

Laboratory and Vehicle Demonstration of “2nd-Generation” LNT + in-situ SCR Diesel NO_x Emission Control Systems

2010-01-0305

Published
04/12/2010

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ABSTRACT

This study extends research previously reported from our laboratory [SAE 2009-01-0285] on diesel NO_x control utilizing a new generation of Lean NO_x Trap (LNT) plus in-situ Selective Catalytic Reduction (SCR) catalyst systems. Key findings from this work include 1) evidence for a “non-ammonia” reduction pathway over the SCR catalyst (in addition to the conventional ammonia pathway), 2) high NO_x conversions utilizing LNT formulations with substantially lower platinum group metal (PGM) loadings than utilized in earlier systems, 3) ability of the downstream SCR catalyst to maintain high overall system NO_x efficiency with aged LNTs, and 4) effectiveness of both Cu- and Fe-zeolite SCR formulations to enhance overall system NO_x efficiency. FTP NO_x conversion efficiencies in excess of 95% were obtained on two light-duty vehicle platforms with lab-aged catalyst systems, thus showing potential of the LNT+SCR approach for achieving the lowest U.S. emissions standards

INTRODUCTION

Emissions control for diesel vehicles requires the ability to capture and/or convert NO_x under the normal lean engine operating conditions of diesel engines. To date, the leading aftertreatment technologies have involved either lean NO_x trapping [1,2,3,4,5,6,7] or selective catalytic reduction [8,9,10,11,12,13,14,15] (either with HC species or urea). Recently, several studies have reported on LNT+SCR systems which utilize the SCR catalyst in a “passive” or “in-situ” mode where the reductant required to convert NO_x that breaks through the LNT is generated over the LNT during NO_x purge or reduction events [16,17,18,19,20]. Generally it is assumed that the primary reductant species formed over the LNT during purge events is NH₃. Hence, SCR catalyst

technology for use in LNT+SCR systems has focused on NH₃-SCR catalyst formulations.

The present study is an extension of work we reported in a 2009 SAE paper [20]. That study focused on the effectiveness of advanced Cu-zeolite SCR catalyst formulations downstream of new generation LNTs having improved de-SO_x characteristics, and hence, improved thermal durability. The combination of new-generation LNTs and Cu-zeolite SCR catalysts enabled up to 30% reduction in platinum group metal (PGM) loadings compared to earlier generation LNTs. The present study reveals new features of the LNT+SCR concept as demonstrated both in laboratory and vehicle experiments. In particular, we provide evidence that not all reduction of NO_x across the SCR catalyst occurs via stored ammonia. Other reductant species contribute to the high conversion efficiencies observed across the SCR catalyst. In addition, the LNT+SCR approach is shown to work with high efficiency over a broad range of engine operating conditions resulting in overall FTP NO_x conversion efficiencies in excess of 95%, as demonstrated on two vehicle platforms.

EXPERIMENTAL

LABORATORY EXPERIMENTS

The laboratory setup, instruments, gas compositions, and evaluation and aging procedures are the same as previously reported [7, 20]. The catalysts were 25 mm diameter by 25 mm long cores cut from larger monoliths (cordierite with 400 cells per square inch and 6.5 mil wall thickness). The catalysts were tested in a quartz tube reactor contained in a tube furnace. Gases were blended synthetically (see Table 1 for composition) and fed to the reactor at flow rates corresponding to a volumetric space velocity of 30K hr⁻¹, which is representative of driving speeds found in the FTP.

Catalyst temperatures were measured at the inlet (6mm in front of the sample), mid (middle of the 25 mm inch sample core), and the outlet (6mm after the sample). Experiments with both LNT and SCR catalyst cores utilized 25 mm samples of each separated by 6mm. All catalyst temperatures reported herein refer to the inlet temperature (unless noted otherwise).

The laboratory experiments utilized a V&F Airsense chemical ionization mass spectrometer, Midac heated FTIR (4m cell), and a Horiba Mexa 9100 Hegr gas bench consisting of a chemiluminescent analyzer (NO_x, NO), combined flame ionization (THC)/Magneto-pneumatic (O₂) analyzer, and non-dispersive infrared analyzer (CO and CO₂). Gases to the mass spectrometer and analyzer bench were passed through heated sample lines and diluted with N₂ in a ratio of about 1:2 to avoid water condensation. Heated, undiluted “raw” gas was fed to the FTIR. For the majority of testing, a standardized set of gas compositions was used (Table 1). The gas runs in the lean condition for a period of time, then switches to the rich composition for a different period of time, and this cycle repeats. The duty cycle used in these experiments was 60 seconds lean and 5 seconds rich (60/5).

Table 1. Standard gas composition

Gas	Lean	Rich
CO	0%	3%
H ₂	0%	1%
C ₃ H ₆	0%	5000 ppmC1
NO _x	200 ppm	200 ppm
O ₂	10%	1%
CO ₂	5%	5%
H ₂ O	5%	5%
λ	1.96	0.92

These gas compositions are not entirely representative of diesel exhaust. NO_x was supplied exclusively as NO at a relatively high level for a part load operating mode, so as to better discriminate between catalyst formulations. A 3:1 ratio of CO:H₂ was used. We utilized propylene (C₃H₆) as our HC - typical of light cracked hydrocarbons in diesel exhaust but not representative of larger unburned fuel species.

All catalysts were provided by Ford's catalyst suppliers and are identified in Table 2 by a code assigning a letter designation to each supplier and a number corresponding to the specific formulation. Catalysts are identified only by their generic type (e.g., Cu-zeolite SCR or LNT) and relative PGM loadings (LNTs) to protect supplier confidentiality. Two reference formulations (B3 and C1) were tested extensively within Ford during the 2003-2005 time frame and are compared to more recent formulations designated as “New.” As shown in Table 2, the new LNT formulations have lower desulfation temperatures than the reference LNT which translates into lower peak aging temperatures and better durability (as described in [20]).

Table 2. Catalysts

Supplier Code	Catalyst type (PGM Loading)	DeSO _x Temp (°C)
A1	New LNT (High)	700-745
A2	New LNT (Low)	700-730
A3	New Cu-zeolite SCR	-
B1	New LNT (Low)	680-700
B2	New Cu-zeolite SCR	-
B3	Fe-zeolite SCR	-
C1	LNT (High)	750-800

VEHICLE TESTING

Two vehicles were tested with similar configurations of the aftertreatment system. The first vehicle tested was a production 2005 MY Land Rover (LR3) diesel vehicle that was Euro 3 emission compliant as new. This vehicle was equipped with a twin turbocharged, common rail direct injected 2.7L V6 (Lion) diesel engine. The front drive shaft was disconnected to convert the original all-wheel-drive system to rear-wheel drive for emission testing on a single roll chassis dynamometer. The powertrain control system was originally modified for lean NO_x trap aftertreatment system development, but was subsequently adapted for evaluation of the LNT+SCR system as depicted in Fig. 1. The catalyst information is shown in Table 3. Both the LNT and SCR were hydrothermally aged at 750°C for 64 hours before installation. The vehicle inertia weight was set to 3780 lbs on the chassis dynamometer to simulate the power to weight ratio equivalent to a light duty diesel truck, with dyno coefficients of 0.07, 1.91 and 11.13. The second vehicle equipped with the LNT +SCR system was a non-production 4.4L V8 TDI light duty pickup truck. The catalysts in this truck are arranged in the same order as on the LR3 (DOC plus LNT and SCR followed by catalyzed DPF). The catalyst information on this truck is shown in Table 4. Three Horiba modal emission benches and two modal FTIR (Horiba 4000 and 6000 with 2.4 meter path lengths) were used to measure the sec-by-sec emissions at various sample locations labeled in Fig. 1 below.

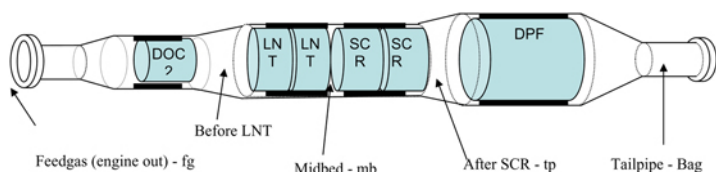


Fig. 1. Schematic diagram of the catalyst system layout used on both the LR3 vehicle and the 4.4L light-duty truck. Catalyst details are given in Tables 3 and 4, respectively. Note that the LR3 has a small metallic DOC (see Table 3) located upstream of DOC 2 that is not shown in the diagram.

Table 3. Catalyst configurations on the Land Rover (LR3) vehicle

Component	PGM Load	Dia. x Length (in)	Calc. Vol (L)	% of Engine Swept Vol	Material	Cell CPSI / Wall
DOC 1*	70g/ft ³	3" x 3"	-	-	Metallic	-
DOC 2	70g/ft ³	4.66" x 3"	0.84	31%	Ceramic	400 / 6 mil
LNT	85g/ft ³	2 - 5.66" x 3.5"	2.88	107%	Ceramic	400 / 6 mil
SCR	-	2 - 5.66" x 3.5"	2.88	107%	Ceramic	400 / 6 mil
cDPF	20g/ft ³	7.5" x 8"	6.0	222%	SiC	200 / 15mil

DOC1 is close coupled to engine exhaust manifold.

Table 4. Catalyst dimensions of the 4.4L V8 Mockup light duty truck

Component	PGM Load	Dia. x Length (in)	Calc. Vol (L)	% of Engine Swept Vol	Material	Cell CPSI / Wall
DOC	90g/ft ³	2 - 4.66" x 4"	2.23	51%	Ceramic	400 / 6 mil
LNT	85g/ft ³	7.5" x 5"	3.6	82%	Ceramic	400 / 6 mil
SCR	-	8" x 6"	4.94	112%	Ceramic	400 / 6 mil
cDPF	5g/ft ³	8" x 8"	6.59	150%	SiC	200 / 15mil

The regulated species (THC, CO, NO_x, NMHC, CO₂, O₂) were measured and reported on a sec-by-sec basis using Horiba 7000 modal emission analyzer systems. Additional species were measured using Horiba 4000 and 6000 model FTIRs including NO₂, N₂O, NH₃, HCHO, C₂H₂, C₂H₄, and C₃H₆. Special consideration was taken to reduce the hang-up of NH₃ and other hygroscopic molecules of interest in the FTIR sampling system. The inline heated filter elements were chosen for their low absorptivity for NH₃. Finally, the entire sampling train from the exhaust probes to the analyzer were preheated and maintained to at least 130°C.

Modal (sec-by-sec) measurements of NH₃, nitromethane, and other potential reductant species were also conducted using a V&F Aircsense mass spectrometer (MS). This instrument uses electron impact ionization to create Hg, Xe, or Kr primary ions with ionization potential energies (I.P.) of between 10.6-

13.9 eV. The primary ions are allowed to interact with neutral gases in a low pressure (10⁻³ to 10⁻⁴ torr) collision cell and the secondary ions that form are extracted into a quadrupole mass spectrometer for mass analysis and detection. The instrument is remarkably selective for ionizing molecules with I.P.'s less than the primary ion used and can measure molecules such as NH₃, H₂S, NO, O₂, H₂O, and a wide variety of volatile organics of interest to the automotive catalyst community. The time resolution of the analyzer is adjustable from as fast as a few msec to tens of seconds. The Aircsense MS was calibrated for NH₃ using a gravimetrically prepared gas standard (Scott Specialty Gases) of 500 ppm concentration. Other species, such as nitromethane, NO, O₂, H₂O, HNCO, etc, were calibrated by dilution into dry nitrogen either from gas standard cylinders or by syringe pump injection (if a liquid) into a 4 L/min flow of pure dry nitrogen.

RESULTS & DISCUSSION

NON-AMMONIA NO_x REDUCTION AT THE SCR CATALYST

Fig. 2 shows a lab reactor comparison of cycled NO_x conversion for the 70K aged, low-loaded (A2) LNT with and without a downstream A3 Cu-zeolite SCR catalyst. As pointed out in our previous study [20], addition of the SCR catalyst results in improved NO_x conversion over the entire temperature range with respect to the LNT alone, but especially in the low-temperature range. NH₃ production over the same LNT is plotted in Fig. 3 as a function of FTIR scans during repeated 60/5 cycling at the temperatures indicated on the graph (each concentration spike represents NH₃ breakthrough occurring during each 5 s rich purge event). In comparing Figs. 2 and 3, the most notable feature is the absence of significant NH₃ production over the LNT at temperatures below 200°C where the SCR catalyst greatly enhances NO_x conversion. These observations suggest the participation of a non-ammonia reductant in conversion of NO_x over the SCR catalyst.

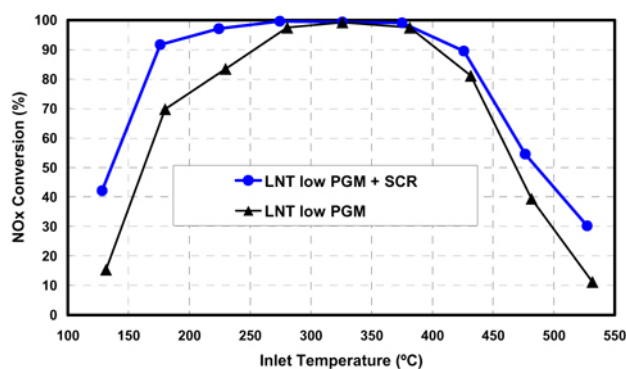


Fig. 2. Lab reactor cycle-averaged NO_x conversion as a function of inlet catalyst temperature over the 70K aged A2 LNT with and without downstream A3 Cu-SCR catalyst.

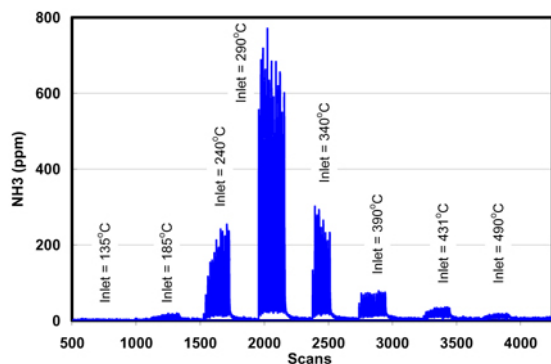


Fig. 3. Same experiment as in Fig. 2 but showing NH₃ production as a function of FTIR scans at the indicated temperatures.

LNT. Beginning at about 1975 s, the tailpipe NO_x emissions decrease to nearly zero and stay there for about 200 s. The effectiveness of the SCR catalyst can be seen by the area between the mid-bed NO_x emissions (indicating NO_x breakthrough from the LNT) and the tailpipe NO_x measurement (i.e. downstream of the SCR catalyst). The area between the two curves can be compared to the area under the NH₃ trace to get a rough sense of the fraction of the enhanced NO_x conversion that can be attributed to NH₃. Quantitative analysis of the data indicates that the NH₃ generated across the LNT only accounts for about 15% of the incremental NO_x conversion associated with the SCR catalyst under these test conditions

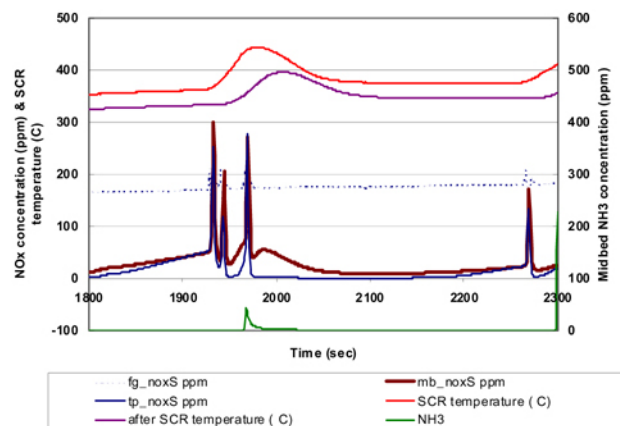


Fig. 4. Steady speed (55 mph) emissions and temperature measurements on the LR3 vehicle through NO_x storage and purge cycles.

Evidence for a non-NH₃ reductant was also obtained in FTP tests on the LR3 vehicle. The FTP test identified as 442 is representative (it was the first test with rich regeneration, thus, there was no reductant pre-stored in the SCR catalyst). Overall, this test showed about a 50% reduction in NO_x (weighted mass basis) over the LNT and an additional 44% reduction of breakthrough NO_x over the SCR catalyst. Very little NH₃ was generated across the LNT over the entire test. Fig. 5 shows a second-by-second plot of NH₃ emissions as measured by the Horiba 6000 FTIR sampling between the LNT and SCR bricks. Only two purge events occurred during the full FTP test - both resulting in NH₃ peaks less than 70 ppm out of the LNT. The NH₃ production across the LNT was integrated over the entire test and is reported in Table 5 as 0.658×10^{-3} moles. No NH₃ was measured downstream of the SCR catalyst, implying that all of the NH₃ produced by the LNT reacted or was stored over the SCR catalyst. In comparison, the integrated amounts of NO_x into and out of the SCR catalyst are also reported in Table 5 and correspond to a NO_x conversion across the SCR catalyst of 4.66×10^{-3} moles. The NH₃ generated by the LNT can theoretically