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Full Length Article

Effects of oxygenated fuel blends on the composition of size-segregated engine-out diesel particulate emissions and on the toxicity of quasi-ultrafine particles

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ABSTRACT

Reformulation of petroleum diesel through its blending with various oxygenated fuels has been explored for reducing emissions of diesel particulate matter (DPM). Such oxygenated fuel blends tend to alter the physico-chemical characteristics of DPM and its toxicity due to changes in the combustion chemistry, caused by the thermo-chemical properties of the oxygenated fuels. However, there is a lack of in-depth investigations on the changes in the chemical composition of size-segregated DPM and its related toxicity, especially for smaller particles, when the blended fuels are combusted in diesel engines. To fill this knowledge gap, we examined the effects of blending ultralow sulfur diesel (ULSD) with five different oxygenated fuels (diglyme (DGM), palm oil methyl ester (PME), dimethyl carbonate (DMC), diethyl adipate (DEA), and butanol (Bu)) at 2% and 4% oxygen levels on the carbonaceous composition of size-segregated engine-out DPM and the toxicity of quasi-ultrafine particles (quasi-UFPs, aerodynamic diameter $< 0.2\,\mu m$). The oxygenated fuel blends are effective in promoting soot oxidation in all size ranges and in reducing the total engine-out DPM mass concentrations, but lead to a significant increase in organic carbon (OC) fractions. Smaller particles had higher fractions of OC, particle-bound PAHs and n-alkanes, which varied with the type and content of oxygenates used. The blended fuels significantly affected the surface areas of both soot and volatile particles in the quasi-ultrafine size range, the cytotoxicity of the quasi-UFPs, and altered the global gene expression with a broad range of biochemical pathways due to the changes in the engine-out particle composition caused by the blended fuels.

1. Introduction

Diesel particulate matter (DPM) originating from both mobile and stationary sources is a major contributor to fine airborne particulate matter ($PM_{2.5}$) in urban atmosphere [1]. Exposure to these particles has been linked to an array of adverse short and long term health outcomes, including cardiopulmonary morbidity and mortality, and lung cancer mortality [2,3]. The blending of petroleum diesel with various oxygenates in the form of alcohols, ethers, carbonates and esters is getting a high priority as the fuel-bound oxygen in the blended fuels has benefits in suppressing soot formation and/or promoting soot oxidation during the combustion process, and therefore reducing the total DPM mass concentrations [4–7]. Since no threshold for DPM-induced adverse health effects has been established, there is a general consensus that an overall reduction of DPM mass concentration is likely to result in reduction of DPM-associated health risks.

However, the adverse health impacts caused by airborne particles are related to the contents of specific toxic species in them and their ability to enter the lungs which in turn depend on their chemical composition, particle size and surface area [8,9]. Elemental carbon (EC) and organic carbon (OC) with diverse functional groups account for a major fraction of DPM, and these carbonaceous components have adverse impacts on urban air quality, human health, and affect global climate change [6]. In particular, some semi-volatile hydrocarbons such as polycyclic aromatic hydrocarbons (PAHs) in DPM are associated with inflammatory potential, oxidative stress and mutagenic potential, and are suspected human carcinogens [6]. Additionally, toxic activities per unit mass of ultrafine particles (aerodynamic diameter $< 0.1\,\mu m$), such as the mutagenic activity and the redox activity, are significantly higher than those of larger particles [10] because of their distinct chemical composition, large lung-deposited surface area (LDSA), increased reactivity, and altered deposition, absorption, translocation, and elimination rates [10,11]. Therefore, emission reduction strategies that take into account the composition of size-segregated DPM rather than the

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Table 1
Properties of tested fuels [7].

Properties	Diesel	Palm oil methyl (PME)	Diglyme (DGM)	Dimethyl carbonate (DMC)	Diethyl Adipate (DEA)	Butanol (Bu)
Chemical formula	–	–	$C_6H_{14}O_3$	$C_3H_6O_3$	$C_8H_{14}O_4$	$C_4H_{10}O$
C wt%	86.6	76.6	53.7	40.0	55.2	64.9
H wt%	13.4	12.2	10.5	6.7	8.0	13.5
O wt%	–	11.2	35.8	53.3	36.8	21.6
Sulfur content, wt ppm	< 10	< 50	–	–	–	–
Aromatic content, wt%	0.6	–	–	–	–	–
Lower heating value (MJ/kg)	42.5	40	24.5	15.8	25.5	34
Heat of evaporation (kJ/kg)	270	300	322	369	295.1	585
Density (kg/m^3) @20 °C	830	875	940	1070	1005	810
Viscosity (mPa·s) @40 °C	2.8	4.6	2.0	0.63	2.5	1.8
Cetane number	52	67	126	35.5	15	17
Boiling point (°C)	185–345	300–350	161.3	91	127	78
Stoichiometric air-fuel ratio	14.7	11.3	8.2	3.5	7.5	11.2

DPM mass are deemed to be effective and efficient in mitigating the adverse health impacts of diesel exhausts.

In this context, the application of oxygenated fuel blends in diesel engines has the potential to alter the physico-chemical characteristics of DPM favorably due to the changes in the combustion chemistry, caused by the thermo-chemical properties of the oxygenated fuels. Although it is well known that a reduction of the mass of particles emitted does not directly imply a reduction of particle toxicity [7,8,12–14], it is no clear that (1) how the reduction of the particulate mass caused by different kinds of oxygenated blended fuels affects particle toxicity; and (2) what the altered particle properties are responsible for changes in the particle toxicity. Furthermore, no systematic field studies have been conducted yet on a comparative evaluation of changes in the chemical speciation of size-segregated DPM emissions, especially for the toxicity of ultrafine particles, when the petroleum diesel blended with oxygenated fuels is used in diesel engines. As a consequence, the potential health effects of DPM emitted from oxygenated fuel blends and the related mechanisms are largely unknown at this stage [2,3,10].

To address these knowledge gaps, we conducted a systematic study to make a comparative evaluation of the effects of blending ultralow sulfur diesel (ULSD) with five oxygenated fuels with different functional groups (DGM, PME, DMC, DEA, and Bu) at 2% and 4% oxygen levels on the carbonaceous contents of the size-segregated DPM (EC and OC) from an off-road diesel engine with no after-treatment technologies. The results shown in this preliminary study represent the direct engine-out DPM measurements. We selected PAHs and n-alkanes as appropriate chemical species of OC for further discussion as PAHs are suspected human carcinogens and n-alkanes represent an important class of the organic compounds originating from unburned fuel and/or lubricating oil. Determination of the concentrations of these species will improve our understanding of the influence of the blended fuels on the toxicity of DPM, and provide insights into how these blended fuels affect the DPM formation and chemical composition, which is vital in designing effective emission control technologies to protect public health. In addition, quasi-UFPs emitted from pure ULSD and from oxygenated fuel blends with 4% oxygen were chosen for the toxicity study as they contain higher fraction of organic compounds, and easily penetrate into cellular targets in the human pulmonary and cardiovascular system [10]. We exposed the human-type II cell alveolar epithelial cell line (A549) to quasi-UFPs derived from both oxygenated fuel blends and pure ULSD and assessed their cytotoxicity by using the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay. The cDNA microarray technique was then used to assess the changes in the expression of genes A549 in an attempt to gain an insight into the complex mechanisms that underlie the health effects induced by DPM from the oxygenated fuel blends in comparison with pure ULSD.

2. Materials and methodology

2.1. Engine and fuels

Experiments were conducted on a single-cylinder, naturally aspirated, four-stroke, direct injection diesel engine (L70AE, Yanmar Corporation) connected to a 4.5-kW generator. The diesel engine has a capacity of 296 cm^3 with bore and stroke of 78 mm and 62 mm, a fixed speed of 3000 rpm (revolutions per min). The reasons for choosing this system for this study are given in Supplementary information (SI). Experiments were performed at about 50% related engine power (2.1 kW). The main specifications of the engine and the schematic of the experimental system adapted in this study are given in Supplementary Table S1 and Fig. S1.

ULSD with less than 10 ppm by weight of sulfur was used as the baseline fuel. The PME used in this study was obtained from a palm oil-based biodiesel plant in Malaysia operated by Vance Bioenergy, while the other four oxygenated compounds (DGM, DMC, DEA and Bu) were purchased from Sigma-Aldrich. These oxygenates were blended with ULSD at 2 wt% and 4 wt% oxygen, which are correspondingly designated as PME2 and PME4 for PME-ULSD blended fuels, DGM2 and DGM4 for DGM-ULSD blended fuels, DMC2 and DMC4 for DMC-ULSD blended fuels, DEA2 and DEA4 for DEA-ULSD blended fuels, and Bu2 and Bu4 for butanol-ULSD blended fuels, respectively. The major properties of the fuels are provided in Table 1. More details have been reported in our previous study [7].

2.2. Particulate sampling and measurement

A two-stage, air ejector dilution system (Dekati mini-diluter, Dekati Ltd) was used for diluting the diesel exhausts for DPM sampling and for online measurement of the particle number size distributions. The dilution ratio for each stage was determined by simultaneously measuring CO_2 concentrations in the raw exhaust, in the background air and in the diluted exhaust, using a non-dispersive infrared analyzer (MRU VarioPlus, Germany, ± 0.5% accuracy). This measurement was done for every test, and all data presented in this article have been dilution-corrected to represent engine-out condition.

A Dekati gravimetric impactor (DGI, DGI-1570, Dekati Ltd.) was used for collecting size-segregated DPM from the first-stage diluter with a moderate flow volume of 70 lpm. The DGI includes four impaction stages and a backup filter, which can classify particles into five size ranges, namely $PM_{>2.5}$ (course particles with aerodynamic diameter (AED) > 2.5 μm), $PM_{2.5-1}$ (inter-modal particles with AED between 1 and 2.5 μm), $PM_{1-0.5}$ and $PM_{0.5-0.2}$ (accumulated particles with AED between 0.5 and 1.0 μm, and with AED between 0.2 and 0.5 μm), and $PM_{0.2}$ (quasi-UFPs with AED < 0.2 μm), respectively [15]. Previous studies have demonstrated that the DGI is a novel sampling system for physicochemical and toxicological characterization of DPM emissions