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## Emissions from a Diesel Engine using Fe-based Fuel Additives and a Sintered Metal Filtration System

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### Abstract

A series of laboratory tests were conducted to assess the effects of Fe-containing fuel additives on aerosols emitted by a diesel engine retrofitted with a sintered metal filter (SMF) system. Emission measurements performed upstream and downstream of the SMF system were compared, for cases when the engine was fueled with neat ultralow sulfur diesel (ULSD) and with ULSD treated with two formulations of additives containing Fe-based catalysts. The effects were assessed for four steady-state engine operating conditions and one transient cycle. The results showed that the SMF system reduced the average total number and surface area concentrations of aerosols by more than 100-fold. The total mass and elemental carbon results confirmed that the SMF system was indeed very effective in the removal of diesel aerosols. When added at the recommended concentrations (30 p.p.m. of iron), the tested additives had minor adverse impacts on the number, surface area, and mass concentrations of filter-out (FOut) aerosols. For one of the test cases, the additives may have contributed to measurable concentrations of engine-out (EOut) nucleation mode aerosols. The additives had only a minor impact on the concentration and size distribution of volatile and semi-volatile FOut aerosols. Metal analysis showed that the introduction of Fe with the additives substantially increased Fe concentration in the EOOut, but the SMF system was effective in removal of Fe-containing aerosols. The FOOut Fe concentrations for all three tested fuels were found to be much lower than the corresponding EOOut Fe concentrations for the case of untreated ULSD fuel. The results support recommendations that these additives should not be used in diesel engines unless they are equipped with exhaust filtration systems. Since the tested SMF system was found to be very efficient in removing Fe introduced by the additives, the use of these additives should not result in a measurable increase in emissions of *de novo* generated Fe-containing aerosols. The findings from this study should promote a better understanding of the benefits and challenges of

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#### SUPPLEMENTARY DATA

Supplementary data can be found at <http://annhyg.oxfordjournals.org/>.

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using sintered metal systems and fuel additives to control the exposure of underground miners and other workers to diesel aerosols and gases.

### Keywords

aerosols; diesel exhaust; fuel additives; sintered metal filter; underground mining

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## INTRODUCTION

Diesel engines are one of the primary contributors to the presence of ultrafine and nano-aerosols in ambient air and occupational environments. Due to mounting concern about adverse health outcomes, extensive efforts are being made to reduce exposures of the general population and workers to diesel aerosols. Retrofit-type diesel particulate filter (DPF) systems are extensively used to reduce exposure of underground miners to aerosols emitted by diesel-powered vehicles. The systems made with sintered metal filter (SMF) media that are regenerated with help of the iron-based fuel borne catalysts (FBCs) and on-board electrical heaters are considered as a potential solution for curtailing emissions from underground mining vehicles operated over light- and medium-duty cycles (Stachulak and Hensel, 2010). The FBCs provide direct contact between catalyst and diesel particulate matter (DPM), and ameliorate the regeneration process.

With high toxicity and oxidative potential, metals containing nanoparticles are believed to be one of the contributors to overall toxicity of diesel aerosols (Sanderson *et al.*, 2014). The traditional sources of trace metals in diesel emissions are lubricating oil, engine wear, and aftertreatment wash-coat deterioration. Warner *et al.* (2003) estimated that trace metals from those sources typically contribute <1% to the total mass of aerosols emitted by diesel engines that are not equipped with exhaust aftertreatment devices.

An additional source of metallic aerosols is the combustion of fuels treated with organometallic fuel additives, also known as FBCs. The FBCs are used to improve the combustion process, decrease particulate mass emissions, increase fuel efficiency (Richards *et al.*, 2006; D'Urbano and Mayer, 2007), and/or to improve the regeneration of DPF systems by providing a nucleus for oxidation of soot trapped in the DPF element (Richards *et al.*, 2006). The DPF systems that use FBCs with base-metal and base-metal/platinum (Pt) formulations that did not show significant potential for oxidation of NO to NO<sub>2</sub> (Richards *et al.*, 2006; Czerwinski *et al.*, 2007) are of special interest to the underground mining and tunnelling industry, where *de novo* formation of NO<sub>2</sub> is one of the major concerns (Cauda *et al.*, 2010; Bugarski *et al.*, 2012).

The metals supplied to the combustion chamber by the fuel additives are linked to elevated emissions of metal-containing ultrafine and nano-aerosols (Richards *et al.*, 2006; Mayer *et al.*, 2010; Sanderson *et al.*, 2014). The emission rates of metals from engines supplied with FBCs are primarily a result of the catalyst dosing rate (Mayer *et al.* 2010) and type of exhaust aftertreatment. Combustion of diesel fuel treated with the Fe-based additive ferrocene was shown to induce high engine-out concentrations of aerosols with a mobility diameter <50 nm (Lee *et al.*, 2006; Richards *et al.*, 2006; Miller *et al.*, 2007). It was

suggested (Lee *et al.*, 2006; Miller *et al.*, 2007) that metallic additives at low, but above threshold, values promote formation of nucleation metallic nanoparticles and subsequent homogeneous and heterogeneous coagulation. In the case of ferrocene, the number and size of the self-nucleated nanoparticles were shown to increase with increased levels of dosing concentrations, and the nucleation threshold for Fe was linked to the available surface area of carbonaceous particles (Miller *et al.*, 2007).

The majority of DPF systems have been shown to be highly efficient in trapping metals originating from lubricating oil, fuel, and the use of FBCs (Hu *et al.*, 2009; Liati *et al.*, 2012). However, a very small fraction of the ash might penetrate the filter wall and may reach the atmosphere (Liati *et al.*, 2012). This is more likely to happen in clean DPF systems in the initial stages of DPF loading before the DPM cake is formed on the walls of the DPF element (Mayer *et al.*, 2010).

The study described in this article is designed to investigate whether a Fe-based FBC added to fuel at manufacturer-recommended rates (~30 p.p.m. of iron) might adversely affect the concentrations and characteristics of aerosols emitted by a naturally aspirated diesel engine retrofitted with a SMF system. With the goal of protecting worker health, it is important to gain this knowledge prior to wider implementation of these types of exhaust aftertreatment systems in confined spaces of underground mines and other occupational settings.

## MATERIALS AND METHODS

### Testing facility, exhaust aftertreatment, and fuels

The schematic of the laboratory layout used in this study is shown in Supplementary Fig. S1. A mechanically controlled, naturally aspirated, direct-injected diesel engine (Supplementary Table S1) was coupled to a water-cooled eddy-current dynamometer (Supplementary Table S2). The testing was done for four steady-state engine operating conditions (Supplementary Table S3) and one transient (TR) cycle (Supplementary Fig S2). The TR cycle was adapted from one that was designed to simulate operation of an engine in underground mining load-haul-dump vehicles. The 988-s cycle was repeated back-to-back multiple times during each of the several-hour-long tests.

The test engine was retrofitted with a full-flow SMF system (Mann + Hummel, M + H, SMF-AR<sup>®</sup>) previously tested in the underground mine (Stachulak and Hensel, 2010). The principal components of the SMF system are a filtration element, fuel additive dosing system, and electrical heater (Supplementary Fig. S3). Two iron-based fuel additives were evaluated in this study: (1) Satacen<sup>®</sup>, Innospec Ltd. (Cheshire, UK) marketed by M + H as DT8i and (2) Eolys Powerflex, Rhodia (La Rochelle Cedex, France) marketed by M + H as DT9. Three test fuels were prepared using ultralow sulfur diesel (ULSD) fuel from a single batch acquired from a local supplier: (i) baseline fuel (ULSD), (ii) baseline fuel treated with DT8i additive (ULSD + DT8i), and (iii) baseline fuel treated with DT9 additive ULSD + DT9. The baseline fuel properties are summarized in Supplementary Table S4. The ULSD + DT8i and ULSD + DT9 fuels were prepared by blending each of the additives with ULSD in 200-l barrels prior to transferring the fuels to the engine supply tank used during the tests. The ULSD + DT8i and ULSD + DT9 blends were obtained by adding 1.65 ml l<sup>-1</sup> of DT8i

and 0.61 ml l<sup>-1</sup> of DT9, respectively, as recommended by Mann + Hummel. The concentration of iron in samples of all three fuels and lubricating oil was determined using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyser and following the NIOSH Method 7300 (NIOSH, 2003). The iron concentrations in the ULSD, ULSD + DT8i, USLD + DT9, and lubricating oil were 1.2, 29.5, 26.2, and 2.5 mg kg<sup>-1</sup>, respectively.

### Sampling, measurement, and analytical methodology

The measurements and samplings were performed during 2-h EOut (engine-out) or 12-h FOut (filter-out) tests, respectively. The results were used to assess the net effects of the system and additives on aerosol and gaseous emissions. The aerosol sample collections and measurements were performed in the diluted exhaust that was consecutively drawn from the exhaust ports located upstream (EOut) and downstream (FOut) of the SMF systems (Supplementary Fig. S1). A two-stage partial dilution system (Dekati, Model FPS 4000) was used to dilute EOut and FOut exhaust ~30 times. Diluted exhaust temperatures after the second stage dilution were between 20 and 22°C.

A fast mobility particle sizer spectrometer (FMPS, TSI, Model FMPS™ 3091) was used to measure size distributions and total number concentrations (TNCs) of submicron aerosols in the diluted exhaust (Supplementary Fig. S1) for both steady-state and TR measurements. The FMPS distributions were fitted with log-normal curves using DistFit 2009 software from Chimera Technologies. The surface area of aerosols in the diluted exhaust that would theoretically be deposited in the alveolar region of human lungs was measured using a nanoparticle surface area monitor (NSAM) (TSI, Model 3550) (Fissan *et al.*, 2007). Total mass concentrations of aerosols in the EOut and FOut diluted exhaust were continuously monitored using a tapered element oscillating microbalance (TEOM) ambient mass monitor (Model TEOM 1405; Thermo Scientific, Franklin, MA). The sampling flow rate was set at 2.0 l min<sup>-1</sup>.

Elemental carbon concentrations (ECCs) in the diluted EOut and FOut exhaust were determined using results of carbon analysis performed on the sample concurrently collected on three sets of tandem 37-mm quartz fiber filters (QFFs; Pall Science, QAT2500). The QFFs were pre-fired at 600°C to minimize filter media contamination and sealed in tandem configuration in the five-piece cassettes (SKC, SureSeal). The five-piece cassettes are used to allow for uniform deposition of the sample on QFFs. Critical orifices (BGI Inc., Model S02) and vacuum pumps (Leybold, SV25b) were used to maintain a constant nominal sampling flow rate of 12 l min<sup>-1</sup> through each of the cassettes. The sampling flow rates were established as an average between measurements performed using a bubble flow meter (SensiDyne, Gilian Gillibrator-2) prior and after the sampling. In the case of the tests used to collect EOut samples, the sampling times were 120 min. In an effort to increase the amount of material on the sampling filters, the sampling times for FOut tests were extended to 720 min. The primary and secondary filters were analysed individually for EC carbon content by the NIOSH OMSHR laboratory using a thermal optical transmittance-evolve gas analysis (TOT-EGA) following NIOSH Method 5040 (NIOSH, 1999). The results performed on three blank samples were used for each group of samples to correct for background

contamination. For I50, I100, and TR engine operating conditions, the average concentration of Fe was determined by analysing filter samples of diluted exhaust collected concurrently onto three sets of tandem 37-mm-diameter, 0.8- $\mu\text{m}$  pore, mixed cellulose ester (MCE) filters. The concentration of Fe in samples was determined using ICP-AES (Spectro, Model Analytical-ICP-AES CIROS) and the NIOSH method 7300 (NIOSH, 2003).

The effects on particle morphology and size-resolved elemental composition were studied on the EOut and FOut samples collected for I50 and I100 steady-state engine operating conditions. Samples for electron microscopy (EM)/energy dispersive spectroscopy (EDS) were collected using an electrostatic precipitator (ESP) (Miller *et al.*, 2010) and a thermophoretic precipitator (TPP) sampler (Miller *et al.*, 2012). The 3-mm-diameter disks made with four different media types were used to sample diesel aerosols. Carbon-filmed EM grids were selected for imaging for their superior transmittance and quality of images. The samples for EDS analysis were collected on three types of carbon-free media, SiO-filmed EM grids, metallic foil (copper), and pure silicon. Samples were analysed using EM and EDS. High-resolution EM was performed using a scanning transmission electron microscope (STEM), either a Hitachi 5500 STEM or Hitachi 2300 STEM, equipped with an EDS system. This system allows for obtaining elemental maps for the samples collected on EM grids with 10–20 nm resolution. Samples collected on foils and silicon media were analysed using a field emissions scanning electron microscope (FESEM, Hitachi S-5500). The basic EM analysis of each sample provided qualitative assessment of the sample and a number of images to show typical particle morphologies. In addition, the EDS spectra were generated for a few particles of different morphologies, to investigate whether different morphologies had different metal/carbon ratios.

## RESULTS AND DISCUSSION

The effects of the fuel additives and SMF system on emitted aerosols were assessed by using the results of various measurements performed in the diluted exhaust. To compensate for slight test-to-test variations in dilution rate (DR), the results were normalized to a DR of 30. The averages of the results obtained using direct measurements with FMPS and NSAM were calculated using data recorded during the last hour of each test. The standard deviations of means were included to show variability between individual tests.

The effects of SMF system and fuel additives on TNC in diluted EOut and FOut exhaust were assessed using the results of FMPS measurements for four steady-state and one TR tests.

Results show that, for all test conditions, the SMF system reduced the average TNC emitted by the test engine by more than 100-fold (Fig. 1a). The additives did not induce any substantial change to the overall effectiveness of the SMF system (Fig. 1a). The effects of additives on EOut TNC were found to be dependent on engine operating conditions (Fig. 1b). For I100, DT8i had adverse and DT9 had favourable effects. The indications were that the additives had an adverse effect on FOut TNC (Fig. 1b). Due to very low FOut TNC, the importance of these changes was relatively minor.

In general, the SMF system had a profound effect on the size distributions of aerosols. The EOut aerosols were primarily distributed in accumulation modes with the count median diameters (CMDs) ranging between ~50 and 70 nm (Fig. 3a and Supplementary Table S5). The CMDs of the EOut aerosols in the accumulation mode were found to be in the following ascending order: R50, R100, I50, and I100. Depending on test conditions, the FOut size distributions were single-modal or bimodal (Fig. 2b and Supplementary Table S5). The FOut aerosols were distributed between accumulation and nucleation modes. The CMDs for aerosols in FOut accumulation modes were consistently higher than the corresponding CMDs for aerosols in EOut accumulation modes, ranging between ~60 and 95 nm (Supplementary Table S5). The relatively minor increase in the concentration of FOut nucleation mode aerosols observed for the R100 and I100 ULSD cases could be linked to penetration of hydrocarbon-rich gases through the system under high exhaust temperature operating conditions and subsequently nucleation of those downstream of the system and to penetration of iron-rich solid aerosols potentially sourced to FBCs.

The effects of the additives on the size distributions of EOut and FOut aerosols were relatively minor and, in general, less pronounced than the effects of the SMF and engine operating conditions. The results show that the DT8i and DT9 additives, when added at the recommended concentrations, had a relatively minor impact on the size distribution of EOut aerosols (Fig. 2a, Supplementary Table S5). For all test conditions, the CMDs for the EOut accumulation mode aerosols were slightly smaller when the engine was fueled with ULSD + DT8i than with the other two fuels. In the case of ULSD and ULSD + DT9, the EOut accumulation mode CMDs were similar. Only in the case of the ULSD + DT9 I50 test did the FMPS measurements indicate some presence of EOut aerosols distributed in nucleation mode, with the CMD of 13 nm (Fig. 2a and Supplementary Table S5). In several cases when the treated fuels were used (ULSD + DT8i R50, R100, I50, and ULSD + DT9 I100) the FMPS measurements indicated some presence of FOut aerosols in nucleation mode. Total and peak concentrations of nucleation mode aerosols (Fig. 2b, Supplementary Table S5) were substantially lower than corresponding total and peak concentrations of accumulation mode aerosols. Apparently, the use of additives at those relatively low dosing rates did not result in high increases in EOut and FOut concentrations of nucleation mode aerosols previously observed by other researches for generally higher dosing rates (Lee *et al.*, 2006).

DR-normalized data collected with a nanoparticle surface area monitor (NSAM) were used to assess the effects of the SMF system and additives on total surface area concentrations (TSACs) of aerosol deposited in the alveolar region of lungs. For all test conditions, the SMF reduced the average TSAC of aerosols by 100-fold. For all but a few cases, the additives slightly reduced EOut TSAC and contributed to slightly higher FOut TSAC. As a result, for all but R50 conditions, the additives had barely quantifiable adverse effects on the effectiveness of the SMF system.

The results of the TOT-EGA carbon analysis were used to assess the effects of the system and additives on ECC, respectively. The FOut ECC were found to be very low at, or in, a number of cases, even below the level of quantification (LOQ) of TOT-EGA analysis ( $0.1 \mu\text{g m}^{-3}$ ). Therefore, the calculated effectiveness of the system in removal of ECC, shown in Fig. 3, should be treated as an estimate. The ECC results corroborate TNC and TSAC results

and confirm that the SMF system was very effective in removal of diesel aerosols (Fig. 3a). With the exception of one case (ULSD + DT9, R100), the additives had favourable effects on concentrations of EOut ECC.

The presence of Fe in aerosol samples was studied using results of ICP-AES analysis performed on EOut and FOut aerosol samples collected for I50, I100, and TR conditions (Fig. 4).

For all three test conditions, the introduction of Fe with DT8i and DT9 additives substantially increased Fe concentration in the EOut aerosols samples. For all three tested fuels, the Fe concentrations in the FOut samples were found to be below the LOQ of applied ICP-AES analysis ( $2 \mu\text{g m}^{-3}$ ). The FOut Fe concentrations for all three tested fuels were found to be much lower than the corresponding EOut Fe concentrations for the case of untreated ULSD fuel. Therefore, it can be concluded that for all test conditions, the SMF system effectively removed Fe aerosols including those originating from the fuel and lubricating oil and those introduced with the additives.

EM and EDS were used to discern the influence of tested Fe-based fuel additives on the morphological and chemical properties of EOut and FOut aerosols. One of the objectives was to investigate if metals introduced with additives could trigger the formation of metal-rich particles during the combustion process, and whether those would penetrate the filtration system and therefore be emitted into the atmosphere.

The EOut aerosols emitted by the test engine fueled with ULSD were found to have primarily fractal-like diesel agglomerated structure (Fig. 5a). This is in general agreement with results previously reported in the literature for aerosols emitted by diesel engines (Park *et al.*, 2004; Mathis *et al.*, 2005; Lapuerta *et al.*, 2007; Mustafi and Raine, 2009). The general morphology of the EOut aerosols was not discernibly affected by the additives and engine operating conditions. Many of the agglomerates collected when fuels treated with the additives were used contained small 'nuggets' of iron-rich material. This suggests that the ratio of iron to carbon during the post-combustion phase was at or above a threshold that would trigger self-nucleation of iron as described in a previous study (Miller *et al.*, 2007). Under one test condition (I50-DT9), the nucleation of iron was prominent enough to produce a separate population of iron-rich nanoparticles (Fig. 5b), which appears as a small nucleation mode in the data of Fig. 2a. EM and EDS analysis of samples from that engine condition verified the existence of iron-rich spherical nanoparticles.

The image analysis software (AnalySIS; Soft Imaging System Inc.) was used to isolate and measure the size of individual particles in agglomerates. For EOut samples, between 15 and 56 primary particles were measured per agglomerate. The primary particle sizes were easiest to ascertain for ULSD samples. The ULSD particle images were the most fractal and the boundaries between individual particles were relatively easy to identify. The ULSD + DT8i and ULSD + DT9 particles were slightly more compacted and therefore it was more difficult to accurately discern primary particle size. The statistical parameters including CMD,  $\sigma$ , and TNC for those distributions are summarized in Table 1.

The CMDs of primary particles observed in this study (29–38 nm) are at the upper part of size ranges of those found for different engines and engine operating conditions by Mathis *et al.* (2005) [17.5–32.5 nm], Müller *et al.* (2006) [25 nm], Neer and Koylu (2006) [28–34 nm], Lapuerta *et al.* (2007) [18–30 nm], and Mustafi and Raine (2009) [25–30 nm]. In all cases, the mean size and number of primary particles were equal or greater for I100 than for I50 conditions.

The EM analysis of FOut samples confirmed that the relatively few (compared to EOut) particles in the post-aftertreatment exhaust were distributed between (i) nucleation and (ii) agglomeration modes. The agglomerated FOut aerosols had a similar morphology to the corresponding EOut aerosols and were possibly a result of minor blow-by caused by imperfections in the filter construction. The nucleation mode particles were typically low-density particles that varied widely in morphology and composition, postulated to have formed from semi-volatile compounds that penetrated the filter as gases and subsequently self-nucleated.

## CONCLUSIONS

The study showed that the SMF system was very effective in reducing TNC (>99%), TSAC (>99%), and ECC (>99%) emitted by the test engine. The results of ICP-AES analysis showed that the system was also very efficient in removing Fe-containing aerosols from the exhaust. When added at the recommended concentrations, the additives had only a minor effect on the size distribution of aerosols emitted by the engine and by the SMF system and on the concentration and size distribution of nucleation aerosols emitted out of the SMF system. The results of ICP-AES analysis showed that in all cases when fuel was treated with the additives, the FOut concentrations of Fe in aerosols were at non-detectable levels and below those determined for aerosols emitted by the engine supplied with untreated fuel. Therefore, the great majority of Fe supplied by the additives should be trapped in the filter media and by design should catalyse the SMF regeneration process.

The results of this study indicate that the system and additives, if used in conjunction and in the recommended fashion, should not introduce significant additional quantities of *de novo* pollutants in the underground environment. However, further toxicology studies on the FOut aerosol samples would be needed to support a more definitive health-related conclusion. The results indicate that those relatively minor increases in the concentration of FOut nucleation mode aerosols can be attributed to the increase in both: (i) the concentrations of aerosols formed via heterogeneous and homogeneous nucleation of hydrocarbon-rich gases downstream of the system and (ii) the concentrations of iron-rich solid aerosols potentially sourced to FBCs. The results of ICP-AES and EM/EDS analyses showed that the additives substantially contributed to Fe concentration in the EOut aerosols samples. Therefore, in order to prevent the release of potentially hazardous iron-rich aerosols into the environment, these additives should not be used in diesel engines that are not equipped with full-flow filtration systems.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

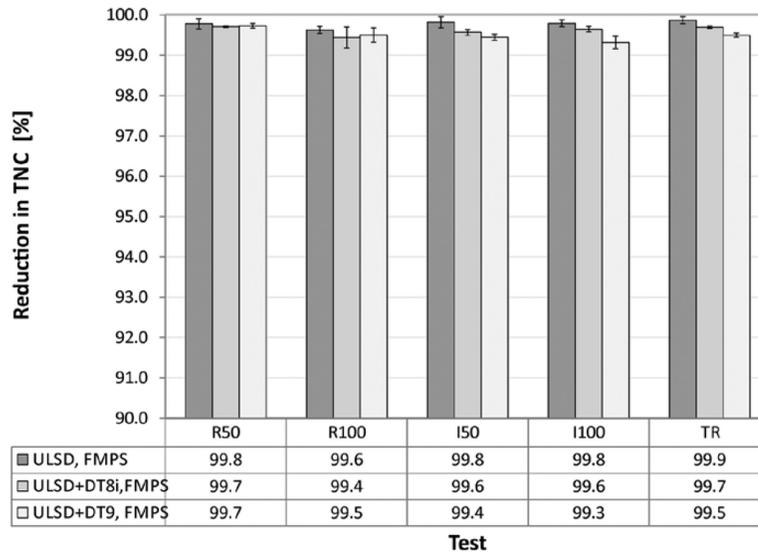
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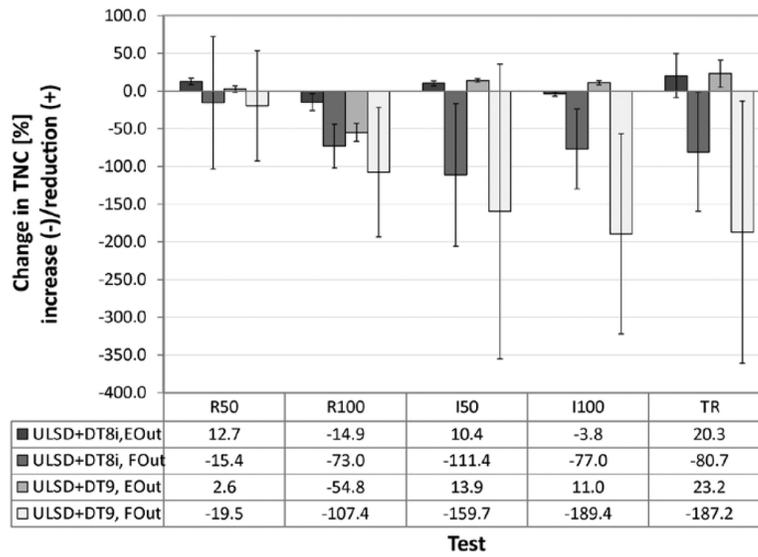
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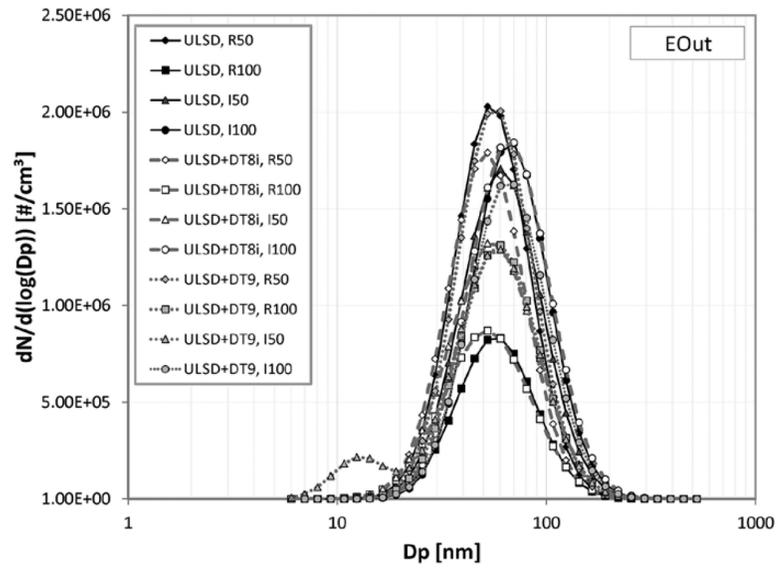


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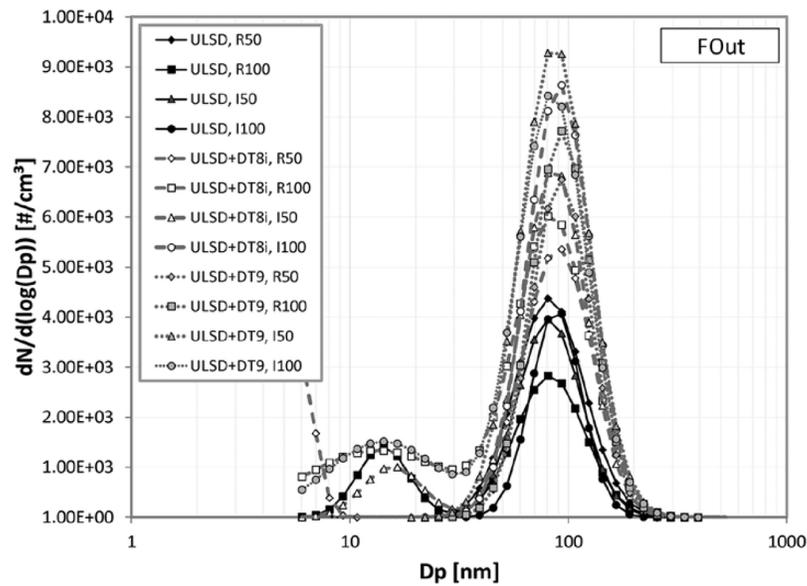


b

**Figure 1.** (a) Effects of SMF system on TNC and (b) effects of fuel additives on EOut TNC and FOut TNC (changes are given with respect to the ULSD case).

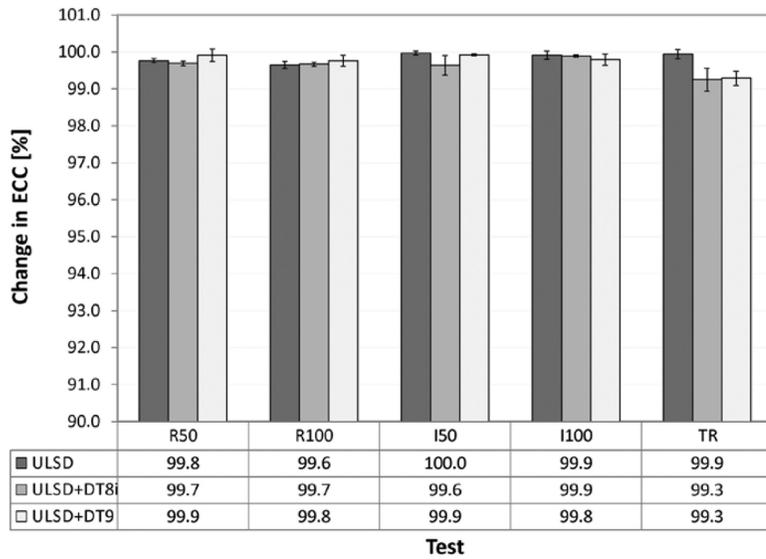


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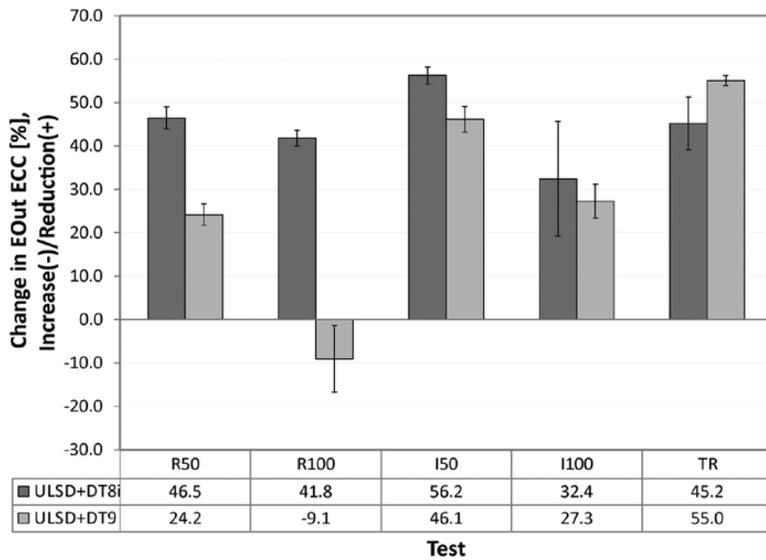


b

**Figure 2.** Size distributions of aerosols measured with FMPS for steady-state operating conditions in the diluted (a) EOut and (b) FOut exhaust.

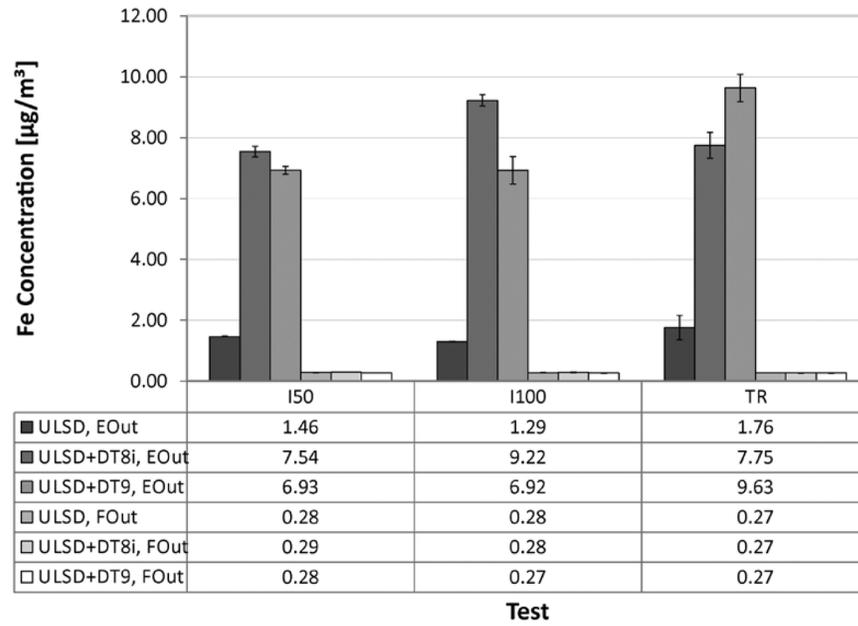


a

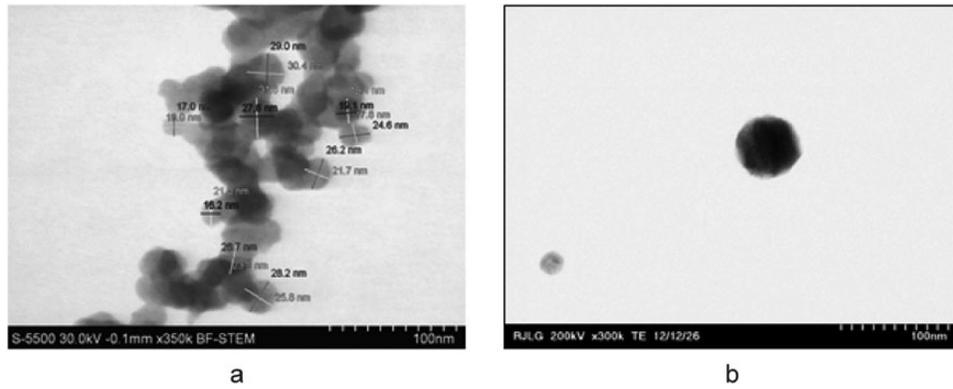


b

**Figure 3.** (a) Effects of SMF system on ECC and (b) effects of fuel additives on EOut ECC.



**Figure 4.** Fe concentrations in the diluted (DR = 30) EOut and FOut exhaust for I50, I100, and TR conditions.



**Figure 5.**

(a) Typical morphology of EOut particles emitted by the test engine fueled with ULSD + DT8i and operated at I50. Note: Image created intentionally using ‘dark field’ TEM to highlight the bright spots, which represent higher density, and were shown with EDS to be iron-rich. (b) Typical iron-rich nucleation mode particles emitted by engine fueled with ULSD + DT9 and operated at I50.

**Table 1**

Primary particle statistics.

Fuel	Mode	CMD	$\sigma$	TNC
		nm	—	#/agglomerate
ULSD	I50	32.5	1.370	39
	I100	32.7	1.374	39
ULSD + DT8i	I50	28.9	1.434	45
	I100	35.0	1.292	57
ULSD + DT9	I50	31.7	1.243	28
	I100	38.2	1.337	41

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