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Impact of high soot-loaded and regenerated diesel particulate filters on the emissions of persistent organic pollutants from a diesel engine fueled with waste cooking oil-based biodiesel

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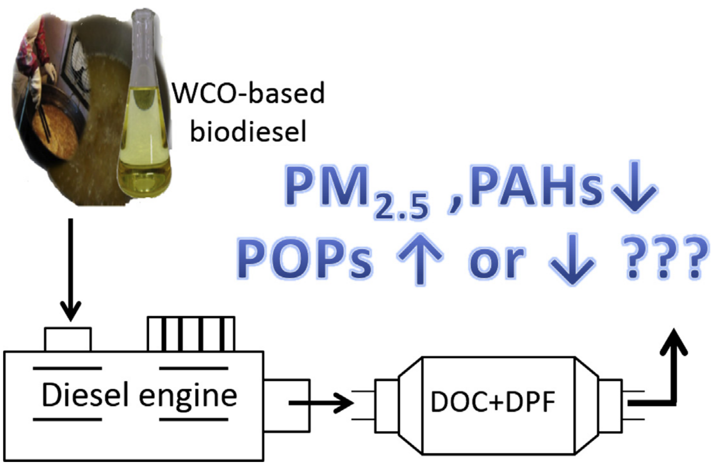
HIGHLIGHTS

- WCO-based biodiesel blends cannot stimulate POPs formation in uncatalyzed DPF.
- Formation mechanism of POPs in diesel engines is homogeneous gas-phase formation.
- The gas-phase POPs are highly dominant in the raw exhausts of diesel engines.
- The regeneration of the DPF can drastically reduce the formation potential of POPs in the DPFs.

GRAPHICAL ABSTRACT



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ABSTRACT

This study evaluated the impact on persistent organic pollutant (POP) emissions from a diesel engine when deploying a diesel oxidation catalyst (DOC) combined with an uncatalyzed diesel particulate filter (DPF), as well as fueling with conventional diesel (B2) and waste cooking oil-based (WCO-based) biodiesel blends (B10 and B20). When the engine was fueled with WCO-based biodiesel blends (B10 and B20) in combination with deploying DOC+A-DPF, their levels of the chlorine and potassium contents could not stimulate the formation of chlorinated POPs (PCDD/Fs and PCBs), although previous studies had warned that happened on diesel engines fueled with biodiesel and deployed with iron-catalyzed DPFs. In contrast, the WCO-based biodiesel with a lower aromatic content reduced the precursors for POP formation, and its higher oxygen content compared to diesel promoted more complete combustion, and thus using WCO-based biodiesel could reduce both $PM_{2.5}$ and POP emissions from diesel engines. This study also evaluated the impact of DPF conditions on the POP emissions from a diesel engine; that is, the difference

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in POP emissions before and just after the regeneration of the DPF. In comparison to the high soot-loaded DPF scenario, the regeneration of the DPF can drastically reduce the formation potential of POPs in the DPFs. An approach was developed to correct the effects of sampling artifacts on the partitioning of gas- and particle-phase POPs in the exhaust. The gas-phase POPs are highly dominant (89.7–100%) in the raw exhausts of diesel engines, indicating that the formation mechanism of POPs in diesel engines is mainly through homogeneous gas-phase formation, rather than de novo synthesis.

1. Introduction

Despite the many advantages that diesel engines offer, they are emission sources for various pollutants, including nitrogen oxides (NOx), sulfur oxides (SOx), particulate matter (PM), hydrocarbons and halogenated persistent organic pollutants (POPs) [1]. Moreover, a number of studies have shown conclusively that diesel engines constitute the dominant source of ultrafine-particle pollution in urban environments [2–4]. Furthermore, in 2012 the International Agency for Research on Cancer (IARC) identified diesel exhaust as a group 1 risk, due to the carcinogenic impact it can have on human health. Toxic and carcinogenic POPs present in the exhaust of diesel engines include PM, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) [5–7].

The World Health Organization (WHO) ambient air $PM_{2.5}$ guidelines (an annual mean of 10 $\mu g/m^3$ and a 24-h mean 25 $\mu g/m^3$), and the increasingly strict air quality standards for $PM_{2.5}$ that are being introduced in a number of countries [8–10], are putting greater pressure on the automotive industry and governments to reduce PM emissions from vehicular exhaust, and especially the fine particulate emissions from diesel engines. Various technologies have been developed and employed to achieve this, including engine innovations [11], aftertreatment devices, like diesel particulate filters (DPFs) [12,13], and the use of cleaner alternative fuels, such as bio-alcohol and biodiesel [14–18]. Among these technologies, DPFs are currently the most effective way to reduce the PM emitted from diesel engines, and can achieve a removal efficiency of greater than 99.8% for nonvolatile core and soot particles, with this result being uniform across all the particle-mode size ranges [13].

Initially, after installation, a DPF employs classical particle trapping mechanisms such as Brownian diffusion, interception, impaction by inertia and gravitational settling [11,19]. After a while a particle layer may develop to form a “cake” which then greatly improves the particle trapping through the phenomenon of cake filtration [11,20]. On the other hand, the overloaded soot has been shown to affect the performance of the engine, due to a high pressure drop, and can lead to clogging of the filter [21–23]. A DPF thus needs to be regenerated after it has been used for a period of time, and this is typically done using one of the following methods: (a) passive regeneration through noble metal-coated substrates or employing fuel borne catalysts (FBCs), which are added to the fuel to reduce the soot burn-out temperature and combust the accumulated soot in the filter [24], and (b) active regeneration through fuel combustion, full-flow burners and electrical devices [23,25].

Heeb et al. [26] tested a bimetallic iron/potassium FBC and found considerable PCDD/F formation (TEQ-based exhaust emissions increased by 51-fold) in an uncoated silicon carbide DPF when adding approximately 10 $\mu g/g$ of chlorine content to the diesel fuel. In a subsequent study, they tested an iron-catalyzed DPF, and found that fatty acid methyl ester (FAME) biofuel containing impurities of potassium also promoted PCDD/F formation (TEQ-based exhaust emissions increased by 23-fold), while the iron-catalyzed DPF remained inactive with commercial diesel fuel [27]. From these studies it is clear that when using a DPF, the presence of iron, potassium and chlorine in fuel can enhance the formation of PCDD/Fs. The role of chlorine on the formation of PCDD/Fs has been extensively studied and is well-known [28,29]. Compared to chlorine, the role of potassium on the formation of PCDD/Fs is seldom addressed. It is believed that potassium can induce the formation of magnetite (Fe_3O_4), which serves as an active catalyst in the Fischer-Tropsch process [27,30], and has a positive correlation with PCDD concentration, indicating catalytic activity for PCDD synthesis [31].

Waste cooking oil-based (WCO-based) biodiesel is obtained from transesterification of waste cooking oil with suitable alcohols in the presence of catalysts. Biodiesel produced from WCO may contain up to five times the chlorine content compared to fossil diesel [32], as well as high Na and K contents due to the salt used in food preparation, while the transesterification processes might also incorporate the KOH or NaOH used as catalysts [33]. Despite the higher chlorine and K contents, the use of WCO-based biodiesel can still reduce the amount of toxic POPs emitted from diesel engines. For example, B20 (80% diesel + 20% WCO-based biodiesel) could achieve 49–73% and 61–83% reductions in PAHs, PCDD/Fs, PCBs, PBDD/Fs and PBDEs based on mass and toxicity, respectively [32]. However, no studies have yet examined whether the use of WCO-based biodiesel combined with a DPF would increase the emissions of chlorine-substituted toxic pollutants from diesel engines.

The objectives of this study were thus to examine the effects on POP emissions when using different proportions of WCO-based biodiesel blends combined with DPFs. This study also evaluated the impact of DPF conditions on the POP emissions from a diesel engine; that is, the difference in POP emissions before and just after the regeneration of the DPF. In order to better understand the removal/formation mechanisms of POPs inside the DPF, an approach was developed for correcting for the effects of sampling artifacts on the partitioning of gas- and particle-phase POPs in the exhaust.

2. Materials and methods

2.1. Test fuel, diesel engine, DOC and DPF

The commercial diesel sold in all gas station in Taiwan, 98% conventional diesel + 2% biodiesel (2% biodiesel was added to conventional diesel fuel by regulation), was used as the base test fuel in this study, referred to as B2 (CPC Corporation, Taiwan). WCO-based biodiesel (B100, Greatec Green Energy Co., Ltd.) was blended with the B2 in volumes of 10% and 20%, and named B10 and B20, respectively, and these blends were also tested.

The experiments were conducted using a 6-cylinder, heavy-duty diesel engine in a direct-injection mode (Hino W06E), coupled with a dynamometer (Schenck W230) which was used to control the engine torque and speed. The engine had a 6-liter capacity