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A comparative analysis of chemical components and cell toxicity properties of solid and semi-volatile PM from diesel and biodiesel blend

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ABSTRACT

Alternative fuel has raised increasing attention in recent years for better fuel economy and emission reduction. The biodiesel fuel is natively produced from vegetable and animal oils with large number of organic compounds with varying groups and characteristics. Particulate Matter (PM) emissions from the biodiesel blend are often complicated by the volatility of the different organic components. We here report the chemical and toxicological characterization of solid-PM and semi-volatile PM (SV-PM) from diesel and biodiesel blend (BD30) exhausts, using front and backup filter, respectively. While total PM emission was lower for BD30 in general, it contained 19% higher organic compounds (OC) in SV-PM compared to diesel, which on the other hand noted 24% more solid-PM. These organic compounds were further analyzed with OCEC thermograph to confirm the dominant existence of highly volatile OC in SV-PM. We further extracted water-soluble components from the solid- and SV-PM samples, and subjected to RAW 264.7 macrophage cell exposure. More than 2-fold increase of oxidative potential was observed in SV-PM samples over solid-PM with elevated levels of cellular reactive oxygen species (ROS) and a significant correlation with OC concentration. Instead, non-cellular assay for ROS quantification showed the change in oxidative potential is greatly influenced by solid-PM. And non-cellular ROS due to SV-PM is 2-fold less than cell-based assay. Hence, the semi-volatiles, though produced in small quantities, need great attention in assessing health hazards and could well be a scope for further research.

1. Introduction

The greater demand of automobiles and feedstock for steadily increasing world population in the past century has resulted in the increased fossil fuel consumption. Though diesel fuel was generally preferred over gasoline for its reduction in greenhouse gases production (MECA, 2009), diesel exhaust has a dominant contribution to the atmospheric particulate matter (PM) pollution, especially in urban areas. It was also reported to cause myocardial damage and lung inflammation in long term (Brito et al., 2010; Libalova et al., 2016) and listed as Category I carcinogen by World Health Organization. In recent years, biodiesel with alternate fuels blended in diesel has been promoted as a means to reduce the emissions (Steiner et al., 2013). While vegetable oil has been often used as the source of biodiesel blend (Roy, Calder, Wang, Mangad, & Diniz, 2016), the high viscosity and low volatile nature of vegetable

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oils had been a concern for incomplete combustion. But its blending with diesel through transesterification process has been the common method to produce clean and environmentally friendly fuel (Roy et al., 2016; Xue, Grift, & Hansen, 2011). A 20% soybean biodiesel blend has been the mostly commonly used fuel (Xue et al., 2011), and earlier studies have reported of decreased NOx emissions in low biodiesel blends compared to pure form (Bari, 2014; Chattopadhyay & Sen, 2013; Fukagawa et al., 2013).

Although there are clear evidences of reduced production of HC and CO emissions from biodiesel exhaust (Lahane & Subramanian, 2015), there still exist concerns in the higher oxygen content of biodiesel and the resulting higher combustion rate (Lapuerta, Armas, & Rodríguez-Fernández, 2008) that may produce more polar and water soluble organics (Biswas et al., 2009; Qi et al., 2009) despite of the reduction in soot emissions (Surawski et al., 2011). The organic carbon, depending on the saturation vapor pressure of individual compounds, may partition between the gas and particle phases and form the semi-volatile particulate matter, which especially in engine exhaust emissions, poses a challenge to the evaluation of potential health impact associated with the PM emissions.

Earlier studies have reported varied health effects from diesel PM emissions via epidemiology and toxicological studies (Brito et al., 2010; Di, Cheung, & Huang, 2009; Jalava et al., 2010; Kooter et al., 2011), but still there are limited reports on the biodiesel emissions. The mechanism whereby PM affects health is believed to be through oxidative stress at cellular level and many studies have investigated on the oxidative potential of PM using abiotic methods (Biswas et al., 2009; Topinka et al., 2012), but it can't be accounted for particle/cell interactions for health-related outcomes.

This study investigates the differences in chemical composition of diesel and biodiesel blend (BD30 – 30% biofuel & 70% diesel fuel) fuel by analysing their elemental carbon, organic carbon, and polyaromatic hydrocarbons (PAHs) concentrations in PM emission across solid particulate phase PM (solid-PM) and semi-volatile PM (SV-PM). In addition, a sensitive macrophage cell-based (endogenous) DCFH-DA assay was employed to quantify the oxidative potential and cell toxicity due to both phases for comparison from the different fueled combustions, along with abiotic method (exogenous). An identical filter based-PM extraction procedures were applied for both the fuel types, assuming the occurrence of similar particle morphological changes while handling the samples.

2. Materials and methods

2.1. Filter collection system

The filter sampling was carried out in PolyU (The Hong Kong Polytechnic University) engine performance lab from October 2014 to February 2015. Four separate filter sampling setups were installed following dilution system from tail pipe exhaust as shown in Fig. 1. The tail pipe exhaust from diesel engine was directly injected into a dilution system where zero air and emission gas were well mixed. The dilution system consisted of a stainless steel chamber employed with sensors to measure CO₂ concentration from zero air inlet, engine exhaust gas inlet and outlet. The dilution ratio was maintained between 5.85 and 7.64 among all the collected filters. Of the 4 filters, two quartz filters (Whatman Inc., Maidstone, UK) were installed in 47 mm in-line filter holders (stainless steel, 2220, PALL Life Sciences, Ann Arbor, MI) on the left hand side of dilution system. Whereas, on the right side, a teflon filter (PALL Life Sciences, Ann Arbor, MI) was loaded in the front filter holder while a quartz filter was loaded in the filter holder behind. The ends of each side were connected to individual piston pumps (Nitto Kohki Co., Ltd, Tokyo, Japan) at flow rate of 10 lpm. The flow rates were checked and calibrated by flow meter (Drycall MI-500, USA) before and after each sampling point. The Q + Q and T + Q filter sets were employed representing Quartz front filter + Quartz backup filter and Teflon front filter + Quartz backup filter, respectively, to facilitate its utilization for varied analysis, and also to understand the pattern of particulate solid-PM and SV-PM collection on front and back filters, respectively.

2.2. Engine operating conditions and gravimetric measurements

Two types of fuel were used in this investigation – Esso Diesel and hybrid BD30. The hybrid fuel BD30 refers to a mixed fuel of biodiesel (Dynamic Progress International Limited, Hong Kong) and Esso Diesel in a volumetric proportion of 3:7. The diesel engine and its fuel burning conditions maintained in this study are as reported earlier by the author (Di et al., 2009). Four filters were

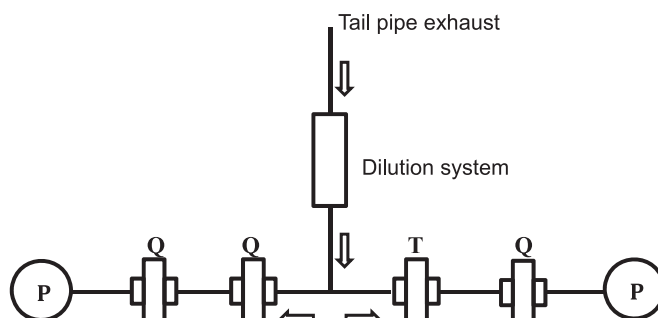


Fig. 1. Filter sampling system. The tail pipe exhaust from diesel and BD30 fuel, following the dilution system, were collected on two different filters sets: Q + Q and T + Q as denoted in the figure. While the front filters in the line collect particulate Solid-PM, the back filters collect gaseous SV-PM.

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