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Influence of an iron-based fuel-borne catalyst on physicochemical and toxicological characteristics of particulate emissions from a diesel engine

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HIGHLIGHTS

- Ferrocene-doped diesel fuels affect DPM characteristics.
- These fuels reduce EC and DPM emissions but increase both WSOC and OC in particles.
- They showed different effects on counts of nanoparticles and larger particles.
- They reduced the ignition temperature and activation energy of soot.
- They slightly increased the cytotoxicity of particles.

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ABSTRACT

Metal-based fuel-borne catalysts (FBCs) have been used with diesel fuels to effectively reduce soot and diesel particulate matter (DPM) emissions from both on-road and off-road applications. However, there is a lack of detailed investigations on the potential changes in the properties of particulates, when FBCs-doped fuels are combusted in diesel engines. This study fully evaluates the potential impacts of ferrocene-doped ultralow sulfur diesel (ULSD) fuels on physical, chemical and toxicological characteristics of the particulates emitted by a single cylinder, direct-injection diesel engine working at a constant speed and at three engine loads. The results indicated that ferrocene-doped fuels could effectively reduce the particulate mass and elemental carbon (EC) emissions, while increasing the proportion of both organic carbon (OC) and water-soluble organic carbon (WSOC) in particles. Particle-phase PAHs and n-alkanes emissions increased with an increase of Fe in the fuels. Ferrocene addition also led to lower soot ignition temperature and activation energy. However, the total number emissions of particles from ferrocene-doped fuels dramatically increased due to the formation of Fe-rich nuclei mode particles. Compared to pure ULSD, the particles emitted from ferrocene-doped fuels showed a slight decline in cell viability. The Fe in the particles and the changes in chemical composition of particulates are thought to be responsible for the variation of cell viability.

1. Introduction

Diesel engines have been widely used in both mobile and stationary applications due to their reliability, durability and high fuel efficiency. Diesel particulate matter (DPM) emissions represent a major contributor to urban carbonaceous aerosols, which have an adverse impact on local air quality and affect global climate change and also human health [1,2]. Modification of diesel engine combustion process and application of after-treatment technologies are critically needed for reduction of DPM emissions and thus mitigation of their influence on the atmospheric environment and human health [3]. Another solution under consideration is to add fuel-borne catalysts (FBCs) in the form of metal organic compounds, or nanoparticles to diesel fuels to suppress particle formation and promote in-cylinder soot oxidation [4–9].

Today, FBCs including Fe, Ce and Pt are commercially available, which have been used internationally in both on-road and off-road applications, although in the U.S., current regulations restrict their on-road use [10,11]. For example, in Europe, these additives have been developed in combination with diesel particle filters (DPFs) to ensure fast and complete regeneration, and to provide solutions that comply with current Euro 5 and Euro 6 requirements that take into account both regulated emissions and optimization of CO_2 emissions [11]. They can also be used without DPFs in retrofit systems for off-road equipment and commercial vehicles to reduce

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soot and DPM emissions [10]. Among these aforementioned FBCs, the soot-suppressing properties of dicyclopentadiene iron (ferrocene, $Fe(C_5H_5)_2$) are well-known from studies on different combustion systems [4]. Ferrocene is readily soluble in liquid fuels, air stable, relatively non-toxic, heat stable, inexpensive, and easy to handle [4,9]. Recent studies suggested that iron-based FBCs doped in diesel fuel and in biodiesel promote complete and more efficient combustion in the diesel engines, resulting in increased power, improved fuel economy and substantially reduced exhaust emissions containing as soot, carbon monoxide (CO) and hydrocarbons (HC) [7–9].

The use of ferrocene in diesel fuels may not only reduce DPM emissions, but also alter the physical characteristics and chemical composition of particulates including emissions of metallic nanoparticles [5,11–15], which might lead to changes in the overall toxicity of DPM. However, no systematic studies have been conducted to make a comprehensive evaluation of fundamental changes in the physico-chemical characteristics of particulate emissions resulting from the use of ferrocene in diesel and relate these changes to the toxicity of particulates in an integrated manner, to the best of our knowledge. In addition, it is still not clear how ferrocene-doped fuels affect particle toxicity and which chemical constituents of DPM are mainly responsible for its health effects. It should be noted that although the current knowledge regarding the influence of FBCs on diesel exhaust composition from vehicle engines is substantial, there are still scientific gaps in understanding the diesel exhaust composition in off-road diesel engines, such as generator sets. These engines are widely used, and emit a substantial fraction of DPM on a global level because they have limited emission control measures. For example, the US Environmental Protection Agency (EPA) estimates that non-road diesel engines contribute to about 44% of the DPM emissions nationwide [16].

The main goal of this study was to identify the impact of using different concentrations of the fuel-borne catalyst, ferrocene, on the characteristics of diesel engine particulate emissions from the protection of the environment and public health viewpoints, rather than estimate the combustion process. Combustion process parameters such as the flame temperature or combustion temperature in cylinder have been provided by previous studies [7,8], and therefore are not discussed in the current study. Apart from particle mass and number emissions, this work further examined the effects of the iron-base catalyst on the elemental carbon (EC), water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WISOC) composition of DPM. The variation of these compounds is important both in helping to elucidate the impact of the modified combustion process on the composition of carbonaceous aerosols and in its determining environmental effects [10]. We have selected appropriate chemical species such as PAHs and alkanes for the discussion as they are important constituents of organic aerosols. In addition, the effects of ferrocene on particle volatility and soot oxidation behavior were also examined since interactions between Fe and nucleation-mode particle formation as well as with the DPF regeneration performance remain poorly known [5,10]. Finally, in order to assess the impact of iron-based FBCs on the toxicity of DPM, cytotoxicity of particles emitted from both with and without ferrocene doped diesel fuel combustion was investigated. Thus, the current study represents the first attempt of its kind to fully evaluate the potential impact of ferrocene doped ultralow sulfur diesel (ULSD) on the physical, chemical and toxicological characteristics of DPM emitted by a single cylinder diesel engine under different load conditions. Results from these tests may offer better insights into the effect of iron-based FBCs on diesel particulate emissions, and prove to be useful for future assessments of environmental and health impacts of this kind of fuel additives.

2. Materials and methods

2.1. Test engine and fuels

A schematic of the experimental system employed in this study is shown in Fig. 1. Experiments were carried out 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 main specifications of the engine are shown in Table 1. The generator is connected with several resistance heaters, and the engine load is adjusted by the variation of the total resistance. Other similar small diesel engines have been used in [6–10,15] for investigating the influence of metal-based FBCs on engine exhaust emissions. ULSD with less than 10 ppm (parts per million) by weight of sulfur was used as a base fuel, the major properties of which have been reported elsewhere [17]. Experiments examined four concentrations of ferrocene in the fuel corresponding to 25, 50, 100, and 200 ppm Fe by weight. The method employed to add ferrocene to the fuel was similar to that used by Miller et al. [14] and Nash et al. [10]. Briefly, a known amount of analytical grade ferrocene (Sigma–Aldrich) was added to approximately 400 mL of diesel fuel in a beaker. This mixture was heated to 60 °C, stirred continuously for at least 30 min, and splash blended with the appropriate mass of diesel fuel to achieve the desired Fe concentration.

2.2. Particulate sampling and testing

A two-stage Dekati mini-diluter (DI-2000, Dekati Ltd.) was used for diluting the engine exhaust gas for DPM sampling. The diluter provides primary dilution in the range of 8:1–6:1, depending on the engine operating conditions, while the secondary dilution system provides a further dilution of 8:1. The actual dilution ratio was evaluated based on measured CO_2 concentrations in the raw exhaust, in the background air and in the diluted exhaust. The CO_2 concentration was measured with a non-dispersive infrared analyzer (MRU Vario Plus, 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.

DPM emissions from the first-stage diluter were collected onto 47 mm Teflon filters (Pall Life Sciences, Ann Arbor, MI) and precombusted (650 °C for 12 h) 47 mm quartz fiber filters (Whatman, USA), by using two Mini-Vol particulate samplers (Air metrics Ltd.; 5 L/min flow rate), respectively. Particles collected on the Teflon filters were used for gravimetric analysis and for toxicological analysis, while those collected on quartz fiber filters were processed for subsequent OC/EC and thermogravimetric

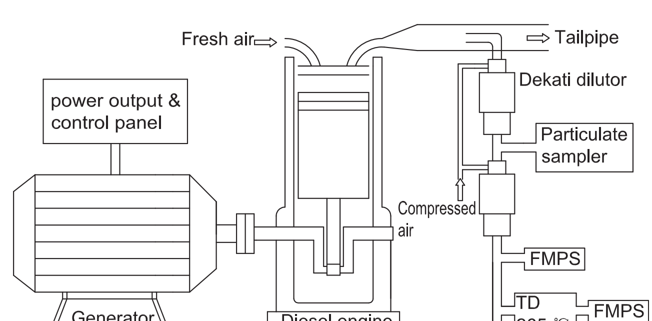

Fig. 1. Schematic of the experimental system (TD: thermal denuder; FMPS: Fast Mobility Particle Sizer).