

Controlling particulate emissions from diesel vehicles

A.P. Walker*

Johnson Matthey plc, Orchard Road, Royston, Herts SG8 5HE, UK

Diesel engines move the world. Their excellent fuel economy makes them the power source of choice in a multitude of applications, such as transportation, excavation and mining. They are used extensively in commercial transport, being employed in trucks, buses, trains and ships. The Diesel engine is also becoming increasingly popular in the passenger car sector, especially in Europe where around 30% of the market is made up of Diesel vehicles; this proportion is expected to increase to 50% by 2010. However, increasing attention is being paid to the particulate matter (PM) emissions from Diesel vehicles, which consists mostly of carbonaceous soot and a volatile organic fraction (VOF) of hydrocarbons that have condensed on the soot. There is growing concern about these emissions, since emerging evidence potentially implicates PM as a major pollutant associated with acute health effects. This article reviews the strategies currently available to control the PM emissions from Diesel vehicles, and outlines the operating principles of the current state-of-the-art systems.

KEY WORDS: active regeneration; CRT[®] system; Diesel oxidation catalyst; Diesel particulate filter; particulate emissions; passive regeneration.

1. Introduction

Diesel engines provide great benefits to society since they are widely used to transport goods, services and people. They are the power source behind commercial transport, being employed in trucks, buses, trains and ships, as well as off-road industrial vehicles such as excavation machinery and mining equipment. These are all applications in which Diesel engines have been used for many years, due to the inherent fuel efficiency and the excellent durability of such engines.

The Diesel engine is being increasingly used to power passenger cars and vans. The application of Diesel engines in these applications is growing rapidly, particularly in Europe where the current penetration of the Diesel engine into the light-duty market is around 30%, and is predicted to grow to 50% by 2010. This rapid growth in these so-called light-duty Diesel (LDD) applications is due in part to the substantial fuel economy advantage of the Diesel engine with respect to the gasoline engine as well as the excellent low-end torque and overall performance of modern high speed Diesel engines.

However, like the gasoline engine, the Diesel engine emits carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NO_x). Diesel engines also produce significant levels of particulate matter (PM) which consists mostly of carbonaceous soot and a volatile organic fraction (VOF) of hydrocarbons that have condensed on the soot. There is growing concern about these PM emissions, since emerging evidence potentially links PM with acute health effects [1,2]. In particular, concern has grown over the effects of fine particulate

material which may be linked to increased instances of asthma, respiratory and cardiovascular complaints.

This article focuses on the PM control strategies that are being used on vehicles today, and outlines the operating principles and issues associated with these technologies.

2. Emissions legislation

The progressive tightening of the emissions standards for LDD vehicles presents significant challenges for the engine development and emissions control communities. As table 1 shows, the legislation is becoming more demanding for all pollutants.

The same qualitative trend is seen in the heavy-duty Diesel (HDD) emissions legislation as shown in table 2. In Europe, the major challenges are in PM control for 2005 (Euro IV) and in both NO_x and PM control for 2008 (Euro V). HDD engines are already so clean that they can meet the CO and HC levels proposed for Euro V without the use of any aftertreatment.

The trends in the PM legislation apparent in tables 1 and 2 make it clear that effective PM control devices need to be developed to enable vehicles to meet the increasingly stringent limits.

Note that PM is currently regulated based on the mass of particulates. This can give a misleading representation of the actual PM emissions. The typical contribution of the small and large particles to the particle number and particle mass is shown in figure 1 [3]. It is clear that the very small particles which make up the nuclei (or nucleation) mode are present in the greatest number, but contribute little to the total mass, while the relatively small number of larger particles

*E-mail: walkeap@matthey.com

Table 1
LDD Emissions legislation limits in Europe (ECE/EUDC test cycle;
 g km^{-1})

Year	CO	HC + NO _x	NO _x	PM
1996 (Euro II) (IDI)	1.0	0.7	–	0.08
2000 (Euro III)	0.64	0.56	0.50	0.05
2005 (Euro IV)	0.50	0.30	0.25	0.025

Table 2
Emissions legislation limits in Europe (ESC test cycle; $\text{g kW}^{-1} \text{h}^{-1}$)

Year	HC	CO	NO _x	PM
2000 (Euro III)	0.66	2.1	5.0	0.10
2005 (Euro IV)	0.46	1.5	3.5	0.02
2008 (Euro V)	0.25	1.5	2.0	0.02

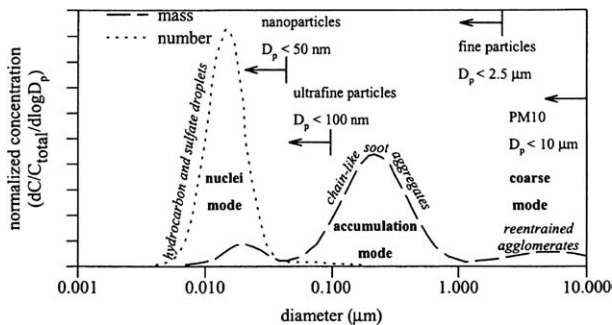


Figure 1. Schematic of mass- and number-based particle size distributions from Diesel engines.

which make up the accumulation mode dominate the particulate mass.

In addition, it is the smaller particles that are proposed to be the ones most harmful to human health, since the larger ones are not ingested into the human system because they become trapped in the nose and throat, from where they are later expelled. These concerns have led to proposals from a number of bodies, such as the German environmental agency, the UBA, that particulate emissions should be legislated not just by mass, but also by number [4].

3. The composition of Diesel particulate matter

Diesel PM is made up of a number of components. The core of the PM is made up of agglomerates of primary soot particles, onto which is adsorbed a layer of condensed hydrocarbons, or VOF. Sulfuric acid droplets, derived from the SO₂ generated from the fuel sulfur during the combustion process, can also condense, and these sulfate species can further adsorb water. Nitric acid, derived from the engine-out NO_x, can also

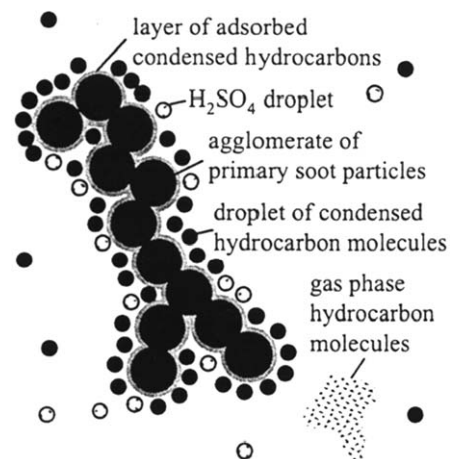


Figure 2. Schematic representation of a chain-like aggregate of primary soot particles and associated adsorbed/condensed species.

condense on the primary soot particles. Finally, oil-derived species such as derivatives of Ca, P and Zn can become entrained in the PM. Figure 2 shows a schematic representation of Diesel particulate [5].

4. Diesel oxidation catalysts

Oxidation catalysts are currently used on LDD vehicles in Europe, principally to control CO and HC emissions. However, these catalysts also reduce the PM mass emissions since they can combust the VOF component of the PM. Table 3 shows the emissions of a Euro III-calibrated LDD vehicle fitted with a catalyst that has been aged for 80,000 km. (Note that in Europe the emissions of a LDD vehicle must meet the legislated standards after 80,000 km, so this catalyst has been aged to full lifetime as stipulated by legislation.)

As table 3 shows, the oxidation catalyst provides significant conversion of CO, HC and PM, such that all of the regulated pollutants are comfortably inside the Euro III legislated levels, even after 80,000 km of ageing.

While oxidation catalysts convert the VOF component of the PM, the carbon component passes through them unconverted. Therefore, the PM conversion obtained by the oxidation catalyst depends strongly on the composition of the PM, with high levels of VOF enabling oxidation catalysts to provide high levels of PM conversion. An oxidation catalyst will typically provide around 20–40% PM conversion, which reflects the usual level of VOF in Diesel PM.

Table 3
Effect of an 80,000 km aged Diesel oxidation catalyst on the emissions of a LDD vehicle over the legislated ECE/EUDC test (g km^{-1})

System	CO	HC + NO _x	NO _x	PM
Engine-out	0.88	0.54	0.37	0.048
Catalyst-out	0.50	0.39	0.35	0.030
Euro III limits	0.64	0.56	0.50	0.05

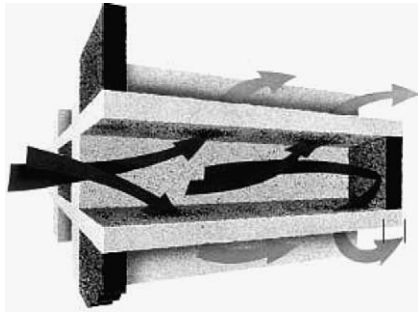


Figure 3. Operating principle of the wall-flow filter.

5. Filtering Diesel particulates

In order to meet future emissions legislation it is essential to control the carbon component as well as the VOF. A number of different strategies have been investigated to filter Diesel particulate species, including wire mesh filters and ceramic foam filters. However, the approach most widely used today to trap PM is the wall-flow Diesel particulate filter (DPF). The operating principle of the wall-flow filter is shown in figure 3.

These filters are usually composed of either cordierite (a clay-derived material, also used as the substrate in catalytic converters) or silicon carbide (SiC). The filter provides channels into which the gas flows, but blocked ends force the incoming gases to pass through porous channel walls before they can exit the filter. The filter walls are designed to have an optimum porosity, enabling the exhaust gases to pass through their walls without much hindrance, in order to minimize the “pressure drop” of the device, whilst being sufficiently impervious to collect the particulate species. These filters have PM trapping efficiencies of almost 100%, making it possible to remove the particulate species from the exhaust stream.

As outlined above, PM is currently regulated by mass. On this mass basis, DPF systems typically provide PM conversions in the 90–95% range. Figure 4 shows the PM trapping efficiency of a wall-flow DPF as a function of particle size at constant engine speed and

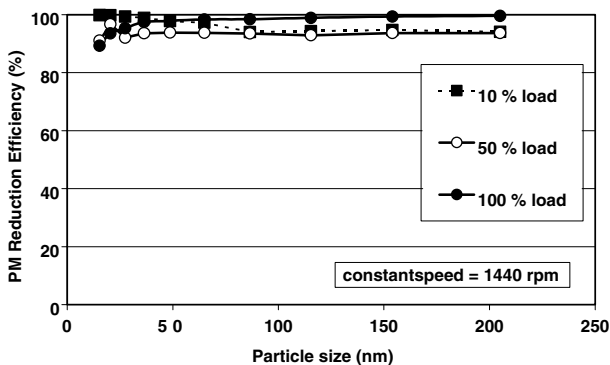


Figure 4. PM removal efficiency of a wall-flow DPF as a function of particulate size.

different engine load conditions. It is clear that DPF systems are extremely efficient at filtering both the small and the large PM species.

So, as well as substantially reducing the PM *mass* level, DPF systems can also decrease the particulate *number* by two to three orders of magnitude.

6. Combusting Diesel particulate

As shown above, it is possible to trap the particulates within the DPF. The next stage is to combust these carbonaceous species, since the filter would rapidly become blocked if these PM species were not removed. There are two basic approaches to the combustion of the trapped PM; these are passive and active regeneration. Both approaches will now be considered in detail.

6.1. Passive regeneration

Passive regeneration involves the combustion of the trapped PM during the normal operation of the vehicle. That is, neither the vehicle operator nor the vehicle’s engine management system has to do anything to induce the regeneration of the DPF.

Clearly this is the easiest way to control PM emissions, but it cannot be applied in all situations, as will be discussed in Section 6.2 below.

There are two principal gaseous species that can be used to combust the collected PM. Oxygen is perhaps the most obvious, and is in plentiful supply in the exhaust from Diesel engines, typically at the 5–10% level. Unfortunately, the combustion of PM in oxygen requires very high temperatures, in the 550–600 °C range, and these temperatures are very rarely accessed in either LDD or HDD applications. However, nitrogen dioxide, NO₂, is far more reactive than oxygen, and can combust PM at a reasonable rate at temperatures as low as 250–300 °C [6]. The respective efficiencies of NO₂ and oxygen at combusting Diesel PM are summarized in figure 5, which shows the CO₂ evolution from PM combustion as a function of temperature in gas feeds

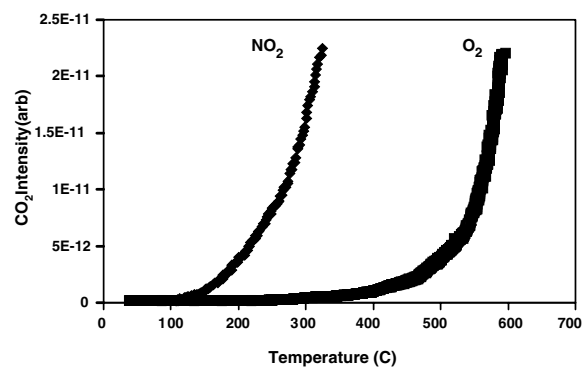


Figure 5. Comparison of the combustion temperature of PM in NO₂ and O₂.

containing in one case NO_2/He , and in the other case O_2/He .

The use of NO_2 to combust Diesel PM is the basis of the passive regeneration strategy, since the NO_2 -carbon reaction occurs at temperatures which are frequently accessed during the normal operation of many Diesel vehicles. This is particularly true of HDD vehicles, which generally operate in the 200–400 °C temperature range.

The majority of the NO_x emissions from Diesel vehicles are in the form of NO , not NO_2 , so some of this engine-out NO must be oxidized into NO_2 to enable passive regeneration. This can be done using an oxidation catalyst, which can either be located upstream of the DPF, or can be coated onto the DPF. The former strategy is the basis of the Continuously Regenerating Trap (CRT[®]) system [7], which is shown schematically in figure 6.

The upstream oxidation catalyst converts a portion of the engine-out NO emission into NO_2 , and this NO_2 reacts with PM trapped in the downstream filter at temperatures much lower than those observed for the oxygen-PM reaction.

The CRT system provides very high conversions of PM which is, of course, its principal function. However, since the CRT contains an oxidation catalyst, it also provides very high conversions of both CO and HC . This is shown in table 4, which details the performance of the CRT system over the European steady-state cycle (ESC, one of the standard legislative cycles for HDD engines). This experiment was performed on an old technology HDD engine which met the Euro I emission levels (which were in force between 1990 and 1996). It can be seen that the CRT system enables this engine to meet the Euro IV emission limits for CO , HC and PM .

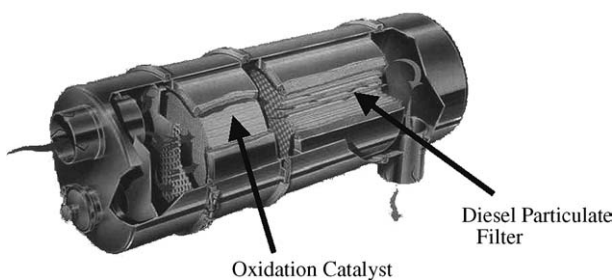
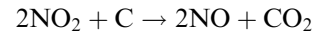


Figure 6. Schematic representation of the CRT[®] system.

Table 4
Performance of the CRT system over the ESC ($\text{g kW}^{-1} \text{ h}^{-1}$)

Technology	HC	CO	NO_x	PM
Engine baseline	0.162	0.989	7.018	0.163
Engine + CRT	0.003	0.002	6.874	0.008
Euro IV 2005 limits	0.460	1.500	3.500	0.020

During the soot combustion process the NO_2 is mainly reduced back to NO , so the system does not provide a significant amount of NO_x conversion:



However, as shown in table 4 a small amount of NO_x conversion (2–10%) is usually seen over the CRT system; it is believed that this is due to the conversion of some NO_2 into N_2 via reaction with carbon in the filter.

Therefore, the CRT system can provide very high conversions of CO , HC and PM . There are currently approximately 70,000 CRT systems in use in a range of HDD applications around the world. The long-term durability of this product has been demonstrated in numerous studies (e.g., [8,9]), in which systems have run successfully for over 700,000 km. Note, however, that these systems require maintenance after typical distances of around 100,000–200,000 km due to the build up of oil-derived ash species in the DPF. All engines consume lubricating oil, and these oils contain performance-enhancing inorganic additives based on elements such as Ca , Zn and P . These species are not combusted on the catalyst or within the DPF, and gradually build up in the filter channels. In order to prevent DPF blockage, these ash deposits must be removed periodically.

6.2. Active regeneration

It is not always possible to regenerate a DPF passively, since the operating conditions of some vehicles are not conducive to such regeneration. For example, if the exhaust temperature is low (e.g., in some low speed urban driving applications), there may not be enough heat in the system to ensure a good rate of NO oxidation over the catalyst and of NO_2 -carbon reaction within the DPF. (Both of these reactions have critical onset temperatures in the 200–250 °C range.) In addition, there may not be enough NO_x available to ensure the generation of sufficient NO_2 to react with the engine-out PM. In general, neither limitation applies to current HDD vehicles, while both limitations frequently apply to current LDD vehicles. This is why the CRT system is only utilized in its completely passive mode on HDD vehicles at this time.

When passive regeneration is not possible, the system needs to be subjected to an active regeneration strategy to raise the temperature to enable the accumulated PM to be combusted periodically. The first vehicle manufacturer to introduce such a system in the LDD sector was Peugeot-Citroen in the year 2000 on their 607 vehicle [10]. The active regeneration system comprises four main components:

- (i) oxidation catalyst,
- (ii) silicon carbide DPF,
- (iii) ceria-based fuel-borne catalyst,
- (iv) sophisticated engine management system and sensors.

Back pressure sensors are used to monitor the pressure drop across the DPF, which increases as the level of PM in the DPF increases. Once this pressure drop reaches a level corresponding to a defined amount of PM, the active regeneration process is initiated. This comprises a change in the fuel injection strategy, which leads to an increase in the temperature of the exhaust gas and of the components within the exhaust. The corresponding increase in temperature of the oxidation catalyst ensures that the temperature of this catalyst is high enough to combust CO and HC with very high efficiency. Once this temperature has been reached (as defined by readings from temperature sensors), the fuel injection process is modified once more, this time to introduce relatively high levels of CO and HC into the exhaust. These species are combusted over the catalyst and the resulting exotherm is used to heat the DPF to the point at which the stored PM will combust rapidly in the plentiful available oxygen. Note that the high mass flow rate of oxygen means that the accumulated PM is rapidly combusted.

As discussed above (see figure 5), the combustion of Diesel soot in oxygen usually requires temperatures in the 550–600 °C range. However, the PM combustion temperature can be reduced by approximately 100 °C by adding a low level of a ceria-based fuel-borne catalyst to the fuel. During the fuel combustion process in the engine this ceria becomes intimately associated with the PM, and subsequently catalyses its combustion during the active regeneration process. This reduction in PM combustion temperature minimizes the fuel economy penalty associated with this active regeneration strategy, by reducing the amount of fuel that needs to be consumed to raise the system temperature. It also limits the temperatures experienced in the DPF, which further minimizes the possibility of thermal damage to the filter during active regeneration.

It is important to note that during the active regeneration process, sophisticated engine management strategies ensure that the driver is totally unaware of the fuel injection changes used to initiate the regeneration. That is, no change in the engine torque or driveability is apparent. This elegant PM control system has now been installed on over 500,000 Peugeot–Citroen vehicles.

One final note on this system is that while the fuel-borne catalyst brings about the significant advantage of reducing the O₂–carbon combustion temperature, the ceria is retained within the DPF, which therefore increases the rate of ash accumulation in the filter. In practice this means that the filter needs to be removed for ash cleaning maintenance after 80,000 km of vehicle use. Due to this negative ash-derived maintenance issue it is expected that future DPF systems will not incorporate a fuel-borne catalyst, but will utilize a precious metal-based catalyst coating on the DPF, ie a Catalysed Soot Filter, CSF.

7. Sulfur and oxidation catalysts

There is one final important consideration when applying these catalyst-based DPF systems on vehicles, and that is the fuel sulfur level.

Diesel fuel contains sulfur, not as a desirable addition, but because it is an unwanted impurity in the original crude oil. The combustion of Diesel fuel within the engine turns this sulfur into sulfur dioxide (SO₂). The oxidation catalyst can further oxidize a portion of the gas phase SO₂ into SO₃. This SO₃ can then form sulfate species which adsorb onto the PM as discussed above, leading to an increase in PM emissions.

Therefore, the sulfur content of the fuel can have a significant impact on the PM emissions of catalyst-based DPF systems such as those discussed in this article. Figure 7 demonstrates this effect by showing the PM emissions of the CRT system as a function of the fuel sulfur level. These experiments were carried out on a HDD engine over the ESC test cycle used to legislate HDD emissions. It can be seen that the measured PM emissions increase linearly with fuel sulfur level, due to this sulfate generation effect. Analysis of the filter papers used to collect the PM within the legislated PM measurement process, confirmed that the increase in PM is due entirely to sulfate generation, as shown in figure 8. Note that very little carbon is detected in the

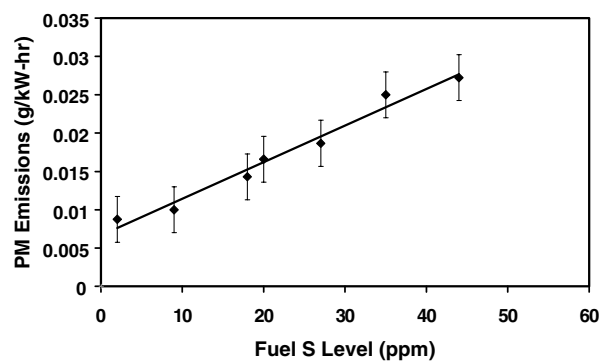


Figure 7. Effect of fuel S level on the measured PM emissions of the CRT system over the ESC test cycle.

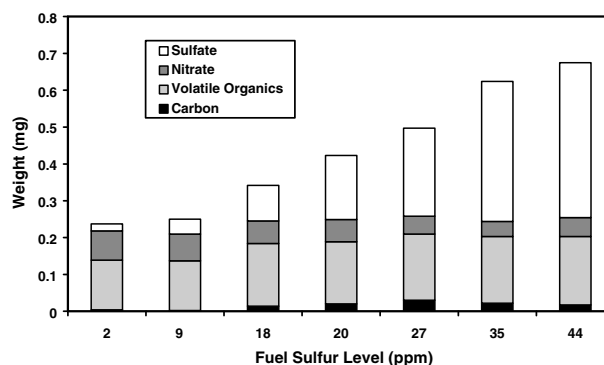


Figure 8. Speciation breakdown of the PM emissions in figure 7.

PM—this is removed by the particulate filter component of the CRT system. The oxidation catalyst component of the CRT system removes most of the engine-out VOF (also called soluble organic fraction, or SOF), but a low level passes through the system, as shown in figure 8.

Similar increases in PM emissions due to sulfate formation are also seen when using the Peugeot–Citroen catalyst-based DPF system [10]. In order to minimize these sulfate emissions the fuel sulfur level should preferably be below 50 ppm. Indeed, the CRT system is only used in combination with fuel whose sulfur level is below 50 ppm. At the present time, such fuel is widely available in parts of Europe (e.g., the UK, Germany and Scandinavia), and is becoming increasingly available in other parts of Europe. Indeed, from 2005 all Diesel fuel sold in the EU will have a maximum sulfur level of 50 ppm.

8. Conclusions

The Diesel engine provides great benefits to society, but recent attention has focussed on the potential health effects of Diesel particulate matter (PM). The volatile organic fraction (VOF) part of this PM can be removed with very high efficiency using a Diesel oxidation catalyst. However, these flow-through catalysts do not convert the carbonaceous core of the PM.

The PM can be almost completely removed from the exhaust stream using a Diesel particulate filter (DPF). This trapped PM can then be combusted using either NO₂ (at low temperatures, 250–300 °C and above), or O₂ (at high temperatures, 550–600 °C). The NO₂-based regeneration process can be implemented passively on current HDD vehicles, as exemplified by the CRT[®] system. There are currently over 70,000 such systems in operation on HDD vehicles worldwide.

The O₂-based regeneration process requires temperatures that are usually well above those accessed during the normal operation of both LDD and HDD vehicles. However, this active regeneration strategy is preferred on LDD vehicles due to the generally low operating

temperatures and NO_x/PM ratios, which make passive regeneration very difficult in such applications. Sophisticated engine management strategies, combined with catalytic processes, are used to raise the temperature of the PM collected in the DPF to the temperature required for the O₂-carbon reaction. The accumulated carbon is then rapidly burned away. This strategy is already in use on over 500,000 Peugeot–Citroen vehicles.

In conclusion, the technology to control the PM emissions from Diesel vehicles has been successfully developed and demonstrated, and many vehicles in use today benefit from the application of these catalyst-based PM control strategies.

Acknowledgments

I would like to thank numerous colleagues for helpful discussions during the writing of this paper, notably Drs. Barry Cooper and Martyn Twigg, and Mr. Robert Evans. Dr. Barry van Setten is gratefully acknowledged for providing figures 1 and 2. I would also like to thank Johnson Matthey for permission to publish this paper.

References

- [1] R.L. Maynard and C.V. Howard, eds., *Particulate Matter: Properties and Effects upon Health*, Oxford, 1999.
- [2] A. Seaton, W. MacNee, K. Donaldson and D. Godden, *Lancet* 345 (1995) 176.
- [3] D.B. Kittelson, *J. Aerosol. Sci.* 29 (1998) 575.
- [4] S. Rodt, *Diesel Engine Emission Reduction Conference*, San Diego, 2002; www.orau.gov/deer2002/presentations.htm.
- [5] J.H. Johnson, S.T. Bagley, L.D. Gratz and D.G. Leddy, SAE 940233, Detroit (1994).
- [6] B.J. Cooper and J.E. Thoss, SAE 890404, Detroit (1989).
- [7] B.J. Cooper, H.J. Jung and J.E. Thoss, U.S. Patent 4,902,487 (1990).
- [8] R. Allansson, B.J. Cooper, J.E. Thoss, A.J. Uusimaki, A.P. Walker and J.P. Warren, SAE 2000-01-0480, Detroit (2000).
- [9] S. Chatterjee, C. McDonald, R. Conway, H. Windawi, K. Vertin, C.A. LeTavec, N.N. Clark and M. Gautam, SAE 2001-01-0512, Detroit (2001).
- [10] O. Salvat, P. Marez and G. Belot, SAE 2000-01-0473, Detroit (2000).