# **Catalytic Coatings for Active and Passive Diesel Particulate Filter Regeneration**

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**Summary.** This paper will give an overview how catalytic coatings are applied in diesel particulate filter systems to support filter regeneration by soot oxidation with nitrogen dioxide or oxygen. Catalytic coatings can be placed on a catalyst substrate in front of a diesel particulate filter, on a filter, or in a combined system on both. Strategies and conditions for successful filter regeneration of those systems will be discussed.

Keywords. Heterogeneous catalysis; Kinetics; Oxidations; Nitrogen dioxide; Soot oxidation.

### Introduction

Diesel engines combust diesel fuel to convert its chemical energy into mechanical power. The primary combustion products of diesel fuel are carbon dioxide and water. More than 99% of diesel emissions consist of CO<sub>2</sub>, H<sub>2</sub>O, and the portion of air left over from the combustion process. As real diesel combustion is not ideal, a fraction of a percent of the total diesel emissions are unwanted combustion by-products [1]. These pollutants are mainly particulate matter (PM), nitrogen oxides (NO<sub>x</sub> = NO and NO<sub>2</sub>), hydrocarbons (HC), and carbon monoxide. Of those, PM emissions are seen as perhaps the most critical. They are of major concern regarding negative health [2–6] and possible climate effects [7–10].

The most effective method to control PM emissions from diesel engines is applying diesel particulate filter (DPF) systems. They are very effective in filtering PM of all sizes out of diesel emissions [11–17]. The main technical challenge for DPF systems in automotive applications is their regeneration from the soot they retain from the exhaust gases. For a large variety of applications ranging from passenger cars, city busses, garbage trucks, delivery trucks, in-door fork lifters, construction machines, tunnel- and mining equipment, to locomotives, various

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DPF systems with soot regeneration technologies are in use today [13, 18]. Whatever the regeneration method, catalytic coatings play a major role in supporting it.

### **Fundamental Principles of DPF System Regeneration**

Particulate matter consists of an agglomeration of primary soot particulates (mainly elemental carbon), adsorbed hydrocarbons (VOF), water, sulphuric and nitric acid, and engine oil derived components like Ca, P, or Zn [19]. The ratio of these components, the microstructure and properties of PM depend on the combustion conditions, the fuel and oil used, and whether and which aftertreatment device is present in the exhaust system.

When trapped in a DPF all of the components present in particulates except the normally very small amount of inorganic oil derived residues can be converted into gaseous products by evaporation (water), decomposition ( $H_2SO_4$ ,  $HNO_3$ ), or oxidation (VOF, soot (=mainly C)). Therefore all technologies commonly used for DPF regeneration are based on some heat treatment and the oxidation of soot to  $CO_2$ . From each regeneration a small amount of "oil ash", which typically consists mainly of zinc phosphate and calcium sulphate, remains in the filter and has to be mechanically removed during vehicle service.

The microstructure of particulate matter influences its reactivity against oxidation [20]. However, a much greater influence on the rate at which PM can be oxidised comes from the concentration and the reactivity of the applied oxidising agent. In diesel exhaust emissions there are two oxidising gases present, which are suitable for soot oxidation: oxygen and nitrogen dioxide. Both play an important role in DPF regeneration. There is much more  $O_2$  present in diesel exhaust emissions than  $NO_2$ , but  $NO_2$  is much more active than  $O_2$ . The difference in reactivity between  $O_2$  and  $NO_2$  as oxidising agent for soot can be seen in Fig. 1, which shows the temperature-ranges at which  $NO_2$  and  $O_2$  start to combust soot.

### Oxygen Based Soot Oxidation

The oxygen comes from the charge air left over from the diesel combustion process and its concentration in diesel exhaust emissions is in the order of around 10%. Exhaust temperatures above  $550^{\circ}$ C are required for soot oxidation by O<sub>2</sub>. With the

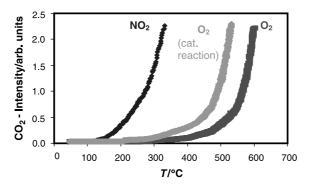


Fig. 1. Soot combustion (to  $CO_2$ ) by  $NO_2$  and  $O_2$  as a function of temperature

application of so-called "fuel borne catalysts" (FBCs), which precursors are added to the diesel fuel, the required temperature can be lowered to around  $400-450^{\circ}C$  [21-33]. Alternatively oxygen could be "activated" by applying non-thermal plasma to generate ozone [34], which could then be used to combust soot at low temperatures [35]. However, this approach has not been used in commercial applications yet.

### Chemistry of Oxygen Based Soot Oxidation

If the temperature exceeds  $500^{\circ}$ C soot oxidation by oxygen becomes significant (Eq. (1)).

$$\mathbf{C} + \mathbf{O}_2 \to \mathbf{CO}_2 \tag{1}$$

The kinetics of soot oxidation is also influenced by the presence of water vapour and adsorbed species like hydrocarbons on the soot surface. A possible influence from water vapour could come from the steam reforming reaction (Eq. (2)) which could be followed by the oxidation of CO and  $H_2$  to  $CO_2$  and water according to Eqs. (3) and (4).

$$C + H_2O \longleftrightarrow CO + H_2 \tag{2}$$

$$\operatorname{CO} + \frac{1}{2}\operatorname{O}_2 \to \operatorname{CO}_2 \tag{3}$$

$$H_2 + \frac{1}{2} O_2 \to H_2 O \tag{4}$$

The CO of Eq. (2) could also react with water in the water gas shift reaction (Eq. (5)).

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (5)

The combination of Eqs. (2) and (5) results in Eq. (6).

$$C + 2 H_2 O \longleftrightarrow CO_2 + 2 H_2 \tag{6}$$

The presence of  $CO_2$  could lead to carbon removal according to Eq. (7) towards the *Boudouard* equilibrium [36], which could be followed by the oxidation of CO to  $CO_2$  (Eq. (3)).

$$\operatorname{CO}_2 + \operatorname{C} \longleftrightarrow 2 \operatorname{CO}$$
(7)

Adsorbed hydrocarbons could help to ignite the soot by its easier oxidation. The oxidation of these adsorbed HCs could lead to local exotherm generation heating up the soot locally to its combustion temperature. Additionally, when HCs are desorbing or burning off from soot particulates, the surface area of the soot particulates accessible to oxygen increases. This activates the soot for its easier combustion.

Whereas sulphur in the fuel has a negative effect on the NO<sub>2</sub> formation and PM emissions (see later), it might have also beneficial effects for the soot oxidation itself. Sulphuric acid adsorbed on particulate matter becomes more concentrated, when the temperature comes close to its boiling point ( $338^{\circ}$ C). H<sub>2</sub>SO<sub>4</sub> is a strong oxidant and might support the soot oxidation according to Eq. (8).

$$H_2SO_4 + C \rightarrow H_2O + SO_2 + CO \tag{8}$$

This reaction might become more important, after a long period of passive regeneration at low temperatures, when some  $H_2SO_4$  has been accumulated within the soot layer.

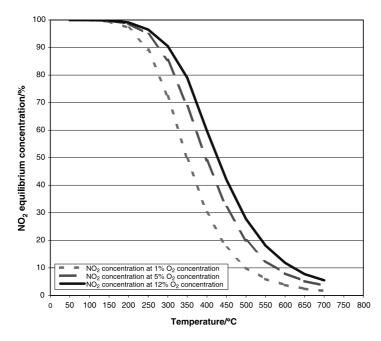
#### Nitrogen Dioxide Based Soot Oxidation

NO is formed under the high-temperature, high-pressure in-cylinder conditions from the nitrogen and oxygen present in the charge air during the diesel combustion. NO<sub>2</sub> forms from NO by reaction with excess oxygen. During the expansion stroke of the piston the temperature decreases rapidly within the combustion chamber, but the NO concentration does not decrease to the NO/O<sub>2</sub>/NO<sub>2</sub> equilibrium concentration as NO is kinetically relatively stable under these conditions [37]. Figure 2 shows the NO<sub>2</sub> concentration at thermodynamical NO/NO<sub>2</sub>/O<sub>2</sub> equilibrium (Eq. (9)) for the temperature range from 0–700°C under typical diesel O<sub>2</sub> concentration levels.

$$NO + \frac{1}{2}O_2 \longleftrightarrow NO_2 \tag{9}$$

The concentration of nitrogen oxides in diesel exhaust gas is around 0.01-0.1%. That is 2–3 orders of magnitude lower than the O<sub>2</sub> concentration. 80–95% of the nitrogen oxides leave the engine as NO and only 5–20% as NO<sub>2</sub>.

In exhaust systems without oxidation catalysts NO is oxidised to NO<sub>2</sub> mainly only after leaving the tailpipe as the reaction of NO with O<sub>2</sub> is very slow under these conditions. The presence of an oxidation catalyst can speed up the NO oxidation reaction and increase the NO<sub>2</sub>-share of NO<sub>x</sub> downstream of the catalyst, where the NO<sub>2</sub> can then be utilised for soot oxidation. An alternative, but not yet



**Fig. 2.** Equilibrium NO<sub>2</sub> concentration for various (diesel emissions typical-) oxygen concentrations as a function of temperature

commonly applied way to increase the rate of the NO oxidation is the application of a non-thermal-plasma reactor [34, 39–42].

NO<sub>2</sub> oxidises soot to CO<sub>2</sub> at reasonable rates at temperatures as low as ca. 250°C [43].

### Design of Diesel Oxidation Catalysts (DOC) for Nitrogen Dioxide Based Soot Regeneration Strategies

A DOC typically consists of a ceramic (most common is cordierite) or metallic (most common is stainless steel) substrate with geometric surfaces of a few square meters. To increase the surface area for a good distribution of the precious metal catalyst material (most common is Pt for DOCs) a so-called "washcoat" consisting of a thermally stable high surface area metal oxide (with a few hundred square meters surface area per gram, *e.g.* Al<sub>2</sub>O<sub>3</sub>) is used. The main function of the washcoat is to stabilise the fine dispersed catalyst material against sintering, but can also be used to enhance the catalytic activity or protect it against poisoning. The aim is to use as much washcoat material as possible without compromising the backpressure behaviour of the catalyst too much. The typical range for washcoat loading is between 3 and  $300 \text{ g/dm}^3$  catalyst volume with typical metal loadings of  $0.1-10 \text{ g/dm}^3$  catalyst.

### Reactions Catalysed by DOCs for NO<sub>2</sub> Based Soot Regeneration

Besides of the NO oxidation further reactions taking place over the DOCs are the oxidation of CO according to Eq. (3) and hydrocarbons (HCs) according to Eq. (10).

$$C_n H_m + (n + \frac{m}{2})O_2 \rightarrow n CO_2 + \frac{m}{2} H_2 O$$
(10)

As CO and HC compete with NO for the active sites on the catalyst, a very high activity for all these oxidation reactions is desired. When sulphur-containing species like SO<sub>2</sub> are present in the diesel exhaust, they will also be oxidised over the DOC to eventually form sulphuric acid and sulphates (Eqs. (11)-(13)).

$$SO_2 + \frac{1}{2}O_2 \to SO_3 \tag{11}$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$
 (12)

$$Al_2O_3 + 3SO_3 \rightarrow Al_2(SO_4)_3 \tag{13}$$

Equation (11) competes with Eq. (9) and therefore limits the NO<sub>2</sub> formation. The formation of sulphuric acid (Eq. (12)) can block the active sites and the formation of washcoat component sulphates (*e.g.* Eq. (13)) can destroy its functionality. Another disadvantage of sulphuric acid and sulphate formation is that sulphuric acid and sulphates can pass DPFs and are measured as particulate matter in legislated emission tests. Therefore the sulphur contents of the diesel fuel as well as the sulphur contents of the engine oil have to be minimised.

#### Chemistry of Nitrogen Dioxide Based Soot Oxidation

The chemistry of nitrogen dioxide based soot oxidation has been subject to several studies [20, 44, 45]. In recent synthetic gas studies with carbon black exposed to a

mixture of NO<sub>2</sub>, O<sub>2</sub>, and water [46] two types of C-oxidation reactions have been identified: direct C–NO<sub>2</sub> reactions (Eqs. (14) and (15)) and cooperative C–NO<sub>2</sub>–O<sub>2</sub> reactions (Eqs. (16) and (17)) in which (+NO<sub>2</sub>) refers to the occurrence of an unstable  $C-(O_2)\cdots NO_2$  complex, which promotes the desorption from the solid carbon surface.

$$-C + 2 \text{ NO}_2 \rightarrow CO_2 + 2 \text{ NO}$$
(14)

$$-C + NO_2 \rightarrow CO + NO \tag{15}$$

$$-C + \frac{1}{2}O_2 + NO_2(+NO_2) \rightarrow CO_2 + NO (+NO_2)$$
(16)

$$-C + \frac{1}{2}O_2(+NO_2) \rightarrow CO (+NO_2)$$
(17)

The contribution of the cooperative  $C-NO_2-O_2$  reaction to the overall oxidation rate increases when the temperature increases. The presence of water vapour promotes the direct  $C-NO_2$  reactions. The main products from these direct (Eqs. (14) and (15)) and cooperative (Eqs. (16) and (17)) reactions are  $CO_2$  and NO, the products of the reactions shown in Eqs. (14) and (16). The amount of CO formed (Eqs. (15) and (17)) is only a few percent of the total amount of products, but increases with temperature increase.

In engine and vehicle tests of CRT<sup>®</sup> applications it is often found that tailpipe  $NO_x$  emissions are up to 2–10% lower than engine out  $NO_x$  emissions [11]. The mechanism of this  $NO_x$  conversion is not fully understood yet. Possible  $NO_x$  conversion products could be HNO<sub>3</sub> or nitrates (which might be stored on the particulates or the filter), N<sub>2</sub>O, or N<sub>2</sub>. PM can contain nitrates, but the amount found on PM is usually very small. N<sub>2</sub>O formation could occur even without the presence of a reducing agent between 200 and 500°C according to Eq. (18).

$$3 \text{ NO}_2 \rightarrow \text{NO} + \text{N}_2\text{O} + 2 \text{ O}_2 \tag{18}$$

The possible equilibrium amount of N<sub>2</sub>O under diesel exhaust conditions (*ca.* 500 ppm NO<sub>x</sub> and 5% O<sub>2</sub>) lies in the lower percent region. However, significant amounts of N<sub>2</sub>O have not been observed. As N<sub>2</sub> is present in large amounts in diesel exhaust a possible NO<sub>x</sub> reduction to N<sub>2</sub> would not be measurable under engine conditions and cannot be excluded. Possible NO<sub>x</sub> reaction pathways could be as shown in Eqs. (19)–(22).

$$NO_2 + C \rightarrow CO_2 + \frac{1}{2}N_2 \tag{19}$$

$$\mathrm{NO}_2 + 2\,\mathrm{C} \to 2\,\mathrm{CO} + \frac{1}{2}\,\mathrm{N}_2 \tag{20}$$

$$2 \text{ NO} + \text{C} \rightarrow \text{CO}_2 + \text{N}_2 \tag{21}$$

$$NO + C \to CO + \frac{1}{2} N_2 \tag{22}$$

There might also be a small contribution of  $NO_x$  reduction by so called "lean- $NO_x$ " reactions with HCs over the DOC. Its ideal pathway can be described by Eq. (23) [47].

$$(2m + \frac{1}{2}n) \text{ NO} + C_m H_n \rightarrow (m + \frac{1}{4}n) \text{ N}_2 + m \text{ CO}_2 + \frac{1}{2}n \text{ H}_2 \text{O}$$
 (23)

However, real lean-NO<sub>x</sub> reactions between HCs and NO<sub>x</sub> over Pt-containing catalysts are very complex [48, 49] and usually lead to a product mix with a major share of  $N_2O$ .

To verify, which of the above or alternative reactions lead to some  $NO_x$  conversion, model gas tests and possible isotopic "labelling" of N or O in  $NO_x$  might help to characterise the reaction pathways.

As shown, there are numerous possible reaction pathways for soot oxidation to regenerate DPFs. Model gas tests can help to verify the conditions, under which these possible reactions might occur, but it seems to be very difficult to fully characterise real world DPF regenerations.

### **Passively Regenerating Diesel Particulate Filter Systems**

In passively regenerating DPF systems the soot oxidation happens during the normal operation of the vehicle without any action required by either the operator or the engine control system. For a passive regeneration strategy using oxygen, the exhaust temperatures have to be reliably frequent above 400°C in case of FBCs present or even 500–550°C without FBCs present. For a passive regeneration strategy using NO<sub>2</sub> the exhaust temperatures have to be reliably frequent above  $250^{\circ}$ C.

Exhaust temperatures of passenger car applications span a wide range during "normal" operation as their duty cycles can be extremely different depending on how and where the vehicle is driven. At high speed driving exhaust temperatures might exceed 500°C, but at low load city driving, temperatures might not even reach 200°C. Because of the unpredictable drive cycle of passenger cars, passenger car DPF regeneration cannot rely on any passive regeneration strategy.

Exhaust temperatures of heavy duty diesel (HDD) engine applications are in the region between 200 and 400°C during normal operation and most of their drive cycles are repeating and very predictable. Under "normal" operation conditions HDD exhaust gas temperatures don't reach the areas, which would be required for oxygen-based regeneration, but most vehicles would reach the temperature region above 250°C frequently enough to allow a passive, NO<sub>2</sub> based regeneration strategy. The following commercially available systems are based on NO<sub>2</sub> based passive PM regeneration: CRT<sup>®</sup> (=Continuously Regenerating Trap: Diesel Oxidation Catalyst (DOC) followed by DPF) [50, 51], CSF (=Catalysed Soot Filter: Catalyst Coated DPF) [52, 53], and CCRT<sup>TM</sup> (=DOC followed by CSF) [54]. They all require ultra low sulphur fuel (max. 50 ppm S, ideally <10 ppm S), the knowledge of the operation temperature profile, and a minimum NO<sub>x</sub> to PM ratio.

### Function Principle of $CRT^{\mathbb{R}}$ , CSF, and $CCRT^{TM}$

The first step for carbon burning at low temperatures by NO<sub>2</sub> is generating NO<sub>2</sub>. This can be done by oxidising NO over an oxidation catalyst upstream of a particulate filter (CRT<sup>®</sup> system) or over a catalytic coating placed on a diesel particulate filter (CSF). NO<sub>2</sub> oxidises soot (mostly carbon) collected on top of and inside the walls of the particulate filter to CO<sub>2</sub>. As a result NO<sub>2</sub> is reduced back to NO.

The main functional requirements for a passive regenerating DPF system are a sufficient temperature profile and a minimum  $NO_x$  to PM ratio. The required values are system dependent and interdependent of each other. The basic factors involved are:

- 1.  $NO_x$  mass flow, depending on speed and load of the engine, combustion conditions.
- 2. NO to NO<sub>2</sub> oxidation kinetics, depending mainly on the catalyst used and its ageing status, temperature, and mass flows of NO, NO<sub>2</sub>, O<sub>2</sub>, CO, and HC.
- 3. PM mass flow, depending on speed and load of the engine, combustion quality.
- 4. Soot oxidation kinetics, depending mainly on temperature, NO<sub>2</sub> mass flow, soot reactivity, soot loading of the filter, and soot distribution within the filter.

A DOC followed by a DPF forms a CRT<sup>®</sup>-system. Figure 3 shows its typical set-up.

Figure 4 shows the pollutant conversion of field aged CRT<sup>®</sup>-systems. Even after very long operating distances the systems tested show still very high CO, HC, and PM conversion similar to the performance of a new one.

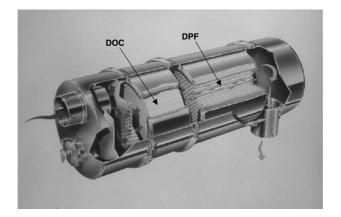


Fig. 3. CRT<sup>®</sup>-schematic

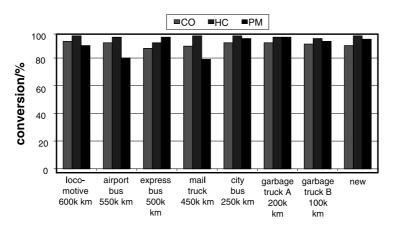


Fig. 4. Pollutant conversion of field aged CRT-systems

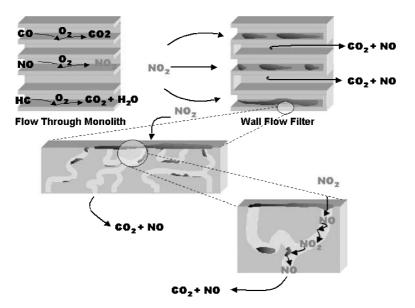


Fig. 5. Scheme of the working principles of  $CRT^{\mathbb{R}}$ , CSF, and  $CCRT^{TM}$ 

In a "coated DPF" or "CSF" (<u>C</u>atalysed <u>S</u>oot <u>F</u>ilter) the role of the oxidation catalyst (CO, HC, and NO oxidation) has been transferred to the filter. As NO<sub>2</sub> is formed along the length of the filter, some NO<sub>2</sub> is only formed downstream of some of the soot. When this NO<sub>2</sub> hits soot particulates collected on the filter, these are oxidised to CO<sub>2</sub>, while NO<sub>2</sub> is reduced to NO. Over the catalytic coating of the filter NO can be re-oxidised to NO<sub>2</sub> by present oxygen, and is therefore available for further soot oxidation.

Combining CRT<sup>®</sup> and CSF results in a CCRT<sup>TM</sup>-system, which allows the maximum use of the NO<sub>x</sub> for soot regeneration. Figure 5 shows the principle of CRT<sup>®</sup>, CSF, and CCRT<sup>TM</sup>. The key reactions shown in Fig. 5 are those given in Eqs. (9) and (14).

The principle difference between CRT<sup>®</sup>, CSF, and CCRT<sup>TM</sup> is the location, where these reactions happen: In a CRT<sup>®</sup> system Eq. (9) takes place over the DOC and Eq. (14) in the soot layer of the DPF. As there is no catalytic coating on the DPF the NO from Eq. (14) cannot be re-used in the DPF. Due to the presence of oxidation catalyst coating within the filter walls of the CSF-only and CCRT<sup>TM</sup>-systems the NO formed in Eq. (14) can be re-oxidised according to Eq. (9) and can be made available for further C-oxidation reactions according to Eq. (14). Depending on the temperature and the availability of C and active sites to re-oxidise NO, this cycle can occur several times. However, in reality the systems are more complex than described above and not all reaction pathways are well understood yet.

## Comparison of CSF, CRT<sup>®</sup>, and CCRT<sup>TM</sup> Systems

# Comparison CSF-CRT<sup>®</sup>

A CSF system is more compact than a CRT<sup>®</sup> system as it requires only one component instead of two. But its compactness requires compromises regarding exhaust backpressure and catalyst loading.

The soot layer on top of the filter walls burns less effectively in a CSF than a CRT<sup>®</sup> system. This is because in a CSF NO is oxidised to NO<sub>2</sub> underneath the soot layer whereas in a CRT<sup>®</sup> system NO<sub>2</sub> is formed upstream of the DPF and has therefore a higher chance to get in contact with the soot layer on top of the filter walls. For the same reason a CSF system has a larger NO<sub>2</sub> slip than a CRT<sup>®</sup> system with the same amount of precious metals applied and requires higher temperatures (>300°C) for significant carbon regeneration.

A CSF system requires less installation space but higher operating temperatures than a CRT<sup>®</sup> system. In a CSF NO<sub>x</sub> can potentially be used more than once for soot oxidation. At high enough temperatures (>350°C) the NO<sub>x</sub>:PM ratio requirements can be lower for CSFs than for CRT<sup>®</sup> systems.

Due to its design a CRT<sup>®</sup> system is less sensitive to ash accumulation and more robust against sintering of the precious metal components. Ash accumulation in CSF reduces efficiency due to blocking of gas pathways as the ash plug builds up. Precious metal sintering is a high temperature ageing mechanism leading to a reduced number of catalytically active sites. To minimise the increase of back-pressure due to the catalyst coating, the amount of washcoat, which stabilises the precious metals in a CSF slightly less protected against sintering than in a DOC. In case of spontaneous thermal regenerations with oxygen the carbon burning creates heat within the DPF. Such heat would not effect an upstream DOC (like in the CRT<sup>®</sup> set-up), but the catalytic coating of the CSF would be fully exposed to it. If the temperature on the CSF surface becomes too high, this could potentially cause some precious metal sintering resulting in catalyst de-activation.

Both systems have advantages and disadvantages. Thus, which system to choose depends on the conditions for its application. In HDD applications, where the low temperature activity is most important, the CRT<sup>®</sup> system seems to be the better choice.

# Comparison of CCRT<sup>TM</sup> with CSF and CRT<sup>®</sup> Systems

Figure 6 compares the pressure rise of an un-coated DPF, a CSF, a CRT<sup>®</sup>, and a CCRT<sup>TM</sup> system with each other in a low temperature cycle ( $T < 270^{\circ}$ C) to assess

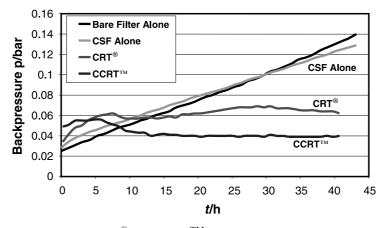


Fig. 6. Un-coated DPF, CSF,  $CRT^{\text{(B)}}$ , and  $CCRT^{\text{TM}}$ ; backpressure behaviour over time during low temperature cycle at  $T < 270^{\circ}C$ 

their low temperature behaviour. The backpressure of these particulate filter systems relates to its soot loading. A higher soot loading results in a higher backpressure. The change in backpressure relates therefore to the regeneration efficiency compared to the soot accumulation.

The CCRT<sup> $\hat{T}M$ </sup> system combines properties of CRT<sup> $\mathbb{R}$ </sup> and CSF. It allows a more efficient use of the NO<sub>x</sub> emitted from the engine for carbon burning and is even at low CSF precious metal loadings superior to CRT<sup> $\mathbb{R}$ </sup>- and CSF-systems. This is especially true for low temperature applications and applications with a low NO<sub>x</sub> to PM ratio. NO<sub>2</sub>-slip can be minimised by applying optimised metal loadings and distributions.

### **Active Regenerating Diesel Particulate Filter Systems**

If applications are too cold (*e.g.* garbage trucks or some city busses) or driving cycles do not reliably frequent cause the exhaust temperature to reach at least  $250^{\circ}$ C (*e.g.* passenger cars) to enable passive regeneration, active regeneration is required. If the NO<sub>x</sub>-emissions of the engine are high enough, the temperature can be raised to burn soot by NO<sub>2</sub>. If the NO<sub>x</sub>-emissions of the engine are low, the soot combustion has to be done by oxygen.

Increasing the temperature to  $300-350^{\circ}$ C for NO<sub>2</sub>-based regeneration can be done in a number of ways, *e.g.* by fuel injection into the exhaust or by engine means. Active regeneration via NO<sub>2</sub> requires a relatively long time (due to low NO<sub>2</sub> concentration in the exhaust) but is a safe strategy, as high temperatures are avoided.

For a temperature increase to 550–600°C, which is required for regeneration with O<sub>2</sub>, "post injection" with a high rate is required. "Post injection" is a diesel fuel injection into the engine combustion chamber at a very late time of the combustion stroke of the engine so that the fuel is not burned as part of the usual combustion process. The aim of a post injection is to put large amounts of unburned hydrocarbons into the exhaust. These hydrocarbons burn over the oxidation catalyst and raise the exhaust temperature via the heat generated. Due to the higher  $O_2$  concentration the reaction rate of  $O_2$ -based soot regeneration is higher than the rate of the NO<sub>2</sub> concentration limited NO<sub>2</sub>-based regeneration. However, there is a risk of destroying the filter. This risk is especially high in situations where the carbon load of the filter is high and the exhaust mass flow low. If a  $O_2$ -based regeneration starts under these conditions, carbon burning creates a lot of heat in the filter, which might not be sufficiently removed from the filter. If too much heat is retained in the filter, it might melt (cordierite, sinter metal) or oxidise (SiC). If the temperature gradient along the diameter or the axis of the filter exceeds the filter material limits, the thermal stress could cause filter cracking. Therefore applying this strategy requires care.

# Active Regeneration of a $CRT^{\mathbb{R}}$ System via $NO_2$ in a Field Trial

In a field trial to study active regeneration by  $NO_2$  [55] the exhaust temperature has been controlled by varying the turbo charger efficiency. Active regeneration was triggered when the system backpressure reached a critical value. The temperature increased and the backpressure dropped. The success of this trial demonstrated that this approach represents a promising strategy. Active regeneration via NO<sub>2</sub> is a safe strategy, but requires a long time due to the low mass flow of NO<sub>x</sub>.

CCRT<sup>TM</sup>-systems offer significant advantages for the NO<sub>2</sub>-based active regeneration compared to CRT<sup>®</sup>- and CSF-systems.

### Active Regeneration via $O_2$

Active Regeneration *via*  $O_2$  is applied successfully in more than 500.000 LDD applications [56] and is the most likely solution for all US HDD-applications (with low temperatures and/or low NO<sub>x</sub> to PM ratio) to meet US 2007 legislation limits. The first LDD-systems with  $O_2$ -based active regeneration used a highly active DOC in front of a SiC-filter and a cerium based additive to lower the  $O_2$ -C-reaction temperature (see Fig. 1). To avoid excessive ash accumulation HDD-applications would have to do without additives. HDD engines are built to run for more than one million kilometres and even with oil ash accumulation only there would be too much ash to store in the filter for the lifetime of the vehicle. Oil ash accumulated in a DPF needs to be cleaned every 100000–200000 km. If FBCs would be used, the frequency of ash cleaning intervals, which cause downtime for the vehicle, would increase, which is highly undesirable.

For the non-catalysed oxygen-carbon reaction (Eq. (1)) temperatures of 550–600°C are required. These temperatures can be obtained by post injection in combination with an oxidation catalyst. Here the unburned fuel is being oxidised over the oxidation catalyst and produces the heat required to heat up the exhaust gases to the desired temperature. The heat production can be done over an oxidation catalyst, which is functioning as a catalytic burner or over a (precious metal containing) filter coating. In both cases a high resistance of the coating against high temperature exposure is required.

The filter coating could also have a role in the catalytic carbon oxidation by oxygen. However, compared to uncoated DPFs coated DPFs have shown only small advantages in supporting  $O_2$  based soot regenerations [30]. These results indicate that catalytic DPF coatings have no major influence on the  $O_2$ -C-reaction. However, catalytic CSF coatings resulted in a faster, more complete regeneration in the temperature range of 540–640°C.

Active regeneration is a fast process and represents a very promising strategy for the filter regeneration.

### **Diesel Particulate Filter Systems as Part of 4-Way-Systems**

For additional nitrogen oxide reduction DPF-systems can be combined with NO<sub>x</sub> emission control technologies. The currently most common technology for NO<sub>x</sub> emission reduction is exhaust gas recirculation (EGR). By combining a CRT<sup>®</sup> with EGR very high (>90%) PM-, CO-, and HC-reduction and *ca.* 40% NO<sub>x</sub>-reduction can be achieved [57]. If a more effective NO<sub>x</sub>-reduction is required, a NO<sub>x</sub>-storage catalyst coating or an SCR-system can be applied. A DPF with a NO<sub>x</sub>-storage catalyst coating is known under the term "DPNR" (created by Toyota) [58, 59]. By combining a CRT<sup>®</sup> with an SCR-system a so-called SCRT<sup>®</sup> system is obtained [51, 60]. Depending on engine out emissions as well as speed/load and

System	НС	СО	$NO_x$	PM
SCRT [48]/Eng. out (conversion) SCRT [57]/Eng. out (conversion)	0.003/0.162 (98%) 0.002/0.123 (98%)	0.000/0.989 (100%) 0.000/0.324 (100%)	1.061/7.018 (85%) 0.562/6.926 (92%)	0.007/0.163 (96%) 0.008/0.022 (64%)
Euro V Limits	0.460	1.500	2.000	0.020

**Table 1.** Emissions data of various SCRT<sup>®</sup> systems obtained by ESC ( $g k W^{-1} h^{-1}$ , %) [48, 57]

temperature conditions, the efficiency of such systems can exceed 90% for all four pollutants, CO, HC, PM, and CO. Table 1 shows emission data of SCRT<sup>®</sup> systems obtained by the ESC tests.

### Conclusions

A variety of DPF systems are available to reduce soot emissions from diesel engine applications. The main challenge associated with DPF systems is the regeneration of the soot retained in them. Soot regeneration is based on soot oxidation. This can be done by oxygen or nitrogen dioxide. If the driving cycle and the exhaust conditions allow, it is possible to use passively regenerating systems. For all other cases active regenerating systems are available. Whatever the regeneration method, catalytic coatings play a key role in supporting them.

DPF systems can also be combined with  $NO_x$  control technologies to form 4way systems. With such systems more than 90% of PM, CO, HC and  $NO_x$  emissions can be removed to meet current and future legislation requirements.

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