

# The Fate of Iron in a Homogeneous Diesel Combustion Catalyst in Compression Ignition Engines

Yu Ma\*, Mingming Zhu and Dongke Zhang

Centre for Energy (M473),  
The University of Western Australia, Perth WA 6009, Australia

---

## Abstract

This study reports a phenomenological and microscopic investigation into the evolution of the iron species in a ferrous picrate combustion catalyst during diesel combustion from a compression ignition (CI) engine. The experiments were carried out using a laboratory-scale CI engine fuelled with diesel, with and without the catalyst, to generate soot particles. The particles were collected and subjected to analyses using SEM, TEM and EDS. Results showed that iron from the catalyst was transformed to iron-decorated soot particles and scattered among the clusters of soot aggregates. Moreover, there were no iron signals found in the primary soot matrix, indicating that iron in the catalyst did not participate in the nucleation of the primary soot during diesel combustion and thus the absence of iron in the internal structures. Based on the observations, a formation pathway for the iron-decorated soot particles was proposed, in that, the ferrous picrate catalyst releases Fe atoms upon thermal decomposition to promote the fuel combustion and affects soot emission by changing the overall combustion environment without intrusively interacting with the formation of primary soot; Fe then condenses from the burnt gas and forms iron-decorated soot particles to be attached to large soot aggregates and included in the exhausts.

*Keywords: Compression ignition engine, Diesel soot, Homogeneous combustion catalyst, Iron, Morphology*

---

## 1. Introduction

Emissions of particulate matters from diesel combustion in the compression ignition (CI, diesel) engines, commonly known as diesel soot, are under increased scrutiny due to their high carcinogenic risk to human health and adverse impacts on ambient air quality [1-3]. Considerable efforts have been devoted to reducing soot emissions over the past decades, including modifications in fuel formulation, improvements in engine design and development in post-combustion treatment devices [1,4,5]. One of the effective approaches is the use of metal-based catalysts in diesel fuel. The catalyst normally contains a metallic part to promote the fuel combustion and an organic part to make the catalyst soluble in hydrocarbons, thus the term homogeneous combustion catalysts (HCCs). Laboratory and modelling studies [6-8] have shown that trace amounts of HCCs can significantly improve fuel combustion and reduce exhaust emissions. Our own work [9-13] have focused on an iron-based HCCs, with ferrous picrate as the active ingredient, which was capable of reducing up to 4.2% brake specific fuel consumption and 39.5% soot emissions in a diesel engine under the experimental conditions. Further analyses using a thermogravimetric analyser and transmission electron microscope (TEM) [11,12] have identified higher oxidative reactivity and smaller sizes of primary soot particles and aggregates possessed by the soot from burning the ferrous picrate treated diesel.

In order to improve the understanding of the role of the catalyst in soot formation and oxidation processes, a large number of studies [9-17] have been performed to

investigate how iron-based catalyst is emitted or incorporated in soot. Hahn et al [14] studied the effect of iron (as iron pentacarbonyl) on sooting process in a fuel-rich premixed propane/oxygen flame and employed X-ray photoelectron spectroscopy to analyse the collected soot particles. They found iron oxide nanoparticles in the early stage of combustion, which acted as nuclei to provide active sites for soot inception and nuclei deposition. Zhang and Megaridis [15] used a laminar ethylene/air diffusion flame to ascertain the effect of ferrocene during the soot formation process. With the assistance of TEM and energy-dispersive X-ray spectroscopy (EDS), it was found that fine iron fragments were incorporated in the carbonaceous soot matrix at the early stage of formation, which subsequently promoted the soot oxidation by a catalytic oxidation mechanism. Moreover, it is claimed by Wong [16] and Marsh et al [17] that the catalyst formulation, to a large extent, has a potential influence on the interaction mechanism of the metal and soot during diesel combustion processes.

Extending our previous work on the ferrous picrate based HCCs [9-13], the aim of this contribution was to investigate how the iron from the addition of ferrous picrate catalyst emitted in the exhausts after catalysing the diesel combustion processes. To this end, the study entailed doping the fuel supply with ferrous picrate to introduce the additional iron and using a laboratory-scale CI engine to generate the soot particles. Samples of these soot particles were collected and analysed using scanning electron microscope (SEM) and TEM in conjunction with EDS. The outcomes of this research have substantiated the transformation of the Fe species in the catalyst in diesel combustion process and provided

---

\* Corresponding author:  
Phone: (+61) 8 64885528  
Email: [yu.ma@uwa.edu.au](mailto:yu.ma@uwa.edu.au)

substantial evidence to understand the mechanisms of the catalyst in the overall soot formation process.

## 2. Experimental

### 2.1 Fuel and the catalyst

A commercial diesel was obtained from a local service station (Caltex Australia Ltd) and used as a reference fuel. The ferrous picrate catalyst (FPC) was provided by Fuel Technology Pty Ltd, which was a liquid solution with ferrous picrate dissolved in the solvent naphtha. In order to produce iron-rich particles, the catalyst dosage ratio of 1:1000 was used, which was ten times higher than the manufacturer recommended ratio. Adding this amount of the catalyst did not noticeably alter the fuel physical properties [9,10].

### 2.2 Sample collection

Soot samples were collected from the exhausts of a four-stroke, single cylinder, direct injection CI engine (YANMAR L48AE, AET Ltd.). The engine had 70mm bore, 55mm stroke, 211cm<sup>3</sup> displacement, compression ratio of 19.9:1. A Zöllner TypeA-100, water cooled, electric dynamometer was coupled to the engine output shaft for providing the load conditions. Details of the engine system have been reported elsewhere [9-11]. During the soot sample collection, the engine was maintained under a speed of 2800rpm and a load of 5.5Nm (75% of the max. load under the specified speed).

When the engine was stabilised under the above conditions, bulk soot particles were collected on a glass fibre filter paper (Whatman GF/A, 1.6 µm pore size) that was located in the exhaust path for 3h. Up to 5mg of each sample was then scratched off from the filter paper and transferred to the conductive tape on a stub for SEM-EDS analysis.

For TEM imaging, the soot particles were directly sampled from the hot exhaust stream using a thermophoretic sampling technique as described elsewhere [11,12]. In brief, the technique involved a 30mm-long grid holder with TEM copper grids (200 mesh, holey carbon film coating) attached to the tip, which was inserted parallel to the exhaust flow by a step motor for a rapid soot sample collection. Three parallel sample grids were taken for each fuel run to ensure the repeatability of the following analysis.

### 2.3 Analytical techniques

The morphology and local compositional information of the soot samples collected were revealed using a Zeiss 1555 SEM, equipped with a secondary electrons (SE) detector, a backscattered electrons (BSE) detector and an energy dispersive X-ray spectrometer (EDS, Oxford Instruments). The instrument was operated at an accelerating voltage of 10-15kV, a working distance of 3-16mm and a range of magnifications (from 5000× to 50,000×) for imaging.

The EDS elemental analysis was carried out at a 10mm working distance and an accelerating voltage of 15kV, and an integration time of 60s was employed to improve the signal to noise ratio.

The structural properties of the soot at a nanoscale were studied using a JEOL 3000F TEM equipped with a field emission gun with a point resolution of 0.16nm at an accelerating voltage of 300kV. High Angle Annular Dark Field Scanning TEM (HAADF STEM) images and EDS maps (using an Oxford Instruments detector) were used to locate the metals in the soot. High resolution TEM (HRTEM) analysis was also carried out to detect the internal structure of the soot particles. A Gatan 694 MSC digital camera was used to capture the images which were then processed using Digital Micrograph software (Gatan Inc).

## 3. Results and Discussion

### 3.1 SEM analysis

Soot samples from the reference diesel and FPC treated diesel were examined using SEM with the SE detector. For both cases, it was observed that the spherical-shaped primary soot particles, generally 20-30nm in diameter spatially coagulated together to form large soot aggregates, which grew into so called grape-like (aciniform) [2] or chain-like [3] clusters. There were no obvious differences in the surface morphology that could be discerned between the two soot samples from the reference diesel and FPC treated diesel. However, slightly smaller sizes of primary soot particles have been identified for the soot from the FPC treated diesel than that of the reference diesel soot as reported elsewhere [11,12], indicating that the FPC catalyst has influenced the sizes of the primary soot particles during the soot formation processes.

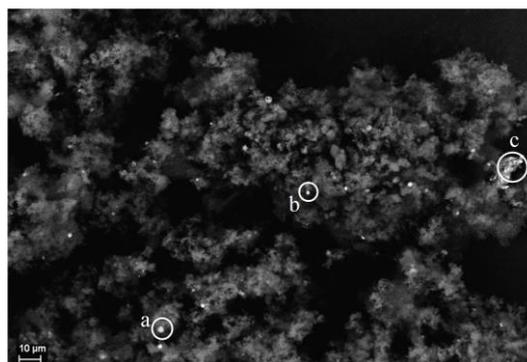


Figure 1 An SEM micrograph of soot particles from the FPC treated diesel

To locate Fe in the soot, the samples were examined with the SEM operating under the BSE detector mode, which produces contrast sensitive to atomic number *Z* variations [18]. In BSE images, metals with high *Z* values appear brighter compared to carbon, which enables the identification of the metal elements.

Results showed that no detectable signal of Fe was found in the soot particles from the reference diesel.

However, for the soot from the FPC treated diesel, elements heavier than carbon were captured, as displayed in the micrograph shown in Figure 1. It can be seen that the clusters of soot aggregates showed a gray-coloured carbon background in the micrograph, while the bright spots scattered among the gray soot backgrounds represented heavier elements than carbon. Three areas containing bright spots were randomly selected and subsequently analysed by EDS. It was found that the Fe peak was distinctly observable from the three areas, indicating that these bright spots were essentially iron-containing particles. The spot *c* where high Fe signal was captured was further examined by the SE imaging at a higher magnification to investigate the surface morphology. As shown in Figure 2, it was found that the Fe-containing particle in spot *c* featured with a smooth surface and a round edge (ca. 2  $\mu\text{m}$  in diameter) and was entangled with the surrounding soot particles, as marked by the arrow in the micrograph. Particles with this distinctive features were therefore named as “iron-decorated soot particles”.

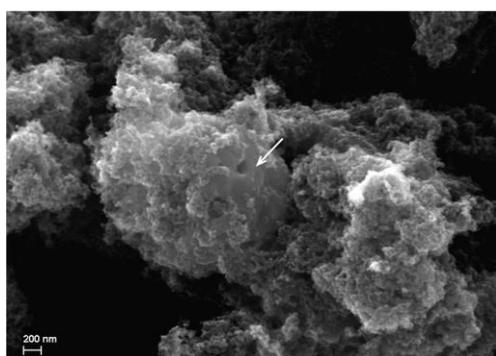


Figure 2 An SEM micrograph for the spot *c* marked in Figure 1 at higher magnification

### 3.2 TEM analysis

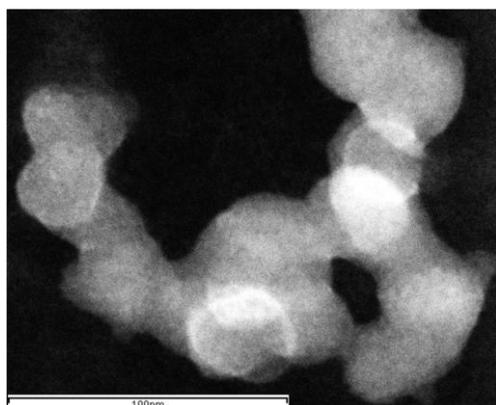


Figure 3 An STEM micrograph of typical primary soot particles in a soot aggregate from the FPC treated diesel

In order to determine if there was any elemental iron incorporated in the primary soot matrix, the soot particles from the FPC treated diesel were examined under TEM. The JEOL 3000F TEM was operated in HAADF-STEM mode. In this technique, the differences in the atomic number *Z* between metal and carbon allowed phase contrasts to be imaged by dark-field

imaging, and an EDS detector was employed to identify the metals when they were located.

Figure 3 displays a typical STEM image of the primary soot in a soot aggregate from the FPC treated diesel. It can be seen that the sample displayed a fairly uniform phase contrast, showing the carbonaceous nature of the soot particles. The EDS analysis of the sample confirmed that the primary soot matrix mainly contained carbon with no presence of Fe. The brighter region in the image was due to the overlapping of the primary soot particles.

Further analysis of the primary soot particle under HRTEM, as shown in Figure 4 (a) and (b), revealed a turbostratic graphitic crystalline structure with no discernible differences in the lattice spacing between the soot samples from the reference diesel and FPC treated diesel, respectively. All the sample grids were carefully examined by STEM and HRTEM and no Fe signals were detected in any primary soot matrix of the FPC treated diesel, which again confirms the absence of iron in the primary soot structure.

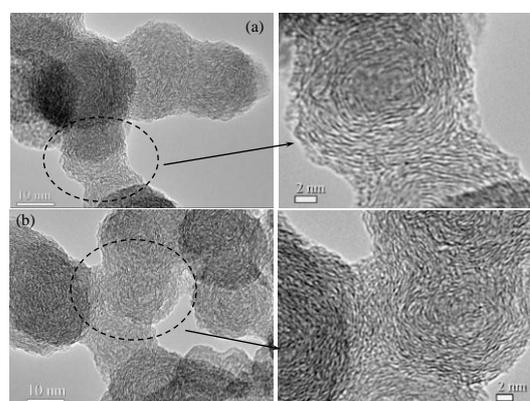


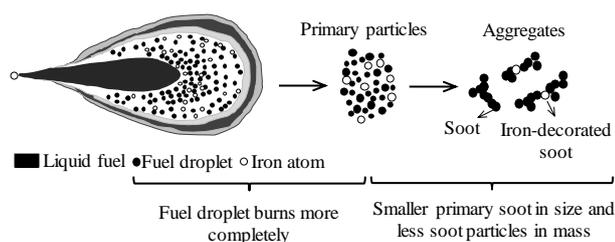
Figure 4 HRTEM micrographs of the primary soot from (a) reference diesel and (b) FPC treated diesel

The observations under both SEM and TEM verify that in diesel engine combustion, iron derived from the FPC catalyst was emitted together with the mature soot particles, without directly affecting the mechanisms of the initial formation of the primary soot particles. These iron-decorated soot particles have further catalytic activity to allow soot to be oxidised at lower temperatures and faster oxidation rates, which was confirmed by TGA tests in our previous study [12]. The possible formation pathway for these iron-decorated soot particles may be proposed as described below, which can also shed light on the interaction mechanism of iron and soot during the combustion processes in diesel engines.

### 3.3 Formation pathway for iron-decorated soot particles

Summarising the aforementioned discussion and interpretation of the present results, along with those reported in the literature, a plausible formation pathway has been proposed for the iron-decorated soot particles observed in engine exhausts, as schematically shown in Figure 5. As the FPC treated diesel fuel is injected into the combustion chamber at a high pressure and

temperature, a plume of fuel vapour with an internal temperature up to 1600K is formed [19]. The ferrous picrate decomposes at 523K [13], so it is reasonably deduced that the FPC thermally decomposes rapidly and ejects Fe atoms into the flame while the fuel droplets vaporise. The released Fe atoms enhance the hydrocarbon combustion, resulting in a higher peak cylinder pressure and faster heat release rate in the chamber [9]. In this changed combustion environment, the gas-phase hydrocarbon fragments burn more completely and form fewer soot nuclei, leading to smaller primary soot particles. In the later stage of combustion, the catalyst effectively accelerates the soot oxidation process, which is inferred by the lower ignition temperatures and higher oxidation rates associated with the soot from the FPC treated diesel, as reported previously [12]. Towards the end of the combustion cycle, Fe atoms condense from the burnt gas phase and form iron-decorated soot particles which were adsorbed onto the surface of large soot aggregates, as displayed by the morphology in Figures 1 and 2. Following the aforementioned mechanism, the fuel combustion in a diesel engine is substantially promoted by the FPC catalyst, resulting in lower fuel consumptions and less incomplete combustion pollutants including soot, as confirmed in our previous engine tests [9-12].



**Figure 5** A schematic showing the formations of iron-decorated soot particles during diesel combustion

#### 4. Conclusions

The ultimate fate of iron in a ferrous picrate based catalyst during CI engine combustion was investigated using a combination of several advanced microscopic characterisation techniques including SEM, TEM and EDS microanalysis. Results showed that the iron in the catalyst formed iron-decorated soot particles and was dispersed on the surface of soot aggregates in the exhausts. The analyses also revealed no sign of iron among the carbonaceous matrix of the primary soot from the catalyst treated diesel, indicating that the catalyst did not intrusively affect the early nucleation of the primary soot during the soot formation processes.

The evolution of iron in the catalyst during CI engine combustion was therefore proposed: upon thermal decomposition, the catalyst releases Fe atoms, which promote diesel combustion and accelerate the soot oxidation without directly affecting the formation of the primary soot, leading to fewer and smaller soot particles; then the iron atoms form iron-decorated soot particles and be attached to large soot aggregates in the exhausts.

#### 5. Acknowledgments

This research has been supported by the Australia Research Council under the ARC Linkage Projects Funding Scheme (Project ID: LP0989368) in partnership with Fuel Technology Pty Ltd and BHPBilliton Iron Ore Pty Ltd.

#### 6. References

- [1] A.C. Lloyd and T.A. Cackette, *J. Air Waste Manage.* **51** (6) (2001), pp. 809–847.
- [2] H. Burtscher, *J. Aerosol Sci.* **36** (7) (2005), pp. 896–932.
- [3] M.M. Maricq, *J. Aerosol Sci.* **38** (11) (2007), pp. 1079–1118.
- [4] W. Knecht, *Energy* **33** (2) (2008), pp. 264–271.
- [5] T.V. Johnson, SAE Technical Paper No. 2006-01-0030, 2006.
- [6] Z. Chlopek, A. Darkowski, L. Piaseczny, *Pol. J. Environ. Stud.* **14** (5) (2005), pp. 559–567.
- [7] G. Skillas, Z. Qian, U. Baltensperger, U. Matter and H. Burtscher, *Combust. Sci. Technol.* **154** (2000), pp. 259–273.
- [8] A. Keskin, M. Guru and D. Altiparmak, *Energ. Convers. Manage.* **52** (1) (2011), pp. 60–65.
- [9] M. Zhu, Y. Ma and D. Zhang, *Appl. Energ.* **91** (1) (2012), pp. 166–172.
- [10] Y. Ma, M. Zhu and D. Zhang, *Appl. Energ.* **102** (2013), pp. 556–562.
- [11] Y. Ma, M. Zhu and D. Zhang, *Appl. Energ.* **113** (2014), pp. 751–757.
- [12] D. Zhang, Y. Ma and M. Zhu, *Proc. Combust. Inst.* **34** (1) (2013), pp. 1869–1876.
- [13] M. Zhu, Y. Ma and D. Zhang, *Proc. Combust. Inst.* **34** (1) (2013), pp. 1537–1544.
- [14] D.W. Hahn and T.T. Charalampopoulos, *Proc. Combust. Inst.* **24** (1) (1992), pp. 1007–1014.
- [15] J. Zhang and C. M. Megaridis, *Proc. Combust. Inst.* **25** (1) (1994), pp. 593–600.
- [16] C. Wong, *Carbon* **26** (5) (1988), pp. 723–734.
- [17] N. D. Marsh, I. Preciado, E. G. Eddings, A. F. Sarofim, A. B. Palotas and J. D. Robertson, *Combust. Sci. Technol.* **179** (5) (2007), pp. 987–1001.
- [18] L. Reimer, *Scanning Electron Microscopy: Physics of Image Formation and Microanalysis*, Springer, 1998.
- [19] P. Flynn, R. Durrett, G. Hunter, A. Loye, O. Akinyemi, J. Dec and C. Westbrook, SAE Technical Paper No. 1999-01-0509, 1999.