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Effect of a homogeneous combustion catalyst on the characteristics of diesel soot emitted from a compression ignition engine

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HIGHLIGHTS

- The effect of a ferrous picrate catalyst on soot characteristics was investigated.
- Primary soot and aggregates from the catalyst treated diesel were smaller in size.
- The soot from the catalyst treated diesel possessed higher C/H and C/O ratios.
- The catalyst promotes fuel combustion, leading to less soot precursors.
- The catalyst actively accelerates the soot oxidation process.

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ABSTRACT

The effect of a ferrous picrate based homogeneous combustion catalyst (FPC), known to improve diesel combustion efficiency, on the morphological and chemical characteristics of diesel soot was studied in detail. Diesel soot samples emitted from a laboratory CI engine fuelled with a commercial diesel, with and without FPC doping, were collected and characterised using a combination of several advanced analytical techniques including a TEM fitted with EELS, an FT-IR, and a solid state ^{13}C NMR, in addition to elemental analysis. Compared to the soot from the reference diesel, the soot particle sizes of both primary soot and aggregates from the FPC treated diesel were consistently smaller and decreased with increasing FPC dosage. Both types of soot showed similar fractal dimensions, indicating that there were no apparent changes in the formation mechanisms of the primary soot particles and their agglomeration processes. Furthermore, the types of the carbon bonds and organic functional groups in the soot were virtually unaffected by FPC, as indicated by the similar degrees of graphitisation and indistinguishable chemical structures in the two types of soot. However, the soot from the FPC treated diesel showed slightly higher C/H and C/O ratios than those from the reference diesel. Based on these observations, it was speculated that FPC enhanced the diesel combustion process, leaving fewer soot precursors, and also promoted the oxidation of soot particles, resulting in smaller sizes of the primary soot and aggregates and reduced the overall soot emissions.

1. Introduction

The emissions of particulate matter, normally known as soot, from compression ignition (CI) engines are under increasing scrutiny because of its eminent risks to human health and the environment [1–3]. Literature reports have shown that the particle size, morphology and chemical composition of soot are directly related to their formation, transport, optical and deposition properties [4,5]. Generally speaking, diesel soot is chain-like clusters or aggregates of spherical-shaped primary particles, varying widely in size. The complex morphologies of soot can be described by fractal dimension [6]. In terms of chemical composition, soot is a solid carbonaceous substance formed in fuel-rich regions during the combustion of hydrocarbons, with unburned hydrocarbons, trace metals and sulphates absorbed on their surfaces [7].

It is widely accepted that during combustion, the formation of soot particles can be depicted in six sequential steps [6–9]: (1) upon intense heating, the pyrolysis of hydrocarbons takes place to generate unsaturated hydrocarbons, acetylenes and polycyclic aromatic hydrocarbons (PAH) as soot formation precursors; (2) the soot precursors nucleate to form larger PAH molecules; (3) the reactive surface of the nucleated soot particles continues to grow by attracting and interacting with gas-phase molecular fragments of hydrocarbons; (4) coagulation and coalescences of the large molecular fragments take place by collision to form spherical primary soot particles; (5) agglomeration of the primary particles occurs to form large aggregates with chain-like structures; and

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finally (6) the oxidation of the soot particles happens concurrently with the soot formation. In diffusion flames (such as those in CI engines), oxidation of soot occurs subsequently to the soot formation process. In CI engine systems, soot normally forms in fuel-rich regions with air deficiencies, and can also be viewed as an indication of poor combustion efficiency [10,11]. The actual soot formation process is complex and associated with many factors, such as fuel structure and composition, engine design, as well as the engine operation and environmental conditions.

To meet the increasingly stringent regulations, numerous efforts have been made to control the diesel soot emissions by modifying the engine systems, developing post-combustion treatment devices, and improving fuel formulations [2,12,13], or by combinations of these approaches. One effective alternative is to add a catalyst to the diesel fuel. The catalyst usually contains a metallic part to promote the fuel combustion and an organic part to make the catalyst soluble in diesel, thus the term homogeneous combustion catalysts (HCCs). Laboratory and modelling studies [14–17] have shown that the addition of trace amounts of such catalysts can significantly improve combustion efficiency and reduce pollutant emissions from CI engines. Some authors [18–20] have also claimed that these catalysts can be used in conjunction with diesel particulate filter (DPF) to help lower the soot oxidation temperature and thus facilitate the DPF regeneration process. In practical applications, HCCs generally feature the following characteristics: (1) they are commercially available, cost-effective, less-corrosive and chemically stable during storage and on-board usage; (2) they can be homogeneously dissolved in diesel fuel without phase separation, acting as catalytic agents to promote the combustion process with substantial fuel savings and emission reduction; (3) they are added to diesel at ultra-low ratios (ppm levels) with no discernible changes in fuel properties and minimal effects on fuel delivery line and injection system and other engine parts and (4) the use of HCCs does not introduce new harmful substances nor incur secondary pollutions to life and the environment [21].

Our previous work [22,23] has focused on an iron-based HCCs, called FPC with ferrous picrate as the active ingredient, capable of reducing up to 39% soot, 21% CO, 13% unburned hydrocarbon emissions and saving up to 4.2% brake specific fuel consumptions from a CI engine under the conditions tested. As the level of smoke emission was determined using an opacimeter [22,23], the measured reduction in the soot is lineally correlated with the particle number density in the exhausts. Therefore, the decreased smoke emission indicates that the total number of soot particles is also significantly reduced due to the use of FPC. Further analyses using a thermogravimetric analyser (TGA) and transmission electron microscopy (TEM) [24] showed higher oxidative reactivity and smaller primary particle size possessed by the soot from the FPC treated diesel. However, there is a lack of knowledge if the FPC addition would alter the detailed physical and chemical properties of the soot particles.

Understanding the characteristics of diesel soot is crucial for evaluating its impacts on human health and the environment [5] and, on the other hand, can also provide insights into the mechanisms of the catalyst in diesel combustion and soot formation processes. There are a number of analytical techniques available for soot characterisations. Transmission electron microscope (TEM) has been extensively used to ascertain the nanostructure and fractal properties of soot particles, as well as to determine the sizes and distributions of the primary soot and aggregates [25,26]. Chemical structure and elemental composition of soot have often been analysed using one or a combination of electron energy loss spectroscopy (EELS), Fourier transform infra-red spectroscopy (FT-IR), solid state nuclear magnetic resonance (NMR) spectroscopy and elemental analysers [27–29]. In the present work, a combination of all of the above analytical techniques was employed to provide more detailed and comprehensive information about the nature of the soot collected from the exhausts of a laboratory CI engine fuelled with a reference diesel and the FPC treated diesel. The detailed morphological, structural and compositional features thus revealed would allow a much improved understanding of the characteristics of soot, providing a thorough assessment of the influence of FPC in diesel soot formation process.

2. Experimental

2.1. Materials

A commercial diesel from a local service station (Caltex Australia) was used as the reference diesel. A ferrous picrate catalyst (FPC) was a homogeneous solution of ferrous picrate dissolved in a solvent mix including high alcohols, short-chain alkyl benzene and other aromatics [18–20]. The catalyst was added to the reference diesel at two dosing ratios, 1:10,000 and 1:1000 by volume. The three fuel samples were then tested in a laboratory CI engine, from which respective soot particles were collected and subjected to subsequent analysis and characterisation. For convenience, the reference diesel was denoted as “RD”, while the two catalyst-treated fuels were abbreviated as “FPC-D (1:10,000)” and “FPC-D (1:1000)”, respectively.

2.2. Test engine and soot collection

The engine and soot collection system have been reported elsewhere [24]. Briefly, a four-stroke, single cylinder, direct injection CI engine (YANMAR L48AE, AET Ltd.) was employed to generate the soot particles. The engine had a 70 mm bore, 55 mm stroke, 211 cm^3 displacement and compression ratio of 19.9:1. A Zöllner Type A-100, water cooled, electric dynamometer was coupled to the engine output shaft to provide the load conditions. During soot collection, the engine was maintained under steady-state with 2800 rpm speed and 5.5 Nm load (equivalent to 75% of the maximum load). Note that key objective of this work was to investigate the effect and mechanisms of FPC in soot formation and oxidation processes in CI engines and it was considered desirable to run the engine at a single operation point of 75% of maximum load to enable consistent sampling of the soot for detailed characterisation also consistent with our previous publication [24]. This is justified as the engine operating conditions would not significantly alter the catalytic mechanisms. When the engine was stabilised, a glass fibre filter paper (Whatman GF/A, 1.6 μm pore size) supported on a ceramic holder was inserted perpendicular to the exhaust path to collect bulk soot for three hours. The soot was scratched off the filter paper and stored in a desiccator for further analysis. For TEM imaging, the soot particles were directly sampled from the exhaust using a thermophoretic sampling technique as described elsewhere [24]. In brief, a 30 mm-long grid holder with TEM copper grids (200 mesh, holey carbon film coating) attached to the tip was inserted parallel to the exhaust stream by a step motor for rapid sample collection. Three samples were taken consecutively for each fuel run to ensure the repeatability of the subsequent sample analysis.

2.3. Analysis and characterisation

The morphological feature and size of soot particles were determined using a JEOL 2100 TEM operating at accelerating voltage of 120 kV and magnifications from 5000× to 50,000×. The images acquired were processed using DigitalMicrograph software (Gatan Inc.). These 2-D images were found to be sufficient to reveal 3-D