Non-thermal Aftertreatment of Particulates

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INTRODUCTION

Modern diesel passenger vehicles employing common rail, high speed direct injection engines are capable of matching the drivablilty of gasoline powered vehicles with the additional benefit of providing high torque at low engine speed [1]. The diesel engine also offers considerable fuel economy and CO_2 emissions advantages. However, future emissions standards [2,3] present a significant challenge for the diesel engine, as its lean exhaust precludes the use of aftertreatment strategies employing 3-way catalytic converters, which operate under stoichiometric conditions.

In recent years significant developments by diesel engine manufacturers have greatly reduced emissions of both particulates (PM) and oxides of nitrogen (NOx) [4,5]. However to achieve compliance with future legislative limits it has been suggested that an integrated approach involving a combination of engine modifications and aftertreatment technology [1] will be required.

A relatively new approach to exhaust aftertreatment is the application of non-thermal plasma (NTP) or plasma-catalyst hybrid systems. These have the potential for treatment of both NOx and PM emissions [6-8]. The primary focus of recent plasma aftertreatment studies [9-12] has concentrated on the removal of NOx. It has been shown that by combining plasmas with catalysts it is possible to chemically reduce NOx. The most common approach is to use a 2-stage system relying upon the plasma oxidation of hydrocarbons to promote NO to NO_2 conversion as a precursor to NO_2 reduction over a catalyst. However, relatively little work has yet been published on the oxidation of PM by plasma [8,13].

Previous investigations [8] have reported that a suitably designed NTP reactor containing a packing material designed to filter and retain PM can effect the oxidation of PM in diesel exhausts at low temperatures. It has been suggested that the retained PM competes with hydrocarbons for O, and possibly OH, radicals. This is an important consideration in plasma-catalyst hybrid schemes for the removal of NOx employing an NO_2 selective catalyst, as the oxidation of PM may deplete the key radicals necessary for NO to NO_2 conversion. It was also suggested that where simultaneous NOx and PM removal are required, alternative catalyst formulations may be needed which may be selective to NO rather than NO_2.

This paper presents the results of recent testing of a prototype non-thermal plasma diesel particulate filter on a Caterpillar C-10 engine exhaust. The results confirm that NTP aftertreatment is applicable to removal of PM from heavy-duty diesel engine exhaust.

The paper also reports on the initial evaluation of NO selective reduction catalysts for application in a combined NOx and PM plasma-catalyst aftertreatment system. The work also highlights a suitable operating strategy for using this approach.

SYSTEM DESIGN

A current prototype Diesel Particulate Filter (DPF), as originally designed for use on a London Taxis International (LTI) taxi [8] was employed in trials on a Caterpillar C-10 engine.

The DPF is a dielectric barrier discharge design, shown in a

diagrammatic form in Figure 1. The design of the DPF incorporates a novel baffle design that causes the exhaust gas to flow through a bed of filter material enclosed between two plasma-generating electrodes. This material has the effect of trapping the PM by a combination of impaction and electrostatic filtration. The DPF system shown is packed with a pelletised material. A filter or monolithic packing material can replace the pellets. The design of the DPF maximises the exposure of the PM to the oxidative radicals whilst keeping the impact on backpressure to a minimum.

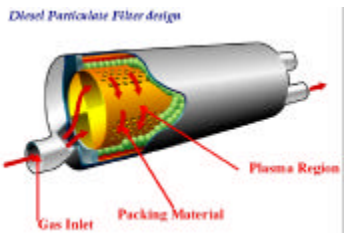


Figure 1: DPF cross-section.

DEMONSTRATION ON A C-10 ENGINE

A demonstration program was conducted to evaluate the particulate removal capabilities of the prototype DPF on a Caterpillar C-10 heavy-duty diesel engine.

EXPERIMENTAL SET -UP

To demonstrate this system on the C-10 engine, tests were performed using a 15% slipstream of the exhaust in order to scale the flow from the C-10 engine to the LDD prototype .
A schematic of the experimental arrangement is shown in Figure 2. Measurements of temperature, pressure, mass , number and size distribution of particulates and exhaust gas composition, were taken both before and after the plasma DPF. The particulate mass was measured using a dilution tunnel (Micro DiLution tunnel giving a dilution ratio of 5:1) and filter papers (70mm Pallflex filters) weighed before and after each test. The gas composition was monitored using a Horiba Mexa 7200 DTR analyser bank. Measurements of ultra-fine (7 ~ 320 nm) particulate number and size distribution were performed using SMPS. Reference fuel AF1313 (SSM-4), which has a sulphur content of 280ppm by mass, was used throughout the tests.

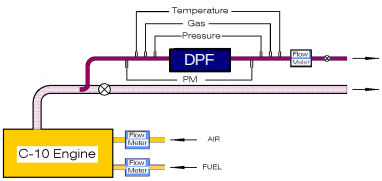


Figure 2. Schematic of the test apparatus.

The prototype was tested over sample points from the 13 mode, European Stationary Cycle (ESC or OICA cycle). The engine conditions of load and speed at these mode points are described in detail in Table 1 and Figure 3 below, along with the weighting factors used to calculate cycle-specific emissions. The weighting factors in Table 1 are represented by the diameter of the circles that show the mode points in Figure 3. The test points represent a range of space velocities through the DPF of 20,000 to 62,165hr^{-1} for the non-idle modes, with the idle mode, mode 1 representing a space velocity of 6,000hr^{-1}.

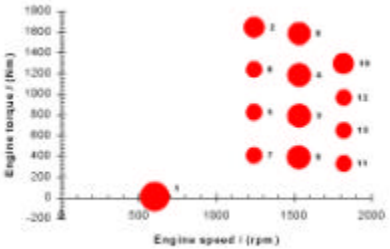


Figure 3: Operating conditions corresponding to the 13 ESC modes

Mode	Code	Engine Speed (rpm)	Engine Torque (Nm)	Engine Power (kW)	Weighting Factor
1	IDLE	[illegible]	[illegible]	[illegible]	[illegible]
2	A	[illegible]	[illegible]	[illegible]	[illegible]
3	B	[illegible]	[illegible]	[illegible]	[illegible]
4	B	[illegible]	[illegible]	[illegible]	[illegible]
5	A	[illegible]	[illegible]	[illegible]	[illegible]
6	A	[illegible]	[illegible]	[illegible]	[illegible]
7	A	[illegible]	[illegible]	[illegible]	[illegible]
8	B	[illegible]	[illegible]	[illegible]	[illegible]
9	B	[illegible]	[illegible]	[illegible]	[illegible]
10	C	[illegible]	[illegible]	[illegible]	[illegible]
11	C	[illegible]	[illegible]	[illegible]	[illegible]
12	C	[illegible]	[illegible]	[illegible]	[illegible]
13	C	[illegible]	[illegible]	[illegible]	[illegible]

Table1: Mode conditions and weighting factors

RESULTS

Figure 4 shows the weighted regulated emissions, over the ESC (OICA cycle), in g / kW-hr before and after the DPF. The mass of PM was reduced by 53% and the total hydrocarbon (THC) by over 70 %. The slight increase in the concentration of CO, which is an operating characteristic of the system, may be as a result of the oxidation of hydrocarbon and PM [8].
No change was observed in the concentration of NOx**.**

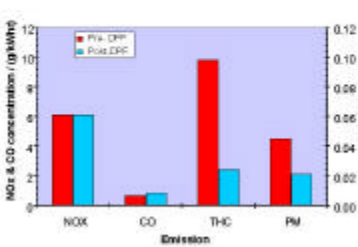


Figure 4: Weighted emissions

Analysis of the individual mode points (Fig. 5) reveals that the level of PM removal varies with engine load and speed. The system appears to be most efficient at removing PM for the lowest engine load condition at each engine speed (modes 7, 9 and 11). These load conditions correspond to the highest PM loadings at each engine speed. The space velocity however is lower at these low load conditions. For example, at mode 7 which has a space velocity of 20,135 hr^{-1}, the DPF shows a 70% of PM but only 27% at mode 10, which has a space velocity of 62,165 hr^{-1} . It is believed that these differences in removal may be partly due to the space velocity limitation of the current prototype DPF which has not been optimised for the engine.

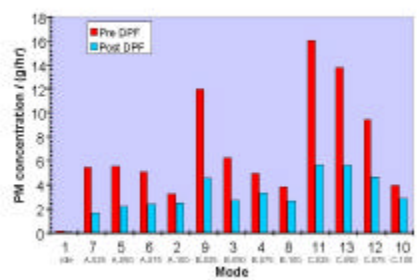
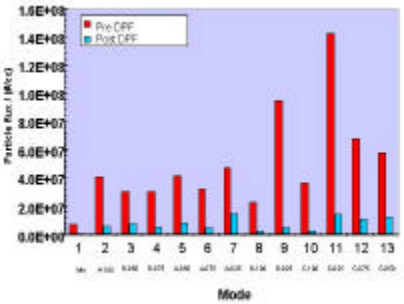


Figure 5: PM removal by mode (unweighted).

Analysis of the particulate number and size distribution for each of the 13 modes of the cycle demonstrates typical removals of 85% (Figure 6) w ith removals for the individual modes ranging between 75% and 95%. Figure 7 shows examples of the size



distribution recorded in modes 1 and 2, mode 1 being idle and mode 2 being a high load mode.

Figure 6. SMPS data by mode.

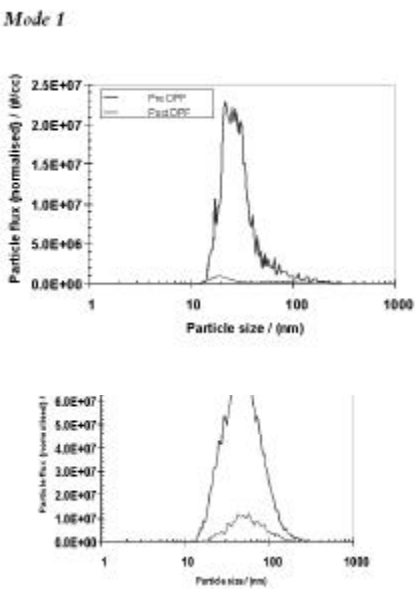


Figure 7: SMPS for selected modes.

The particulate number and size distribution measurements demonstrate a consistently good removal across the size range, without any significant change to the particulate size distribution.

INTERPRETATION OF PARTICLULATE REMOVAL

The evaluation program successfully demonstrated that the DPF was able to remove PM from a heavy-duty engine exhaust. The DPF demonstrated PM removals of 53% by mass and 85% by number. By comparison in light duty engine exhaust tests, typical PM removals of 60-70% by mass and up to 90% by number were recorded [8]. The drive cycles used in testing the device on light and heavy duty engine exhausts were different, however, these cycles do include conditions such as PM load and space velocity that are sufficiently similar to allow comparison. The space velocity through the DPF in the C-10 tests ranged up to 60,000hr^{-1}, tests on the taxi gave a space velocity through the device of up to approximately 80,000hr^{-1}.

INTERPRETATION OF OXIDATIVE PROCESS EFFICIENCY

A constant power of 1.5kW was used in each of the 13 modes. This corresponds to a process efficiency (power per gram of PM) ranging from 0.15 to 2 kW-hr/g for modes 2-13. This data shows reasonable agreement with the process efficiency limit of 0.34 kW-hr/g calculated previously [8] from work on the taxi engine exhaust. In practice an active power management strategy could be employed to vary the applied power according to the PM loading.

By applying the 0.34 kW-hr/g limit to the weighted PM emissions from the C-10 engine over the ESC cycle, it can be calculated that 90% of the PM could be oxidised using approximately 2% of engine power (weighted

average). This figure does not take into account power transmission efficiency.

IMPLICATIONS FOR COMBINED PM / NOx AFTERTREATMENT

It has been suggested previously [8] that where simultaneous PM and NOx removal is required, an approach employing alternative catalyst formulations that are selective to NO rather than to NO_2 may be needed

The proposal would be to use a two-stage approach where initially PM is filtered from the exhaust and oxidised by the plasma. NOx would be subsequently reduced over an NO sensitive catalyst. It is believed that by using this approach the catalytic NO reduction can be enhanced by plasma production of reductants from the exhaust. The result of this enhancement may be to improve the low temperature performance, or extend the activity window of the catalyst.

Catalysts were screened using a two-stage plasma-catalyst arrangement consisting of a packed bed plasma reactor and a pellet catalyst reactor. Various catalysts were studied including mixtures that can be tailored to perform different functions depending upon how the plasma reactor is configured and the nature of the exhaust stream.

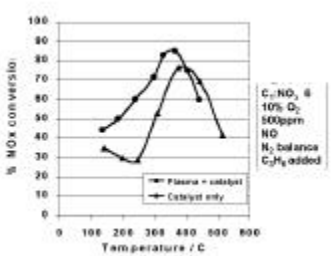


FIGURE 8: Catalyst test set-up

The energy density of the plasma was typically varied between 0 and 50 joules per litre. The temperature of the catalyst could be controlled between 150 and 550 °C. The synthetic exhaust gas mixture used in these tests comprised 10% oxygen, 500ppm NO and 500ppm propene in balance nitrogen. Typically, the experiments were conducted at catalyst space velocities of 10,000 hr^{-1}. A diesel generator set was also available for engine exhaust evaluation. The product gases were analysed using a chemiluminescent NOx / NO analyser, FID hydrocarbon analyser and a Fourier Transform Infrared spectrometer (FTIR - Nicolet).

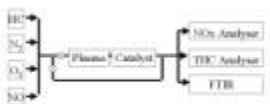


Figure 9. Typical plasma effect on NOx reduction by catalyst.

Figure 9 illustrates the typical effect of the plasma, operating at an energy density of 30 joules per litre, on the NOx conversion by an NO selective catalyst over the 150-550°C temperature range in synthetic exhaust. The proprietary catalyst was thermally aged in a 10% steam-air gas mixture at 723-823 K for 24 hours before testing. Analysis of the product gases using the FTIR reveals good agreement with the chemiluminescent analyser for NOx, NO and NO_2. Additionally, FTIR analysis does not detect other nitrogen oxides such as HNO_3 or HNO_2 and the concentrations of and N_2O is typically <10ppm. Integration of thermal desorption profiles for this catalyst indicates that around 5% of the converted NO is reversibly desorbed as NOx at elevated temperatures. The catalyst performs well over a broad range of

temperatures with peak conversion at 400°C at a space velocity of 10,000hr^{-1}. The results indicate that the main effect of the plasma is to enhance the NOx conversion between 150 and 400°C, above which the effect appears to be minimal and the thermal activity dominates. The effect is not due to the plasma conversion of NO to NO_2 as operating the packed reactor at an energy density of 30 J/L in these conditions does not apparently interconvert the two [8]. It is believed that the low temperature enhancement is as a result of the plasma activation of reductants from the exhaust. There is evidence of plasma production of partially oxidised hydrocarbons that appear to react over the catalyst [14]. It is however unclear as to what role these species may have and whether others are of more importance. The effect of the plasma does however depend upon the nature of the reductant in the exhaust. Results indicate that the plasma enhanced NOx reduction effect can also be achieved using diesel engine exhaust although the C1:NOx ratio usually requires elevating to >4:1.

The enhancement of low temperature NOx reduction increases the activity window of the catalyst and highlights a possible control strategy for NOx reduction. At the lower exhaust temperatures the plasma may be used to enhance catalytic NOx reduction. The plasma could then be turned off when its effect diminishes as the exhaust temperature reaches a critical point where the thermal activity of the catalyst dominates.

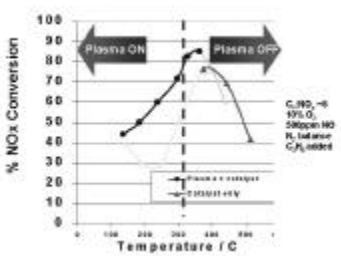


Figure 10: NOx removal strategy

For combined removal of PM and NOx the plasma can be controlled via a power management unit to maintain the PM oxidation and enhance NOx reduction when required
The typical NOx conversions reported here support the proposed strategy [8] to use a NO selective catalyst. Further enhancements are being made by optimising the catalyst composition and by using novel catalyst combinations.

CONCLUSIONS

The DPF prototype has been shown to remove PM and hydrocarbons from heavy-duty diesel engine exhaust. In tests on a C-10 engine, the DPF removed 53% of PM by mass, 85% by number of particulates. This demonstrates that the technology is applicable to Heavy duty diesel engine exhausts as well as light duty applications as reported previously [8].

The power required to oxidise PM trapped from this heavy-duty exhaust has been shown to be similar, in terms of process efficiency, for this heavy-duty exhaust to that required in light-duty exhausts.

Further development of a Heavy-duty diesel specific prototype will allow the DPF to be better matched to the flow and exhaust characteristics of the heavy-duty engine. An active power management strategy could be employed to vary the applied power according to the PM loading and so reduce the overall power requirement

The use of NO selective catalysts for NOx reduction, as proposed earlier [8] has been investigated. These catalysts have been shown to give NOx removal over a suitable temperature range, suggesting that this proposed NOx removal strategy is viable for diesel exhaust aftertreatment application.

This method of NOx removal appears to have the added benefit of maintaining very low concentrations, less than 10 ppm, of N_2O.

A strategy for operating both a NOx only and combined PM and NOx treatment system has been proposed and shows potential for further development.

Acknowledegments

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References:

1. Crosse, J.,
2. "Prepare to vanquish anti-diesel prejudice", *F.T. Automotive World*, p. 25, September 1999.

Dunne, J.M., "Application of powertrain and fuel technologies to meet emissions standards", *Proc. International Seminar on The Status of Emissions Legislation* , IMechE (1996).

3. Greening, P., "Future legislation on vehicle emissions and fuel quality", Paper 12 in *Proc.1st International Conference on Health effects of Vehicle emissions,* (1999).
4. Monaghan, M.L., "Particulates and the diesel- the scale of the problem", Paper S491/001/98 in *Diesel Engines- Particulate Control*, IMechE Seminar Publication 1998-16 (1998).
5. UK Department of the Environment, *3rd Report of the Quality of Urban Air Resources Group*, May 1996.
6. Penetrante, B.M., and Schulthesis, S.E., (Eds.), " Non-Thermal Plasma Techniques for Pollution Control: Part A: Overview, Fundamentals and Supporting Technologies, and Part B: Electron Beam and Electrical Discharge Processing", NATO ASI Series, Series G: Ecological Sciences, Vol. 34, Part B, Springer- Verlag, 1993.
7. Hall, S., "From Lab To Reality, Plasma Engineering For Pollution Control",
8. .Thomas, S.E, Martin A.R., Raybone D., Shawcross J.T., Ng K.N., Beech P., Whitehead J.C., " Non-thermal aftertreatment of particulates- Theoretical limits and impact on reactor design" *SAE* Paper 2000-01-1926 (2000).
9. Broer, S., Hammer, T., and Kishimoto, T., "Silent discharge plasma induced removal of NOx and hydrocarbons from diesel engine exhaust", *Proc. 3rd Int. Conf. On Advanced Oxidation*
10. Hemmingway, M.D.,Goulette, D., Ripley, G., Thoreson, T., Kupe, J., Herling, D., Basharan, S., Smity, M., Lessro, D., and Virden, J., "Evolution of a non-thermal plasma system for remediation of NOx in diesel exhaust", *SAE Paper* 1999-01-3639 (1999).
11. Balmer, M.L.., Tonkyn, R., Yoon, S., Kolwaite, A., Barlow, S., Maupin, G., and Hoard J., "NOx destruction behavior of select materials when combined with a Non-Thermal Plasma", *SAE Paper* 1999-01-3640 (1999).
12. Fanick, E.R., Grothaus, M.G., Bykowski, B.B., Raybone, D., and
13. Hall, S.I., "Reduction of diesel NOx/PM emissions using a Non-Thermal Plasma", p. V57 in *Proceedings of the 1995 DEER Workshop*.
14. Hall, S.I., Winterbottom, F., Inman, M., Segal, D.L., Raybone, D., Shawcross, J.T., Morgan, R.A., and Martin, A.R. *WO99/12638*