

NO_x and PM Reduction from Diesel Exhaust Using Vanadia SCRF[®]

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ABSTRACT

Future heavy-duty diesel (HDD) engines are designed to have higher engine out NO_x, for improved fuel economy, while reduction of the emission control technology footprint is also desired. Consequently, higher NO_x reduction across compact emission control systems is required. Selective catalytic reduction (SCR) catalyst coating combined with a wall flow particulate filter (SCRF^{®1}) is a technology that enables abatement of NO_x emissions in addition to oxidation of soot from diesel engine exhausts. Vanadia based-SCR is well known for NO_x reduction and is active for hydrocarbon (HC) and particulate matter (PM) oxidation. This dual functionality (oxidation and reduction reactions) of the V.SCR catalysts plus the filtration achieved by the filter substrate can help certain diesel engine applications achieve the legislative limits with a reduced packaging volume.

In this work, the NO_x reduction and PM oxidation over filters coated with V.SCR coating (V.SCR-DPF) were studied independently and simultaneously. The effect of various parameters such as washcoat loading, filter type, ANR, and NO₂/NO_x were investigated on engine. The V.SCR-DPF catalyst was tested with a diesel oxidation catalyst (DOC) upstream. The results confirm that significant NO_x and PM reduction can be obtained over transient cycles and at steady state conditions. In general, more than 70% NO_x conversion was obtained over a degreened V.SCR-DPF on hot NRTC (Average Temperature = 300°C) and more than 90% NO_x conversion when it is coupled with a V.SCR catalyst and ammonia slip catalyst (ASC). After aging at 550°C for 50 hours, a slight improvement in NO conversion was obtained over the SCR-DPF. Passive filter regeneration was investigated starting with both a clean and a soot loaded (3g/L) V.SCR-DPF. Good passive regeneration was obtained for both cases during consecutive NRTC test cycles, where the backpressure stabilized after ca. 20 cycles. In addition, good particle number (PN) filtration was obtained over V.SCR-DPF while meeting expected 2019 EU regulation targets for non-road applications.

Furthermore, computational modeling tools were developed, which are able to predict NO_x reduction and passive regeneration for this technology over different engine test conditions. The model was developed by combining kinetics for a V.SCR catalyst, originally developed for a flow through monolith, with a physical model for a coated particulate filter. The reaction kinetics were developed using reactor data. The model has been successfully validated against engine data.

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1.0. INTRODUCTION

Diesel engines are widely used in the transportation, construction, agricultural and other sectors due to their high power output, reliability and fuel efficiency. Engine emissions contribute to air pollution [1] thus aftertreatment systems are used to reduce the air pollutants. Typical pollutants coming from diesel engines are carbon monoxide (CO), unburned hydrocarbons, particulate matter, and nitric oxides (NO_x). Typically, HC and CO are controlled by a diesel oxidation catalyst, particulate matter by a diesel particulate filter (DPF), while NO_x is controlled by a selective catalytic reduction catalyst. Depending on the application operating conditions, different types of SCR (Cu, Fe and V-based) have been applied for efficient NO_x reduction [2-3]. However, further NO_x reduction will be needed to meet future stringent emission regulations [4]. In addition, there is great interest in combining aftertreatment components to reduce packaging volume and cost and to bring the SCR catalyst closer to

the engine to improve cold start NO_x reduction performance, by early attainment of the temperature requirement for urea injection. In addition, an increase in SCR volume may be needed to achieve higher NO_x conversions for higher engine out NO_x emissions that could return substantial fuel consumption benefits [4]. SCR-DPF system compact designs are already applied in diesel passenger cars. In the case of heavy duty and non-road applications, the SCR-DPF design depends on the NO_x and soot oxidation interaction that takes place in close vicinity [5]. It has been demonstrated that Cu zeolite applied on a DPF (Cu.SCR-DPF) efficiently removes NO_x under different conditions and test cycles [6, 7, 8, 9, 10, 11, 12]. In addition, the interactions between the SCR and DPF functionalities have been investigated by engine testing and modeling tools [5-6]. It was shown that the soot present on SCR-DPF does not have a significant impact on NO_x conversion, whereas the SCR activity significantly retarded the rate of soot removal by oxidation with NO₂ [6].

Vanadia based SCR catalysts are well known for their NO_x reduction capability and have been the subject of extensive reviews [13-14]. V. SCR catalysts are also active for HC and PM oxidation [3, 15, 16, 17, 18, 19]. This dual functionality (oxidation and reduction reactions) plus the filtration obtained on the filter substrate can help certain diesel engine applications achieve the legislative emissions limits together with reduction of the aftertreatment packaging volume. V.SCR catalysts are also well known for their sulfur resistance, where no active regeneration is needed to remove sulfur and recover the SCR performance. As of today, only few works have reported V.SCR coated on DPF (V.SCR-DPF) [20, 21]. Johnansen et al. [20] showed that vanadia based SCR formulations on cordierite filters achieved similar NO_x conversion to that of conventional flow through SCR above 300 °C. Wolff et al. [21] described vanadia SCR coating and performance on a high porosity silicon carbide filter. They evaluated the performance of three different coatings. Higher performance was obtained for the parts that were coated with higher washcoat loading with a single layer of coating.

In the present work, the performance of V.SCR-DPF will be discussed for different engine conditions. Some testing was carried out for the DOC + SCR-DPF configuration to examine the SCR-DPF performance separately from SCR. The addition of SCR and ammonia slip catalyst was examined to determine the NO_x conversion performance of the complete aftertreatment system. NO_x reduction and PM oxidation were tested independently and simultaneously for the SCR-DPF. Steady state testing was conducted to determine the NO_x reduction as function of temperature and space velocity. The effect of various parameters such as washcoat technology, filter type, ammonia to NO_x ratio (ANR), and NO₂/NO_x was investigated under transient test conditions, such as the non-road transient cycle (NRTC). The NRTC test is required by a number of emission standards for non-road engines, including the EU Stage III/IV regulation, the US EPA Tier 4 rule and Japanese 2011/13 regulations [22] and will be required for future regulations. In addition, WHTC tests were carried out to examine the SCR-DPF performance under different engine conditions. The WHTC test is a transient engine dynamometer schedule defined by the global technical regulation [23]. Lastly, computational simulation tool was used to predict NO_x reduction and soot oxidation on this technology at different operating conditions.

2.0. EXPERIMENTAL SECTION

2.1. Samples Description

Vanadia based SCR catalysts were coated on different commercially available cordierite DPF substrates. The SCR-DPF samples are summarized in Table 1. Samples were tested after degreening on an engine at 500 °C for 4 hours and some were aged hydrothermally in an oven for 50 hours at 550 °C in air with 10% water. As mentioned above, V.SCR-DPF catalysts were tested with a DOC in front. Most of the tests were carried out with a 7.4L Pt based DOC (8g/ft³). A larger DOC (11.1L) with a higher PGM loading (Pt-Pd) was utilized for higher NO₂/NO_x tests. In addition, a 7.1L Pt-Pd DOC (total of 35g/ft³) was utilized for additional testing. SCR and ASC samples used are described in Table 2.

Table 1. SCR-DPF samples description

SCR-DPF Catalyst ID [†]	V.SCR-DPF Technology	Filter Volume, L	Substrate cell density and wall thickness (mil)
A.1	I	19.5	200/12
A.2	I	17.0	200/12
B.1	I	22.2	300/12
B.2	I	17.0	300/12
C.1	II	22.2	300/12
C.2	II	17.0	300/12

[†]Number indicates engine used.

Table 2. Description of other aftertreatment components

Catalyst ID [†]	Volume, L	Substrate cell density and wall thickness (mil)
DOC_A.1	7.4	400/4
DOC_B.1	11.1	400/4
DOC_B.2	7.1	400/6
V.SCR_A.1	8.5	400/4
ASC_A.1	5.7	400/4
V.SCR/ASC_A.2	13.1	400/6

[†]Number indicates test cell used.

2.2. Engine Bench Testing Description

Engine testing was carried out using standard procedures and equipment. Testing was carried out in two different engine test cells to examine the SCR-DPF performance under different engine out conditions on two different engines.

For the first test cell, ultra-low sulfur diesel (ULSD) fuel was used during all tests. NH₃ was supplied in the form of an aqueous urea solution injected in front of the SCR-DPF catalysts using an air-assisted Grundfos pump. A static mixer was placed after the urea injector to maximize urea mixing and to facilitate decomposition to NH₃. Tests were carried out on a US 2007, 8.9L diesel engine. Intake air flow was measured using an ABB air flow meter ranging from 0-2400 kg/h. Backpressure was measured using pressure transducers (Setra Model 206). Temperatures were monitored through the system utilizing K type thermocouples. Soot loadings weights were measured by weighing the SCR-DPFs while still hot at 180 °C. The scale used for weighing the filters was by Mettler Toledo, ranging from 0 - 64 kg with 0.1g resolution. Exhaust emissions were measured using a Horiba 7400D dual bench and a MKS 2030-HS Series FTIR. In addition, a heated flame ionization detector was utilized to measure HCs. The sample lines were constantly heated at 190 °C. The sampling system setup allowed measurement at multiple locations depending on the test. Emissions were measured at either engine out, DOC out, SCR-DPF out and/or SCR/ASC out to determine SCR-DPF inlet conditions, SCR-DPF outlet and/or system NO_x reduction efficiency, in addition to NH₃ and N₂O slip.

Steady state testing was carried out at different engine speeds and loads to achieve several SCR-DPF inlet temperatures and exhaust flow rate points. Each set point was run as long as needed to achieve

steady state conditions. NRTC tests were carried out to represent a transient driving cycle for mobile non-road diesel engines. For these tests, five repeat tests were performed with a 20 min soak after each of the first two NRTCs; while the three subsequent tests were run consecutively without soak. For the purpose of this publication, the first NRTC test is termed a “cold” test, the second a “warm” test and the subsequent tests “hot” tests. For the hot tests, the average of the three consecutive test will be reported, unless noted otherwise. For these tests EGR was turned off which resulted in ~ 6.5 g/kWh engine out NO_x with a NO_x/PM ratio of ~ 110 (mass based). Before the first NRTC, the catalyst was preconditioned by running a C100 mode without urea injection for at least 30 min to desorb any stored NH₃; the NH₃ concentration at the SCR-DPF outlet was measured during this process to verify all the NH₃ was removed. The engine was allowed to cool until the SCR bed temperature reached 50 °C before running the first test.

Engine out PM during NRTC was measured using a full dilution tunnel. The PM was measured on 47 mm TX40H120-WW Emfab filter using a full flow dilution tunnel that utilizes a Horiba particulate sampling system. The filter was conditioned in the cleanroom for 8 h prior to performing the blank weight, following the CFR Section 40 protocol [24]. The filter was put into a filter holder that goes into the Horiba secondary dilution box. The box temperature was controlled to 47 °C. Both the total sampling flow and the secondary dilution air flow were carefully selected to ensure the filter face temperature was within the 47 ± 0.5 °C range. The filter face temperature was also monitored throughout the entire test. After the test, the filter was put back into the cleanroom and was stabilized for 8 hours before taking the final weight.

The second test cell was equipped with an EU VI, 8L diesel engine. Exhaust emissions were measured with two Horiba Mexa 7100D benches and an ECO Physics CLD 900 RE ht. NH₃ was measured at the tailpipe with a Siemens LDS 6 laser. Ultra-low sulfur diesel fuel (EU VI-B7) was used during all tests in this test cell. NH₃ was supplied in the form of an aqueous urea solution injected in front of the SCR-DPF catalysts using an air-assisted doser. A static mixer was placed after the urea injector to ensure good mixing. Emissions were measured before and after the SCR-DPF catalyst. World harmonized transient cycle (WHTC) tests were carried out. For these tests, three tests were run consecutively. Before the first test, the SCR-DPF was preconditioned at 450 °C for 1 hour without urea injection. For these tests the engine out NO_x was ~ 5.0 g/kWh with a NO_x/PM ratio of 60 (mass based). Similarly, NRTC tests were carried on this engine (~ 4.8 g/kWh with a NO_x/PM ratio of 40). In addition, PN was measured during these cycles. PN measurements were made using a solid particle counting system (Horiba Mexa-2100SPCS). The particle number was measured continuously directly from the engine exhaust after the SCR-DPF. This system is capable of measuring the number of particles larger than 23 nm and smaller than 2.5 μ m.

The last digit of the sample IDs indicates where the samples were tested; 1 for the test cell equipped with the 2007 8.9L engine and 2 for the test cell equipped with the EU VI, 8L engine.

3.0. DEVELOPMENT OF A COMPUTER MODEL

This section of the paper discusses the development and validation of a one-dimensional model for a V.SCR-DPF.

Computer simulation has become an important tool for designing aftertreatment systems, enabling a wide range of parameters and scenarios to be investigated more quickly and cost effectively than a purely experimental, “trial and error” approach [25, 26]. Computer models can be used for optimizing catalyst dimensions, filter substrate type, urea solution dosing strategy, etc. Simulation also can be used to look at optimizing SCR washcoat loading and distribution (e.g. whether the coating is on the inlet or outlet channel) to obtain high NO_x conversion, while keeping the washcoat loading to a minimum to reduce material costs and limit backpressure. Modelling has already been used to investigate the interaction between the NO_x reduction and soot regeneration functionalities of the SCR-DPF, i.e. whether removal of NO_x by the SCR coating adversely impacts soot oxidation due to lower availability of NO₂ and whether the change in NO₂/NO_x ratio due to reaction of soot by NO₂ impacts the rate of NO_x reduction [5-6, 31].

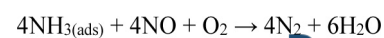
3.1. Approach

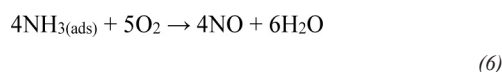
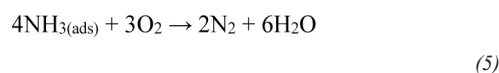
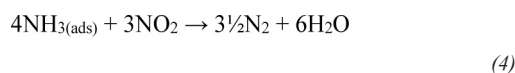
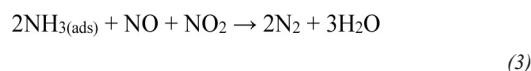
The model for a V.SCR-DPF presented here was developed by combining kinetics for a V-based SCR catalyst developed for a flow-through monolith [27, 28] with a physical model for coated DPF [29,30]. This approach has already been used by this group to develop models for Cu-zeolite and Fe-zeolite SCR-DPFs [6]. It was found that the SCR kinetics could be used without modification, apart from allowing for the different washcoat loading; SCR activity was assumed to be linearly proportional to the washcoat loading. A similar approach has been taken by other workers [5, 31-32].

The model for a coated filter [29, 30] is based on the work of Bissett [33], but incorporates more recent advances [34]. The model treats the solid (filter wall, catalytic coating and soot) and gas phases separately and includes equations for the mass, momentum and energy balances of the gas in the inlet and outlet channels, the pressure drop across the soot cake and filter wall (assuming Darcy’s Law), the solid energy balance and the soot mass balance. An important feature in the DPF model is the description of the way reactants reach the catalytic coating. Thus, in the current DPF model, reactants reach the catalytic coating by diffusion from the bulk flow from both the gas flowing along coated channels and the gas passing through the filter wall. This diffusion is described using mass transfer terms similar to those used for modeling flow-through monoliths.

3.2. Reaction Scheme

In the model, the following reactions occur over the SCR coating:





The first reaction (Eq. 1) is the adsorption and desorption of NH_3 . This is important as all the NH_3 that reacts in the subsequent reactions is NH_3 that has adsorbed on the catalyst ($\text{NH}_{3(\text{ads})}$). The model includes “standard” or NO SCR (Eq. 2), fast SCR (Eq. 3) and SCR of NO_2 (Eq. 4). The model also includes NH_3 oxidation to N_2 and NO (Eq. 5 and 6, respectively). In reactor tests, oxidation of NH_3 to N_2 occurs at temperatures above 300–350°C and oxidation to NO at temperatures above 400°C [27]. The final reaction (Eq. 7) is NO_2 decomposition to NO, which is reversible. This reaction is the reverse of NO oxidation; the main effect observed is decomposition of NO_2 at higher temperatures, rather than oxidation of NO to NO_2 . Similar reaction schemes for V.SCR have been used by other researchers [35, 36, 37].

The model uses Eley-Rideal type kinetics for the NO_x reduction and NH_3 oxidations, as are typically used for modelling SCR reactions. The kinetics were developed using laboratory reactor data and were validated against engine data for the SCR catalyst coated on a flow-through monolith [27]. The reactor tests used the catalyst in the form of a packed bed (crushed and sieved monolith) to minimize the influence of heat and mass transport on the data.

Finally, it should be noted that the model does not include urea hydrolysis, i.e. the formation of NH_3 from urea is assumed to be fast.

3.3. Model Validation

Before a model can be used to make predictions, it is crucial to validate the model against engine data over the widest possible range of conditions. This is important to ensure the model gives reliable predictions, to understand the limitations of the model and to identify if/where the model needs to be improved. The validation of this model will be discussed below in section 4.4.

4.0. RESULTS AND DISCUSSION

4.1. NO_x Reduction Performance

The main focus of the following section is the NO_x reduction efficiency over the SCR-DPF catalysts under different test conditions. The NO_x reduction and NH_3 slip control achieved using a complete system, including SCR and ASC, will also be discussed.

4.1.1. SCR-DPF Performance in Steady State Tests

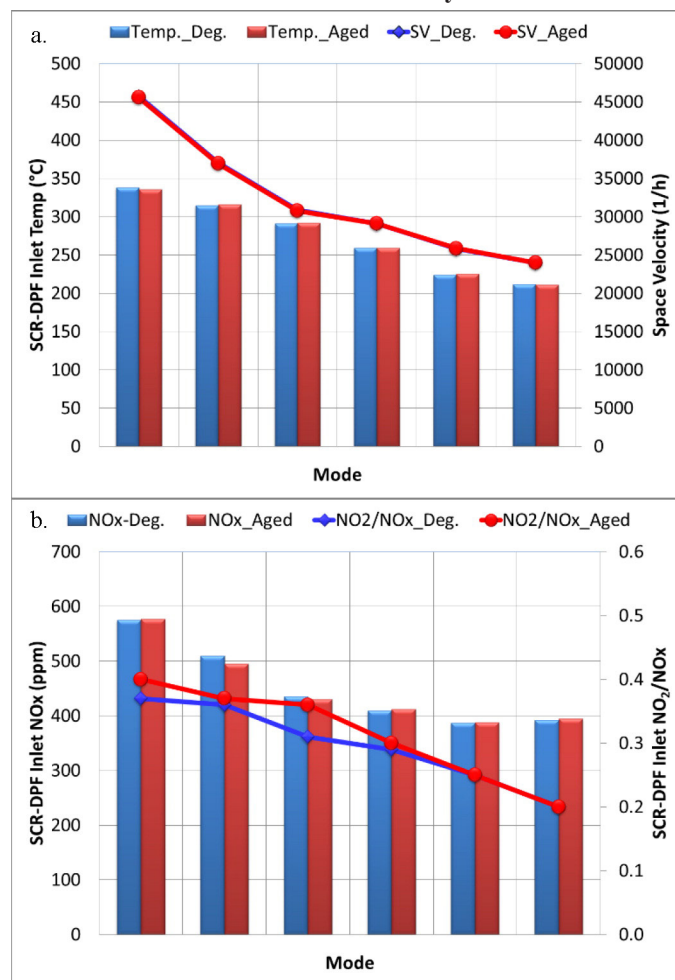


Figure 1. Steady state test conditions; a) temperature and space velocity (based on SCR-DPF volume) and b) NO_x and NO_2/NO_x at the SCR-DPF inlet.

Degreened (Deg.) and aged V.SCR-DPF (A.1) catalysts were evaluated at six discrete steady state points with different temperature and engine exhaust flow rates as shown in Figure 1a. The tests were carried out with DOC_A.1 in front to produce additional NO_2 . The SCR-DPF inlet temperature and gas hourly space velocity (SV) varied from 210–340 °C and 24 000–46 000 h^{-1} , respectively. In addition, the NO_x concentration and NO_2/NO_x at SCR-DPF inlet for each of the test points are shown in Figure 1b. Urea was injected for the six test points targeting ANR ~ 1.0 , however the average ANRs were ~ 0.98 and ~ 0.94 for the degreened and aged tests, respectively. Under these steady state test conditions, 28–70% NO_x reduction was obtained over the degreened SCR-DPF (Fig. 2). Higher NO_x reduction was obtained with the aged SCR-DPF; 3 to 11% points higher depending on the test point. This trend has been reported previously on vanadia based SCR catalysts [38, 39], where increase in polymeric vanadyl surface species was observed upon aging. Went et al.’s SCR studies suggested that polymeric species are 10 times more active than monomeric species [39]. As shown here, a significant amount of NO_x can be reduced by either using a degreened or aged SCR-DPF brick under these test conditions. Nevertheless, to achieve additional NO_x reduction over an SCR