty diesel engine particles in relation to biodiesels, aftertreatments and engine loads

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HIGHLIGHTS

- We study particulate OC and EC under 3 fuels, 2 aftertreatments and 4 engine loads.
- Negligible to minor OC and EC changes with low, ultralow sulfur and 10% biodiesels.
- Moderate reductions of EC and particularly OC from diesel oxidation catalyst (DOC).
- Large reductions of OC and particularly EC from DOC plus diesel particulate filter.
- Highest at idle, whereas OC decreases but EC increases from low to high load.

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ABSTRACT

Three biodiesels and two aftertreatments were tested on a heavy-duty diesel engine under the US FTP transient cycle and additional four steady engine loads. The objective was to examine their effects on the gaseous and particulate emissions, with emphasis given to the organic and elemental carbon (OC and EC) in the total particulate matter. Negligible differences were observed between the low-sulfur (B1S50) and ultralow-sulfur (B1S10) biodiesels, whereas small reductions of OC were identified with the 10% biodiesel blend (B10). The use of diesel oxidation catalyst (DOC1) showed moderate reductions of EC and particularly OC, resulting in the OC/EC ratio well below unity. The use of DOC plus diesel particulate filter (DOC2+DPF) yielded substantial reductions of OC and particularly EC, resulting in the OC/EC ratio well above unity. The OC/EC ratios were substantially above unity at idle and low load, whereas below unity at medium and high load. The above changes in particulate OC and EC are discussed with respect to the fuel content, pollutant removal mechanisms and engine combustion conditions. Overall, the present study shows that the carbonaceous composition of PM could change drastically with engine load and aftertreatments, and to a lesser extent with the biodiesels under study.

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1. Introduction

Diesel engine exhaust is a complex mixture that contains gaseous pollutants and particulate matter (PM) with diameters primarily less than 2.5 μm ($PM_{2.5}$). The key gaseous pollutants consist of nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide, sulfur dioxide (SO_2), and light hydrocarbons (HC). The PM components are composed predominantly of carbonaceous material in the form of organic carbon (OC) and elemental carbon (EC) [1]. The OC has recently been found to be highly associated with the oxidative potential of PM, which is an indicator of cell toxicity [2,3]. Diesel engine particles (DEP) are considered as the major source of EC in

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the atmosphere [4,5]. Collectively, the diesel engine exhaust contributes to adverse human health effects, restricted visibility, acid rain, and global climate change [5–7]; more recently, it has been reclassified as “carcinogenic to humans” [8].

The EC in DEP is formed by the pyrolysis of the unburnt fuels at temperatures above 1300 K, while the OC is produced as a result of incomplete combustion of fuel and lubricant oil [9,10]. The EC and metal ashes make up the agglomerated nearly spherical solid particles, with their surface coated with semivolatile OC and sulfate. The emission rates of particulate EC and OC from engines are shown to vary considerably, depending on the sampling conditions, engine type, mode of engine operation, fuel type, and the presence of aftertreatment [11–13]. Unlike the nonvolatile EC that forms in the engine, the gas/particle partitioning of semivolatile OC varies with dilution ratio, temperature and residence time [14,15].

The major contributor to the EC in $PM_{2.5}$ is heavy-duty diesel engines (HDDE), followed by light-duty diesel engines, and then gasoline engines; on average, the EC contributed to 75% of the DEP and ~25% of gasoline engine particles [5]. From in-use heavy heavy-duty diesel trucks, Shah et al. [11] showed that the OC/EC ratios were below unity under cruise and transient operation, whereas, above unity under creep and cold-start/idle operation. Sharma et al. [16] reported the fraction of EC in DEP increased from 25% to 48% with increasing load from idling to 70% load. Ålander et al. [12] showed that reformulated low-sulfur, low-aromatic fuel as well as diesel oxidation catalyst (DOC) reduced the particulate OC in DEP; additionally, the OC contributions to the total carbon (TC) from an indirect injection engine was significantly greater than that from a direct injection engine. Tsai et al. [17] tested soy-biodiesel blends of 0–50% (B0, B10, B20 and B50) on a diesel generator and showed that the OC and EC decreased with increasing biodiesel blend to a minimum with B20 and then sharply increased to a maximum with B50. Similarly, Lin et al. [18] reported that the soluble organic fraction decreased to a minimum with palm-biodiesel blend of 20% (P20) and reached a maximum with neat P100. Biswas et al. [19] have shown that significant reductions (>90%) of PM, EC, OC and water-soluble OC were achieved with catalyzed or uncatalyzed diesel particulate filters (DPF), between which only catalyzed aftertreatments were found to decrease the OC solubility. In addition, the DEP was dominated by TC in which a higher fraction of OC was observed for HDDE vehicles retrofitted with selected catalyzed continuously regenerating traps or electric particle filter that emits less or insignificant nucleation mode particles.

With increasing stringent PM emission standards, the development and application of advanced emission control technologies are an area of active research in recent years. Although new vehicles are required to meet the new emission standards, emission reductions from in-use vehicles are an integral part of an effective reduction strategy. Among those in-use vehicles, HDDE buses and trucks are of special interest as they contributed to ~50% of the total PM_{10} emitted from mobile sources, despite making up only a minute fraction of the total fleet in Taiwan [20]. In addition, diesel engine commonly has a life expectancy of 20–30 years or more. Therefore, retrofitting in-use vehicles with high-efficiency aftertreatments as well as the use of biofuels have become attracting options for air pollution abatement and energy conservation. However, the impact of control strategies on the emissions needs to be evaluated for changes in human and environmental health implications. Although there are numerous publications on similar subjects, the study focuses vary substantially with respect to engine types, pollutants, fuels, aftertreatments and engine operating conditions. This study therefore supplement earlier studies by focusing on how the carbonaceous composition of diesel engine particles changes in relation to three biofuels and two aftertreatments under transient cycle and during steady engine loads. In addition, this study addresses practical applications as to how the selected biofuels and aftertreatments perform when retrofitted to old, high-emission in-use engines.

Table 1
Engine test modes under steady cycle.

Load	Torque (Nm)	Speed (rpm)
Idle	–	810
Low	210	1200
Medium	255	1635
High	255	2065

2. Experimental methods

2.1. Test engine, fuels and aftertreatments

This study was carried out in the testing facility of the Refining and Manufacturing Research Institute, Chinese Petroleum Corporation in Taiwan. The test engine was a 6-cylinder, 6 L, turbocharged air aspiration, water-cooled, direct-injection 1996 Cummins HDDE (Table S1). At the time of study, the market diesel fuels all contain ~1% waste cooking oil biodiesel (B1) supplied by the Chinese Petroleum Corporation in Taiwan. Three test fuels under study included a premium low-sulfur (<50 ppmw) diesel (B1S50), an ultralow-sulfur (<10 ppmw) diesel (B1S10), and a biodiesel blend containing 10% volume (B10) of neat waste cooking oil (B100). The fuel properties of the B1S50, B1S10 and B100 are given in Table S2. The biodiesel fuel quality and diesel fuel quality standards for use in mobile vehicles in Taiwan, the Chinese National Standards (CNS) 15072 and CNS 1471, are comparable to the European standards EN 14214 and EN 590, respectively. The above fuel selection was due to our national policy changes in 2010 and 2011 to further increase the biofuel content to above 2% and to lower the diesel sulfur contents, respectively. As a result, B1S50 and B1S10 could serve as the base cases for evaluating how policy changes might impact mobile pollutant emissions. The two aftertreatments under study included a DOC (denoted as DOC1) and a prototype DOC+DPF (denoted as DOC2+DPF). The DOC1 is of length (L) 40 cm and outer diameter (o.d.) 21 cm, whereas the DOC2 is of L 10 cm and o.d. 24 cm, made of a ceramic straight-through honeycomb catalyzed with a mixture of platinum and palladium. The DPF is an uncatalyzed ceramic wall-flow honeycomb (L = 30.5 cm, o.d. = 24 cm) with porosity of 45–50% and pore size of 2–3 μm.

2.2. Duty cycles and emission factor calculation

The HDDE was tested with the US Federal Test Procedure (FTP) heavy-duty transient cycle and four steady cycles that include idle, low, medium and high load. The engine torque and speed were controlled by an engine dynamometer (Schenck GS-350). Prior to each transient cycle emission test, the engine was given an overnight cold soak, after which the experiments were conducted in the order of a cold-start emission test and then 3–5 hot-start emission tests, with a 20 min hot soak in between. In the steady cycle emission tests, the engine was maintained steady for 20 min with four sets of torque and speed given in Table 1, denoted as idle, low, medium, and high load. As shown, with the exception of idle, the engine loads differed mainly in the speed (1200–2065 rpm), while the torque was similar (210–255 Nm). In each steady cycle, the emission tests were repeated three times.

With the transient cycle, the emission tests were conducted with the engine running on the three biofuels without any aftertreatments (denoted as B1S50, B1S10 and B10) and with the B1S50 in combination with one of the two aftertreatments (DOC1 and DOC2+DPF). With the steady cycle, all the emission tests were conducted with the engine running on B1S50

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