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Original Article

Effects of oxygenated fuels on the particle-phase compounds emitted from a diesel engine

Chun Guan [a, b], C.S. Cheung [b, *], Xinling Li [a], Zhen Huang [a, **]

[a] Key Laboratory for Power Machinery and Engineering of M. O. E, Shanghai Jiaotong University, China
[b] Department of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hung Hom, Hong Kong, China

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ABSTRACT

In the present work, emission characteristics of soot particles and particle-phase organic compounds emitted from a diesel engine fueled with different oxygenated fuel blends were investigated. Two groups of oxygenated fuels with different oxygenated functional groups were selected as the target fuels to be blended with the diesel fuel. The results indicate that both of the diesel-biodiesel (DB) blends and the diesel-biodiesel-ethanol (DBE) blends could reduce particle mass emission rate and particle total number concentration at either low or high engine load. The DBE blends present more significant impacts on suppressing the soot particles on both physical and chemical aspects as compared to the DB blends. The geometrical mean diameter of the particles from either the DB blends or the DBE blends is decreased with the increase of the blending ratio of the oxygenated fuels. Both of the DB blends and the DBE blends have an effective suppression impact on almost all the measured n-alkanes at the high load, but present a promotional impact on the short carbon chains compounds at the low load. Polycyclic aromatic hydrocarbons (PAHs) are significantly suppressed by using the oxygenated fuels, and OH functional group in the DBE blends is observed to have higher oxidation effect on the PAHs than O—C=O in the DB blends. Moreover, oxygenated fuel blends have a promotional impact on the total measured oxy-PAHs, but present a suppression impact on the total measured nitro-PAHs. However, the impacts of the oxygenated fuels on the individual PAH derivative (oxy- and nitro-PAH) differ among each other.

1. Introduction

Previous studies have indicated that diesel engines are the major contributors to the ambient fine particulate matters (PM, diameter size < 2.5 μm). These fine particles, especially the ultrafine particles (diameter size < 100 nm), could penetrate into human lungs and interstitial tissues, resulting in severe asthma and acute pulmonary emphysema (Mazzarella et al., 2007). The engine PM are mainly comprised of the element carbon (EC) and the organic carbon (OC). The OC further includes n-alkanes, hopanes and steranes, polycyclic aromatic hydrocarbons (PAHs) and some other PAH derivatives, e.g., nitro-PAHs and oxy-PAHs (Lim et al., 2005; Borrás et al., 2009; Miller-Schulze et al., 2010). Commonly, n-alkanes are derived from the unburned fuel and lubrication oil due to the incomplete combustion and could occupy a major proportion in the organic emissions from the diesel engines. The release of the alkanes, especially the low-volatility n-alkanes with long carbon chains, would create serious environment problems (Binazadeh et al., 2009). Compared to the n-alkanes, PAHs and their relevant derivatives have much lower concentrations, but they are mostly observed carcinogenic and mutagenic in epidemiological studies (Schauer et al., 1996; Flowers et al., 2002). Furthermore, among all the above organic pollutants, the semi-volatile and low-volatility organic compounds could be absorbed or adsorbed on the surface of the EC during the cooling and dilution processes, forming the primary organic aerosols (POA) (Presto et al., 2012; Ranjan et al., 2012). When spreading in the atmosphere, the soot particles with those POA would further undergo a series of aging processes through the heterogeneous reactions towards the atmospheric oxidation gases on the particles surface, and hence affecting the atmospheric composition (Zhang and Zhang, 2005; Han et al., 2013). Consequently, the particulate-phase pollutants emissions

* Corresponding author.
** Corresponding author.
E-mail addresses: tomzhengguan@sjtu.edu.cn (C. Guan), mmcsc@polyu.edu.hk (C.S. Cheung), z-huang@sjtu.edu.cn (Z. Huang).

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from diesel engines draw much attention and a better method is needed to solve the emission problems.

So far, there have been an increasing number of publications on the engine combustion, emissions as well as particles properties by using biodiesel of different feedstock, especially in this decade (Cetinkaya and Karaosmanoglu, 2005; Stevanovic et al., 2013; Özener et al., 2014; Yu et al., 2014). Moreover, researches have also systematically investigated the impacts of different alcohols on emissions from diesel engines by using fumigated or blended methanol (Zhang et al., 2010), ethanol (Zhu et al., 2010; Surawski et al., 2012; Guarieiro et al., 2014) and pentanol (Wei et al., 2014). Other oxygenated additives such as dimethyl carbonate (DMC), dimethyl ether (DME) and dimethoxy methane (DMM) are also considered as alternative choices to improve the diesel pollutants emissions, especially on the soot emissions (Arcoumanis et al., 2008; Rounce et al., 2010; Xu et al., 2013). Therefore, oxygenated fuels, such as biodiesel, alcohols, ethers and other oxygenated additives, can be promising alternative fuels for the diesel engines due to their low costs and positive contribution to the reduction of the soot particles.

Generally, the suppression effect of oxygenated fuels on soot formation is attributed to the oxygen content in the fuel. However, even if the blended fuels have similar oxygen content, their impacts on diesel particles are still different among each other, implying the importance of the oxygenated functional groups to the properties of the oxygenated fuels. Xu et al. (2013) and Song et al. (2006) investigated the oxidation reactivity of the exhausted particles derived from different oxygenated fuels with different oxygenated functional groups by using Fourier transform infrared spectroscopy and suggested that the different impacts among different oxygenated fuels on the chemical-physical characteristics of soot particles were associated with the oxygenated functional groups. Beatrice et al. (1998, 1999) investigated three types of oxygenated fuels, including ethers, glycolethers and alcohols. They also found significant differences on the combustion performance and sooting tendency among ethers, alcohols and glycolethers even if the oxygen content in the fuel are the same, and suggested that the molecular structures of the oxygenated fuels could also chemically affect the soot formation.

Nevertheless, there are still lack of investigations on the impacts of oxygenated fuels on the organic aerosols emissions from the diesel engines. The oxygenated functional groups or molecular structures might also play important roles on the decomposition and the formation of the organics during either the in-cylinder combustion or the out-cylinder heterogeneous reactions, such as the decomposition of the alkanes and the formation of the oxy-PAHs (Karavalakis et al., 2010a) and the nitro-PAHs (Miet et al., 2009). Therefore, more independent studies are needed to investigate and compare the emissions characteristics of the particle-phase compounds from the diesel engines when the engines are fueled with different oxygenated fuels. Based on this consideration, two oxygenated fuels with different oxygenated functional groups, namely, waste cooking oil biodiesel and ethanol, were selected as the target fuels to be blended with the diesel fuel by different blended ratios for the present work. The objective of this paper is to assess the effects of oxygenated fuels on the particle-phase compounds emitted from the diesel engine, involving both soot particles and organic aerosols.

2. Materials and methods

2.1. Test engine and fuel properties

The experiments were conducted on a naturally aspirated, water-cooled, 4-cylinder, direct-injection diesel engine. Although the engine is not the most advanced diesel engine, similar type of this engine is still in use on diesel trucks as well as most of the commercial engineering machineries all over China mainland and other developing countries. The specifications of the engine are shown in Table 1. The engine was connected to an eddy-current dynamometer and a controller was available for adjusting the engine speed and engine load. The base fuel used in this study was the commercial ultra-low sulfur diesel (sulfur, <10 ppm-wt), which could meet the limit of China V fuel regulation for the heavy-duty diesel vehicles, represented as D100 (diesel, 100%). Composition of the waste cooking oil biodiesel was measured using Agilent GC 7890A with FID and the method was described elsewhere (Man et al., 2015). Briefly, the biodiesel contains mainly methyl palmitate (C16:0, 11.5%), methyl oleate (C18:1, 35.2%), and methyl linoleate (C18:2, 39.7%). Furthermore, diesel was blended with different volume percentages of the biodiesel and ethanol, resulting in two series of oxygenated blended fuels, represented as DB20, DB50, DBE5, and DBE10. Meanwhile, 10% volume percentage of biodiesel was chosen as the co-solvent to help the blending process of diesel and ethanol, so DBE5 represents the blended fuel of 75% diesel, 10% biodiesel and 5% ethanol in volume percentage and DBE10 represents the blended fuel of 70% diesel, 10% biodiesel and 10% ethanol in volume percentage. The major properties of the test fuels are listed in Table 2. Two engine loads (25 and 75% of the maximum engine load) at a constant engine speed of 1800 r/min, at which the maximum torque output for this engine could be achieved, were chosen as the target engine operating conditions with the brake mean effective pressures of 0.2 and 0.6 MPa.

2.2. Experimental setup and analysis method

2.2.1. Experimental setup

Schematic diagram of the experimental setup is shown in Fig. 1. An insulated flexible tube, which was heated at around 150 °C to prevent thermophoretic deposition of particles and condensation of water and volatile organic carbon on the tube wall, was used to connect the exhaust pipe and the diluter. Through the tube, diesel exhaust gas was drawn into a two-stage diluter (Dekati® diluter) and was diluted by filtered and heated compressed air. The first-stage diluter was also heated at 150 °C to avoid the condensation of the water. After the first-stage diluter, the exhaust gaseous-particle phase compounds were cooled to 52 °C according to the EPA regulation for sampling procedures (Kittelson, 1998). Previous study has demonstrated that quartz filters would have substantial positive sampling artifacts during source sampling tests due to the unavoidable vapor adsorption (Robinson et al., 2010), while Teflon filters could have better property on sampling particle-phase pollutants. May et al. (2013) also pointed out that Teflon filters captured only particle-phase substances. Therefore, in the present study, the samples were collected by Teflon filters. The sampling flow rate was set at 25 L/min by controlling a flow rate valve, and the sampling duration time was varied from 10 to 30 min according

Table 1
Engine specifications.

Model	Isuzu 4HF1
Type	In-line 4-cylinder
Maximum power	88 kW/3200 rev/min
Maximum torque	285 Nm/1800 rev/min
Bore × stroke	112 mm × 110 mm
Displacement	4334/cc
Compression ratio	19.0:1
Fuel injection timing (BTDC)	8°
Injection pump type	Bosch in-line type

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