

Performance and Sulfur Effect Evaluation of Tier 4 DOC+SCR Systems for Vanadia, Iron, and Copper SCR

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ABSTRACT

Non-road Tier 4 Final emissions standards offer opportunities for engines to be certified with DOC + SCR aftertreatment systems (ATS), where particulate matter (PM) emissions will be controlled by engine measures. These non-filter systems will not experience high thermal conditions common for filter regeneration and, therefore, will not have the secondary benefit of thermal events removing sulfur from the DOC and SCR aftertreatment. An experimental program was conducted on DOC + SCR systems in which the DOC was selected for the anticipated NO₂ and sulfur management requirements of a fixed volume of 3 SCR types (vanadia, copper and iron). Each system was optimized to NO_x conversion levels of 90%+ on NRTC cycles then exposed to accelerated sulfur poisoning and various cycles of increasing temperature after each poisoning to observe the performance recovery of the system. Specific sulfur management strategies are defined, depending on technology. Though each system has its own unique sensitivity to sulfur and conditions where it recovers, all SCR systems are capable of sustaining 90%+ NO_x conversion levels. In the case of the copper SCR (Cu-SCR), a new DOC formulation has been developed that noticeably decreases the sensitivity to sulfur, while still allowing the necessary durability for periodic desulfation events.

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INTRODUCTION

As with the various worldwide highway emissions standards over the past decade, the non-road emissions standards have been tightened such that significant reductions of NO_x and PM over the previous engine systems are required by the Tier 4 interim/final and Stage 3B/3A emissions standards in US and Europe, respectively (Table 1). It was expected that much of this reduction will be through the use of aftertreatment as is universally the case for US and European current highway vehicles. Due to the ability to partially tradeoff the particulate and NO_x emissions in a diesel combustion system and controls, it is feasible to meet one of the reduction requirements by purely engine measures. This creates an opportunity to choose between aftertreatment emphasizing the reduction of either PM or NO_x. Tier 4 interim standards were met in different ways by the various manufacturers. Some used particulate reduction aftertreatment and controlled NO_x with engine measures, and some used SCR to reduce NO_x while controlling the particulates within the engine. Some OEMs offered both methods within their product line depending on the market and application. The more stringent Tier 4 final emissions standards also offer the opportunity to develop different aftertreatment options. While full aftertreatment systems containing both a DPF element for PM reduction and an SCR catalyst are offered from various OEMs in

a number of applications, there will be Tier 4 final systems that primarily reduce NO_x with high SCR conversion and do not contain a DPF.

Table 1. Tier 4 Emission Standards - Engines between 56 and 560kW, g/kWh (g/bhp-hr). [1]

Engine Power	Year	CO	NMHC	NO _x	PM
56 ≤ kW < 130 (75 ≤ hp < 175)	2012-2014	5.0 (3.7)	0.19 (0.14)	0.40 (0.30)	0.02 (0.015)
130 ≤ kW < 560 (175 ≤ hp < 750)	2012-2014	3.5 (2.6)	0.19 (0.14)	0.40 (0.30)	0.02 (0.015)

One SCR based approach for Tier 4 interim was to use vanadia SCR (V-SCR) catalyst only, which had the advantage of the low cost, simple urea calibration, no DOC cost, and high tolerance of sulfur, both long term exposure at low levels or accidental high sulfur fuel exposure during the regulated fuel sulfur transition period. However, for the Tier 4 Final NO_x standards, higher conversion than a V-SCR catalyst alone would likely be necessary, similar to the trend for on - highway engines under stringent NO_x standards. This may lead to move to Cu- or Fe- zeolite SCR catalysts for Tier 4 final for systems that either used DOC + CDPF or V-SCR Tier 4 interim /Stage 3B emissions solutions.

It is well known that the low temperature performance of all the common SCR types is improved by the addition of some NO₂, although the sensitivity to increased (<50%) and excess NO₂ (>50%) varies among them. Cu-SCR has the best low temperature performance in the absence of NO₂ but is highly susceptible to sulfur poisoning, especially SO₃ [2], and is somewhat sensitive to excess NO₂. Iron SCR (Fe-SCR) is less sensitive to sulfur and tolerant of excess NO₂, but needs more NO₂ for good low temperature conversion. V-SCR is also helped by the addition of NO₂, but is particularly sensitive to excess. A comparison of the NO₂ effects on the three types is shown in Figure 1. However, in any system that depends in part on NO₂ from a DOC for SCR efficiency, the system sensitivity to sulfur is increased due to the potential for sulfur poisoning of the DOC in addition to the SCR itself.

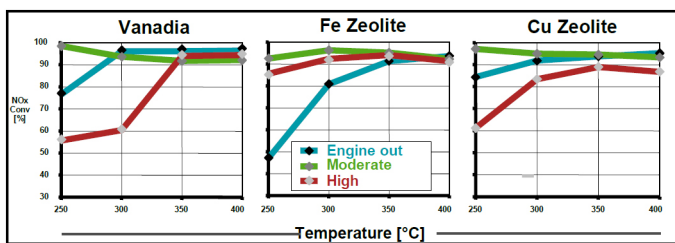


Figure 1. The steady state NO_x conversion for three SCR catalyst types under different NO₂ ratio conditions by temperature.

In many of the first generation heavy duty Fe- and Cu- SCR applications where an actively regenerated filter is present in the system, the sulfur sensitivity of NO_x conversion of these SCR systems has not been an issue since the DPF regeneration frequently exposes all components in the system to sufficient temperature to desulfate. In a DOC + SCR system, especially with a cold engine exhaust profile and a low duty cycle, it may be that certain SCR catalysts will need intervention by engine controls to insure sufficient desulfation.

Given the significant differences in NO₂ sensitivity, sulfur sensitivity and to identify the NO_x conversion potential between DOC+SCR systems based on the 3 SCR types, a program to compare them was devised. A target NO_x conversion of 90% for a potential future 3+ g/kW-hr NO_x engine with low PM was chosen and a reasonable SCR volume was assigned. The ~3 g/kW engine out NO_x target was based on announcements of the Ricardo Twin Vortex combustion system for smaller HD diesels, and subsequent announcements of engines introduced without DPF with engine out NO_x meeting the interim NO_x standard of 2.3 or 3.4 g/kW-hr. [4,5,6] Each catalyst type was matched with an appropriate DOC to meet its NO₂ and anticipated active desulfation requirements, and various aging, performance testing and sulfur poisoning tests were applied.

The project was intended to show the conversion potential for each type in a reasonably well developed system, the sensitivity to sulfur under various conditions, and in the case of catalysts with a significant sensitivity to sulfur, to suggest an appropriate desulfation / sulfur management strategy.

EXPERIMENTAL SETUP

The engine used for this study was a 4.5L turbocharged diesel Tier 3 John Deere engine without EGR. The engine has a peak power of 104 kW @ 2400 rpm and a peak torque of 525 Nm @ 1500 rpm and is certified to meet the Tier 3 NO_x standard of 4 g/kW-hr.

For this experiment, the engine was run on cycles based on its full rated power and also de-rated to 55 kW over the NRTC in order to present a challenging lower exhaust temperature profile. The comparison between these exhaust temperatures is shown in Figure 2. A 68 kW ramped 8 mode cycle was also used to look at desulfation at operating temperatures between the highly transient NRTC and the full load temperature of the 104 kW rating of the engine. The temperature profile for this cycle is shown in Figure 3. The brake specific NO_x for the various rating cycles was in the range of 2.5-3.5 g/kW-hr.

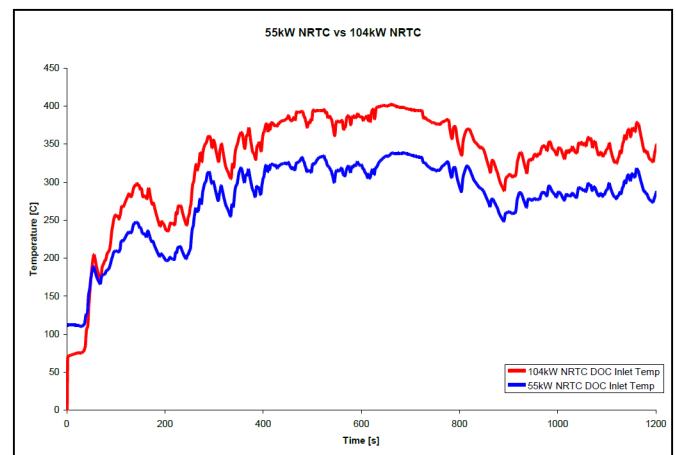


Figure 2. DOC inlet temperature profile of full rated 104 kW NRTC compared to the de-rated 55 kW NRTC.

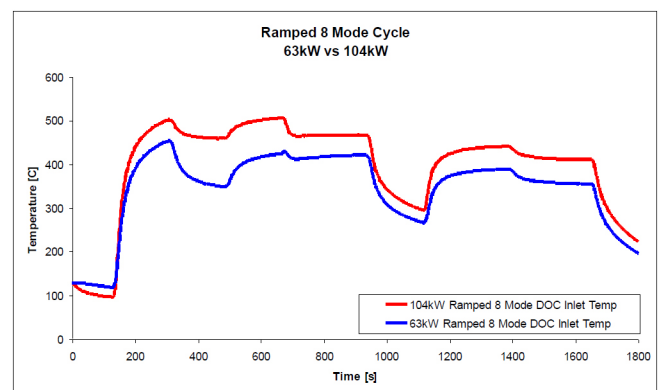


Figure 3. DOC inlet temperature profiles of full rated 104kW ramped 8-mode cycle compared to the de-rated 63kW ramped 8-mode cycle.

System Layout

The test layout, shown in Figure 4, was established to promote complete mixing and ideal sample probe placement. For sulfur poisoning, SO₂ was injected downstream of the turbo and passed through a process gas mixer before reaching the DOC. A production Ford F250 urea mixing section was used for

decompose the urea and provide adequate mixing before entering the SCR. It was found that the NRTC cycle flow velocities for this lower power engine were similar to the velocities for the pickup over its certification cycles. It was anticipated that it could adequately represent a future Tier 4 final DOC + SCR system. Emissions were recorded using traditional emissions benches before the DOC and in the tailpipe section of the exhaust. Additionally, 2 FTIRs were used to observe NO₂ emissions from the DOC and ammonia slip from the ASC. Finally, temperatures before and after each component as well as inside each component were measured.

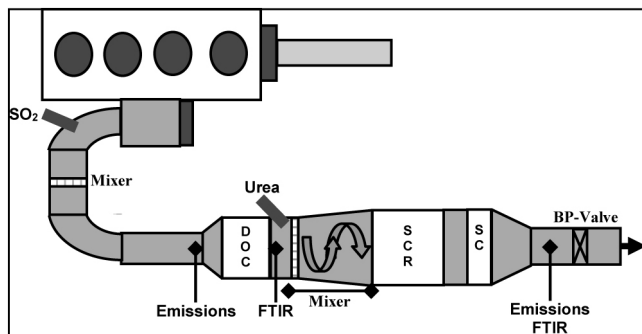


Figure 4. Exhaust system layout. The exhaust system used for testing consisted of a DOC, SCR, and ASC. Emissions were collected in the indicated positions.

Catalyst Selection

Because each SCR catalyst type has unique requirements for NO₂ and different sulfur sensitivity, it was attempted to put together appropriate DOC + SCR + ASC systems for each type to be able to achieve an anticipated minimum 90% NO_x conversion after simulated lifetime aging, sulfur poisoning and desulfation (if required). In addition, in the case of the V and Cu systems, a reference system was evaluated with a Pd-only DOC of appropriate size that would exclude the effect of sulfur poisoning of NO₂ production by the DOC. It is understood that this will also affect the amount of SO₃ delivered to the SCR catalyst, but this did not affect the conclusions of this study. [2]

Component Aging

All systems were tested at an end-of-life estimated hydrothermal oven aging. In the case of the V-SCR and Fe-SCR systems, this was 100 hours at 525°C for both the DOC and SCR components. For the Cu-SCR, it was estimated that the system would require a lifetime 200 desulfation events lasting 15 minutes each with the assumption of 0.5 g/L SCR volume exposure between desulfations and a lifetime fuel usage estimate for the representative application. The desulfation temperature target assumption was based on previous internal testing and published literature for modern small pore Cu-SCR catalysts [3]. Therefore, the Cu-SCRs were aged an additional 50 hours at 625°C. The primary 4:1 Pt:Pd DOC for the Cu-SCR system had been aged 72 hours at

750°C. Table 2 shows the various system catalyst combinations used in the DOC+SCR system experiments described herein.

Table 2. Details of the catalysts in each system used for this experiment.

DOC + SCR System Descriptions				
System Type	DOC Pt:Pd	DOC Vol	SCR 10.5L	ASC 3.5L
Pd DOC + V-SCR	40 gpcf 0:1	4.3L	Vanadium	Pd DOC
Pt DOC + V-SCR	40 gpcf 1:0	2.5L	Vanadium	V - Pt
Pd DOC + Cu-SCR	40 gpcf 0:1	4.3L	Copper	Cu - Pt
Pt/Pd DOC + Cu	48 gpcf 4:1	5.0L	Copper	Cu - Pt
Pt DOC + Cu-SCR	40 gpcf 1:0	2.5L	Copper	Cu - Pt
Pt DOC + Fe-SCR	20 gpcf 1:0	4.3L	Iron	Fe - Pt

Sulfur Poisoning

The poisoning phases of the experiment were accomplished by injecting SO₂ gas into the exhaust ahead of a mixer upstream of both the DOC and SCR. SO₂ was added to the full system at steady state conditions at a rate of ~20 ppm until system exposure of 1 g/L of SCR volume in most cases. It was understood that a certain amount of sulfur is actually stored in the DOC and does not reach the SCR during the poisoning. Two poisoning temperatures of 270 and 390 °C were used initially to represent low and high operating temperature applications, however only the 270°C point exhibited significant sulfur poisoning for any of the systems. Therefore the higher temperature sulfur poisoning results are not included in this paper.

Urea Dosing Strategy

Since the different SCR types would also be expected to have somewhat different urea dosing control requirements, an attempt was made to tune a simple dosing control for each system. Urea dosing proportional to engine out NO_x was applied to repeated NRTC cycles for each SCR type at different nominal Ammonia to NO_x ratios (ANR) until repeated cycles had good performance without excessive NH₃ slip. That ANR was applied to all subsequent testing with that SCR type. The results reported reflect cycles for which the NH₃ slip is below 25 ppm except for certain cases of the first 55 kW NRTC after a poisoning cycle for the Pd DOC cases.

Experimental Procedure

For each system, a sequence of initial aged emissions cycles, poisoning, and a series of post-poisoning emissions cycles were run. In the case of Cu-SCR sequence, additional desulfation events were performed. The poisoning and following cycles / desulfations were repeated 3 times to look for evidence that the apparent recovery of the systems might not be sustainable. The emissions cycle sequences after each poisoning started with the coldest included cycle, a "hot" start 55 kW NRTC, followed by cycles with progressively higher temperatures to see when and whether the sulfur poisoned system would effectively desulfate under some level of normal