Driving Down On-Highway Particulate Emissions

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Abstract

It has been reported that particulate emissions from diesel vehicles could be associated with damaging human health, global warming and a reduction in air quality. These particles cover a very large size range, typically 3 to 10 000 nm. Filters in the vehicle exhaust systems can substantially reduce particulate emissions but until very recently it was not possible to directly characterise actual on-road emissions from a vehicle. This paper presents the first study of the effect of filter systems on the particulate emissions of a heavy-duty diesel vehicle during real-world driving. The presence of sulfur in the fuel and in the engine lubricant can lead to significant emissions of sulfate particles < 30 nm in size (nanoparticles). We have demonstrated that when using low sulfur fuel in combination with a uniquely formulated low sulfur lubricant and a suitable filter system that the particulate emissions of a heavy-duty vehicle were reduced to the levels already present in the ambient environment.

PM emissions and diesel particulate filter (DPF) technology

Diesel Particulate Matter (PM) consists primarily of carbonaceous soot and a Volatile Organic Fraction (VOF) composed mainly of hydrocarbons with lesser amounts of nitrate and sulfate species. It is becoming increasingly recognised that PM emissions from diesel-powered vehicles may have adverse environmental effects. For example, it was proposed that the elemental carbon fraction can increase global warming effects. In addition, the medical community is closely examining the effects of PM on human health as a function of particle size. Reports in scientific literature suggest that there is a link between environmental exposure to fine particles less than 2.5 \( \mu \text{m} \) in size to adverse health effects. These studies elucidated a range of causal mechanisms but have not developed a quantitative understanding of their relative importance. Studies that are more recent investigated the hypothesis that ultrafine particles <100 nm in size are detrimental to human health. It has also been reported that the relationship between ultrafine particles and health may be at least partially due to the high efficiency of particle deposition in the respiratory tract for the very small particles (Alveolar deposition is highest for particles approximately 20 nm in size).

Regulatory agencies such as the U.S. Environmental Protection Agency (EPA) have adopted mass-based air pollution regulations for particulate matter. Other metrics, such as particle number or surface area, may be more important in characterising the physical properties of aerosol related to health effects. Figure 1 illustrates relationships between combustion aerosol number, surface area and mass weighted size distributions. In this case the distribution typifies a diesel aerosol distribution. The shape of the aerosol size distribution from a spark ignition engine would be similar but with relatively less material in the accumulation mode region.
Figure 1.  Typical PM Size Profile of the Emissions from a Diesel Engine Indicating the Nuclei and Accumulation Mode Size Regions.

Figure 1 also shows the relationships between the coarse, accumulation and nuclei modes for the three weighted size distributions. Combustion aerosol follows a lognormal, trimodal size distribution with the concentration in any size range being proportional to the area under the corresponding curve in that range. Nuclei-mode particles typically range in diameter from 3 to 30 nm and consist of volatile organic compounds, sulfate, metallic compounds and carbonaceous compounds. Nuclei mode particles are formed during exhaust gas dilution and cooling. For diesel aerosol the nuclei mode typically contains a few percent or less of the particle mass and more than 90 % of the particle number. The accumulation mode ranges in size from roughly 30 to 500 nm. Most of the mass, primarily carbonaceous agglomerates and adsorbed materials, is found here. The coarse mode consists of particles larger than 1 µm and contains 5-20 % of the mass. These relatively large particles are formed by re-entrainment of particulate matter which has been deposited on cylinder and exhaust system surfaces. Also shown in Figure 1 are size range definitions for atmospheric particles: PM10 (diameter < 10 µm), fine particles (diameter < 2.5 µm), ultrafine particles (diameter < 0.10 µm or < 100 nm), and nanoparticles (diameter < 0.05 µm or < 50 nm).

In recent years substantial improvements in diesel engine technology have led to huge reductions in the mass of PM emissions. However, further reductions are required both to minimise the environmental impact of diesel vehicles and to enable them to meet future legislation. Substantial reduction of the PM emissions can be achieved by fitting a diesel Particulate Filter (DPF) to the exhaust gas system. Many types of DPFs are available based on both ceramic and metallic materials. A wall-flow filter monolith, in which alternate channels are blocked, as shown schematically in Figure 2, is frequently used.

Figure 2.  Schematic Representation of the Mode of Operation of a Wall-Flow Diesel Particulate Filter. The Filter Walls Can Be Ceramic or Metal-based.

The walls of the filter material are highly porous so the exhaust gases pass through with relatively little resistance while the PM is retained in the filter. Using such DPF’s particulate trapping efficiencies of over 99% are possible. Therefore, this technology can be used to collect the PM. However, it is vital to be able to remove this trapped PM from the filter. If this cannot be achieved the filter would block and adversely affect engine performance by increasing exhaust gas back pressure on the engine. This would degrade the engine’s performance, and in extreme cases, could even prevent the engine from starting. PM removal from filters can be achieved via combustion using either oxygen (O2), or nitrogen dioxide (NO2). Oxygen is readily available in diesel exhaust gas, typically it is present at the 5-10% level, but the oxygen-carbon combustion process requires temperatures of above 550 °C to proceed at a practically high rate; this is well above the typical exhaust temperature of a diesel powered vehicle. In contrast, the oxidation of carbon by NO2 occurs at just 250 °C, which is a temperature often accessed under normal driving conditions, particularly within heavy duty diesel applications. Therefore, this low temperature, NO2-based combustion makes possible the development of filter systems that will continuously burn the PM (that is, continuously regenerates and so maintains an acceptably low back pressure) as the vehicle drives along. To use this principle an additional step needs to be realised on the vehicle since the majority of the NOx produced in the engine is in the form of nitric oxide (NO) formed as shown in Reaction 1. This NO can be oxidised to NO2, as shown in Reaction 2 by using a suitable oxidation catalyst placed upstream of the DPF. The key reactions taking place within such a Continuously Regenerating Diesel Particulate Filter (CR-DPF) system are given in Reactions 2 and 3.
In the engine:
$$O_2 + N_2 \rightarrow 2 \text{ NO}$$  \hspace{1cm} (1)

Over the catalyst:
$$2 \text{ NO} + O_2 \rightarrow 2 \text{ NO}_2$$  \hspace{1cm} (2)

In the filter:
$$2 \text{ NO}_2 + C \rightarrow 2 \text{ NO} + \text{ CO}_2$$  \hspace{1cm} (3)

The oxidation catalyst has the additional advantage that it virtually eliminates carbon monoxide (CO) and hydrocarbon (HC) exhaust emissions by oxidising them to CO$_2$ and water. When a CR-DPF system is installed on a vehicle it effectively removes the CO, HC and PM emissions and can potentially regenerate the DPF continuously by combusting the filtered PM during normal driving. Table 1 summarises the typical performance of the CR-DPF system on a heavy-duty engine of a type in use today.$^{24}$

<table>
<thead>
<tr>
<th>CO Conversion</th>
<th>HC Conversion</th>
<th>NOx Conversion</th>
<th>PM (Mass) Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.70%</td>
<td>98.20%</td>
<td>2.10%</td>
<td>95.10%</td>
</tr>
</tbody>
</table>

**PERFORMANCE OF THE CR-DPF SYSTEM AS A FUNCTION OF FUEL SULFUR LEVEL**

As outlined above, to enable continuous regeneration the DPF system must contain an oxidation catalyst. This converts NO into NO$_2$ which is the basis of low temperature passive regeneration. Unfortunately, diesel fuel contains some sulfur compounds which are converted into SO$_2$ during the fuel combustion process. The catalyst can oxidise this SO$_2$ to SO$_3$ which can lead to an apparent increase in the PM mass emissions because the SO$_3$ is collected (as sulfate) on the filter papers used to collect the PM in the legislative PM measurement process. Figure 3 shows the PM emissions, measured in a test cell, over the legislative European Steady state Cycle (ESC) for a heavy duty diesel engine fitted with a CR-DPF system as a function of fuel sulfur level. Both the total PM mass emissions and the speciation of these emissions are shown.

The measured PM emissions increased monotonically as the fuel sulfur level increased. Analysis of the PM showed the amount of carbon, VOF and nitrate emissions were virtually independent of fuel sulfur level but the sulfate emissions increased monotonically with fuel sulfur content. The observed increase in PM emissions was predominantly due to increased sulfate formed by oxidation of SO$_2$ into SO$_3$ over the oxidation catalyst. Indeed, approximately 50% of the fuel sulfur was converted into sulfate in these experiments. It is important to note that the ESC test cycle is principally a high temperature cycle with CR-DPF temperatures of between 300 °C and 500 °C throughout the test. These high temperatures strongly promote the SO$_2$ oxidation process; at lower temperatures significantly less sulfate is formed.

Therefore, it is clear the CR-DPF system can provide very high levels of CO, HC and PM (mass) conversion in laboratory tests. However, the system can convert sulfur compounds from the diesel fuel into sulfate that can lead to increased PM emissions under some circumstances. These performance characteristics have now been studied in on-road tests for the first time. In most on-road applications the conversion of SO$_2$ to sulfate would be expected to be much less than 50%.

**THE MOBILE EMISSIONS LABORATORY**

The on-road PM emissions from a truck with and without a CR-DPF device were studied using a novel Mobile Emissions Laboratory (MEL). The MEL is mounted on a 1998 tractor unit powered by an emission year 2000 diesel engine. The 6 cylinder, 12 litre engine was rated at 287kW @ 1800 rpm, 1964 Nm. The MEL itself was housed in a standard box container mounted on a roll-on/roll-off platform. The gross vehicle weight was 17 400 kg. Power was supplied to the MEL by two 12.5 kW diesel generators that had their exhausts venting at the lower rear of the MEL.
The sampling system allowed samples to be collected from probes located in the upper right or left rear corners of the MEL. The exhaust pipe of the tractor unit split into two vertical stacks that took the engine exhaust up the back of the tractor unit before emitting the exhaust into the atmosphere just above the trailer unit of the MEL. Emissions from these stacks were effectively sampled by the rear sampling probes on the MEL. These rear-sampling probes were adjustable and are about 7 m behind, and in-line with the exhaust stacks as shown in Figure 4. Electronically actuated valves allow the MEL operator to switch between front and rear sample positions. The front probe position collects background samples and the rear probe positions collect engine exhaust plume samples. When the CR-DPFs were fitted, one was installed in each of the vertical exhaust stacks.

Figure 4. Photograph of the Mobile Emissions Laboratory Used In The Present work.

Aerosol size distributions were determined using a TSI 3934 scanning mobility particle sizer (SMPS). The SMPS was configured to size aerosol from 8 to 300 nm. A TSI 3025A condensation particle counter (CPC) determined total particle number concentration for particles between less than 3 nm and approximately 1 µm in size. Three ambient gas analyzers were used to measure exhaust plume or background gas concentrations. Two were Rosemount Analytical 880A non-dispersive infrared (NDIR) analyzers used to measure carbon monoxide (CO) and carbon dioxide (CO₂) concentrations. The third gas analyzer was an EcoPhysics CLD 700 AL chemiluminescence analyser to measure oxides of nitrogen (NOx). Measurement ranges for these instruments were as follows: CO analyzer 0 - 100 ppm, CO₂ analyzer 0 - 2500 ppm and NOx analyzer 0 - 10 ppm. The instruments all had a response time of about 1 s. The CO analyzer had a 20 s time delay to minimize vibration associated scatter.

A portable ECOM AC raw exhaust gas analyzer was used to measure raw exhaust gas concentrations [O₂, CO, NO and NO₂]. The ECOM AC used electrochemical cells to measure gas concentrations and had a relatively slow response time compared to the other gas analyzers. The ECOM calculated CO₂ concentrations from measured O₂ concentrations and assumed fuel properties. A stainless steel probe located in the passenger-side exhaust stack and connected to a Teflon line conducted the exhaust gas to the ECOM analyzer through an in-line particle filter. Exhaust temperatures and pressures were measured using thermocouples, sensors and a data logger. Data acquisition and instrument control were provided by National Instruments hardware using LabView software.

ON-ROAD PM EMISSIONS WITH A CR-DPF SYSTEM

The emissions measurements were made during actual on-road driving in rural Minnesota. During the measurements reported here the truck was driven at a reproducible steady state cruise condition (105 km h⁻¹) to ensure the conditions within all of the measurements were as constant as possible. The work program was designed to evaluate the PM emissions of the truck with and without the CR-DPF systems in place and to determine the impact of fuel sulfur and lubrication oil sulfur on the PM emissions. This latter part of the study was carried out for comparison with the engine test cell data shown in Figure 3, in which the measured PM mass increased significantly as the fuel sulfur level was increased due to sulfate production over the catalyst of the CR-DPF system. Two specially prepared fuels were used during on-road tests: one with relatively high sulfur content and one with relatively low sulfur content. The properties of the specially prepared fuels are detailed in Table 2. As well as standard commercially available lubrication oil a specially formulated low sulfur content lubrication oil was used that had been used in a previous DPF study. Details of the specially formulated fuels and lubrication oil are given in Table 2 and 3. Measurements were compared to estimates derived from another study in which commercial fuel containing approximately 350 ppm sulfur and commercial lubrication oil containing approximately 5,000 ppm sulfur were used.

Table 2. Properties of the specially formulated fuels used in this work.

<table>
<thead>
<tr>
<th>Property</th>
<th>“Low Sulfur Fuel”</th>
<th>“High Sulfur Fuel”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density/g cm⁻³</td>
<td>0.8304</td>
<td>0.8342</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>54.3</td>
<td>54.7</td>
</tr>
<tr>
<td>T₉₅%/ºC</td>
<td>343</td>
<td>340</td>
</tr>
<tr>
<td>Carbon Content/%</td>
<td>86.3</td>
<td>86.8</td>
</tr>
<tr>
<td>Hydrogen Content/%</td>
<td>13.7</td>
<td>13.3</td>
</tr>
<tr>
<td>Sulfur Content/PPM</td>
<td>10</td>
<td>49</td>
</tr>
</tbody>
</table>

Figure 3. Photograph of the Mobile Emissions Laboratory Used In The Present work.
Table 3. Properties of the low sulfur synthetic lubrication oil used in on-road experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity SAE</td>
<td>5W-30</td>
</tr>
<tr>
<td>Base oil type</td>
<td>Synthetic mixture Group IV/Group V type</td>
</tr>
<tr>
<td>Performance level</td>
<td>ACEA E6 type</td>
</tr>
<tr>
<td>Sulfur/%</td>
<td>0.13</td>
</tr>
<tr>
<td>Sulfated Ash/%</td>
<td>0.8</td>
</tr>
<tr>
<td>Phosphorus/%</td>
<td>0.04</td>
</tr>
<tr>
<td>NOACK</td>
<td>7</td>
</tr>
</tbody>
</table>

The following combinations of fuel and lubricating oil are compared:

(a) no CR-DPFs with current US market fuel (350 ppm S) + market sulfur oil (~0.5 wt %)

(b) no CR-DPFs with low sulfur fuel (15 ppm) and low sulfur oil (0.152 wt %),

(c) with CR-DPFs and low sulfur fuel (15 ppm) and low sulfur oil (0.152 wt %),

(d) with CR-DPFs and high sulfur fuel (50 ppm) and high sulfur oil (0.512 wt %)

Figure 5 compares the average number size distribution of the on-road PM emission profiles under each condition (a) – (d). In each case, the truck was cruising at a steady speed of 105 km/hr.

The PM emissions from the truck without the CR-DPF when running on current US market fuel and oil had a peak at low particle size (Dp ~ 10 nm) followed by a broad peak at high particle size (Dp ~ 30 - 300 nm). This trace is representative of the particle emission profile of current US trucks operating under steady-state, 105 km/hr cruise conditions. Figure 5 also shows reducing the fuel S level to 15 ppm and moving to a specially formulated low S oil led to a significant decrease in the number of smaller particles but had no effect on the larger, accumulation mode particles. Installing the CR-DPF systems resulted in a substantial reduction in the particulate emission at Dp > 30 nm. This reduction in the particulate concentration by two orders of magnitude effectively took the particulate concentration downstream of the CR-DPF to the background air levels. That is, within the limits of detection, all of the accumulation mode PM was eliminated. Thus the system removed practically all of the particulate matter emitted by the engine. Note that this near total particulate elimination was observed regardless of the fuel sulfur level within the range probed.

The second observation associated with the presence of the CR-DPF system was the increase in particulate concentration in the very small particle size range (< 20 nm) with respect to the level seen in the low sulfur fuel without the CR-DPF. This was the case with both the low sulfur fuel/low sulfur oil and the high sulfur fuel/high sulfur oil combinations, although the magnitude of the increase was considerably greater with the high sulfur combination. It seems likely, therefore, that this observed increase in the concentration of very small particles was due to the conversion of fuel-derived and oil-derived sulfur compounds into nanoparticle-sized sulfate species over the catalyst component of the CR-DPF system (that is, the process shown in the data presented in Figure 3). As the amount of sulfur in the system increased so did the concentration of sulfate particles produced. The analysis system may have been measuring the sulfate directly or perhaps the sulfate was acting as nucleation sites for the condensation of other species such as hydrocarbons. However, the former explanation seems most likely since the oxidation catalyst within the CR-DPF removed the vast majority of the hydrocarbon species emitted by the engine as shown in Table 1. Furthermore, calculations revealed that only approximately 3-10% of the sulfur in the fuel would need to be converted into sulfuric acid/sulfate to account for the observed increases in particulate emissions in the nuclei mode region (less than 30 nm). This level of conversion is consistent with the relatively low temperature of the system – under these driving conditions the CR-DPF temperature was operating between 300°C and 320°C where the catalyst will only be capable of low conversion of sulfur into sulfate. Therefore, it follows that the observed increase was due to the conversion of a low level of fuel sulfur into sulfate over the oxidation catalyst. Direct measurements of the composition of the particles are in progress and will be reported in full at a later date; however, preliminary analysis indicates the particles are predominately sulfate species.

The observed increase in the concentration of very small particles emitted with the low sulfur fuel and lubricant
combination when the CR-DPF was fitted gave a level approximately the same as that from current US trucks operating on today's US market fuel without the CR-DPF fitted. The CR-DPF system completely eliminated the larger particles and the nature of the very small particles was very different with the CR-DPF system fitted. Moreover, the life of such particles in air is relatively short due to self-coagulation, adsorption and other natural processes. Recent measurements indicated that the life-time of these particles is a few minutes.

Data from Figure 5 were re-plotted in Figure 6 in which the average number size distributions were converted into average volume size distributions. Here the dominant contribution of the larger particles to the volume of the PM emissions measured without the CR-DPF system is clearly seen. A negligible level of volume-based PM was emitted from the CR-DPF systems at particle sizes greater than approximately 25 nm regardless of the fuel and oil sulfur levels. However, the impact of fuel and oil sulfur is clearly seen in the particle size range below 20 nm. Here there was a significant contribution when the high sulfur fuel and high sulfur oil combination was used. Conversely there was a very low contribution with the low sulfur combination. Figure 6 clearly shows, when used with low sulfur fuel and low sulfur oil, the CR-DPF removed effectively all of the PM (within the limits of detection) when considered on a volume basis. In addition, an enormous reduction in the particle emissions is seen with respect to the emissions from current US trucks operating on US market fuel. This data strongly supports the current legislative moves to reduce the fuel sulfur level to below 15 ppm in the US and 10 ppm in Europe. This, when combined with the CR-DPF system, and the low sulfur oils being developed by the lubricant companies will result in real reductions in the emissions of nanoparticles from diesel vehicles.

ON-ROAD PM EMISSIONS WITH A MODIFIED CR-DPF SYSTEM

A further on-road experiment was conducted to see if the virtually total removal of particulate species from diesel exhaust gas was possible. The system used in this test was a modified CR-DPF system in which a special catalytic coating was applied to the diesel particulate filter as well as to the upstream oxidation catalyst. The additional catalyst on the filter provided further reduction of hydrocarbon-derived species from exhaust gas and contained a component capable of trapping sulfate species. The 15 ppm S fuel and low sulfur engine oil combination was used in this set of experiments.

Figure 7 compares the total on-road particulate emissions from this new catalysed CR-DPF system with those from the reference CR-DPF system. The total average concentration of particles is plotted against the average exhaust temperature. The data are grouped into bins 10 °C wide. The average daily background particulate concentration is also shown in Figure 7 together with the experimental data points and a power law fit for each data set derived by weighting each bin datum according to the number of measurements involved.

The particulate emissions from the reference CR-DPF system increased with temperature. This was as expected for an activated catalytic process such as the oxidation of gas phase SO₂ into SO₃ (and hence sulfates). This pronounced temperature dependence provides further evidence that the ultrafine particulate emissions are associated with sulfate species. In a separate study we are experimentally obtaining the kinetics of catalytic sulfate formation in diesel exhaust gas and relating this to the onset of particulate formation in the present study. The particulate concentration from
the CR-DPF system rises above the background level which is consistent with the particulate number data from the CR-DPF system presented above.

In marked contrast essentially no particulate species were measured downstream of the improved catalysed CR-DPF system regardless of the temperature of the system. It could be argued that the particulate emissions from this system were below those in the ambient environment. The sulfur-based species formed and emitted by the upstream oxidation catalyst were trapped in the downstream-catalysed DPF. Further work is being carried out to generate a more complete understanding of this phenomenon. However, within the limits of detection the present results demonstrate it is possible to obtain virtually total removal of particulate species from a diesel engine by optimising the filter-based emission control system.

CONCLUSIONS

1. A mobile laboratory carried on a heavy-duty truck chassis was used to characterize to exhaust of the truck itself under real world atmospheric dilution conditions.

2. This system was used to perform unique measurements of particle emissions from a heavy-duty vehicle fitted with a catalyzed particle filtration systems under real-world on-highway conditions, successfully and with good repeatability.

3. Accumulation mode particles which constitute nearly all of the particle mass were removed with the use of a CR-DPF system.

4. The level of nucleation mode particles was increased by the use of the CR-DPF.

5. Nucleation mode particle numbers were found to be affected by the level of fuel sulfur and lubricant formulation.

6. The combination of a catalysed, continuously regenerating diesel particulate filter, low sulfur fuel and a uniquely formulated lubricant reduced the number of nucleation mode particulates to background levels.

7. With this combination of particulate filter, fuel and lubricant a near zero particulate emission vehicle is a reality.

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