

TWC+LNT/SCR Systems for Satisfying Tier 2, Bin 2 Emission Standards on Lean-Burn Gasoline Engines

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ABSTRACT

A laboratory study was performed to assess the potential capability of TWC+LNT/SCR systems to satisfy the Tier 2, Bin 2 emission standards for lean-burn gasoline applications. It was assumed that the exhaust system would need a close-coupled (CC) TWC, an underbody (U/B) TWC, and a third U/B LNT/SCR converter to satisfy the emission standards on the FTP and US06 tests while allowing lean operation for improved fuel economy during select driving conditions. Target levels for HC, CO, and NO_x during lean/rich cycling were established. Sizing studies were performed to determine the minimum LNT/SCR volume needed to satisfy the NO_x target. The ability of the TWC to oxidize the HC during rich operation through steam reforming was crucial for satisfying the HC target. Temperature studies indicated that the CC TWC needed to operate at a minimum of 500°C to provide good steam reforming activity, while the LNT/SCR needed to operate between 300 and 350°C to satisfy the NO_x slip target while minimizing the slip of NH₃, N₂O, and HC during the purges. Sulfur poisoning increased the HC slip by degrading the steam reforming reaction, and the sulfur increased the NO_x slip by decreasing the NO_x storage capacity of the LNT. Both the TWC and LNT/SCR could be desulfated with rich exhaust at 700°C. However, it was projected that the ability to obtain 700°C at the underbody LNT/SCR location would be difficult without additional exhaust hardware, such as fuel injectors or air pumps. Consequently, development of the LNT/SCR system was terminated in favor of a passive TWC+SCR approach because of its superior sulfur tolerance. Investigations into the passive TWC+SCR approach are discussed in a companion SAE paper.

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INTRODUCTION

Automakers are working diligently to improve the fuel economy of their gasoline-powered vehicles to improve customer satisfaction and to satisfy future governmental regulations. Simultaneously, the California LEV III regulations and the Federal Tier 2 and Tier 3 regulations are requiring carmakers to lower the emissions of hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matter (PM) from their vehicles. One strategy that can provide better fuel economy is the use of lean operation during select driving modes such as cruises, as lean operation lowers the pumping losses and improves the thermodynamics of combustion. Depending on the engine and combustion strategy, lean operation can improve the fuel economy by as much as 5 to 15% relative to stoichiometric operation. However, it is well known that the three-way catalyst (TWC) cannot reduce NO_x under lean conditions. Therefore, to allow lean operation while satisfying strict emission regulations, the TWC converter(s) must be supplemented with catalysts that can reduce NO_x during lean operation or during lean/rich cycling. Selective catalytic reduction (SCR) catalysts [1] with urea injection systems are currently being used to reduce the NO_x emissions from diesel engines. Here an aqueous solution of urea is pumped from a storage tank into the exhaust, where the urea decomposes into NH₃. The NH₃ and NO_x react over the SCR catalyst under lean conditions to produce nitrogen (N₂) and water (H₂O). A popular SCR formulation used on

production diesel trucks contains copper in a chabazite zeolite which provides high NO_x conversion and good thermal durability. One issue is that this system requires the customer to maintain a sufficient supply of the urea solution in the storage tank. Typically, the urea tank is refilled during vehicle service appointments.

An alternative catalyst for treating NO_x under lean conditions which does not require the urea injection system is the lean NO_x trap (LNT). The LNT contains platinum group metal (PGM) such as platinum (Pt), palladium (Pd), and rhodium (Rh) along with NO_x storage materials such as barium (Ba) and cerium (Ce). During lean operation, the platinum oxidizes the NO in the exhaust to NO₂, and the NO₂ reacts with the NO_x storage materials to form nitrates [2]. Periodically, the A/F ratio is driven to a rich condition, and the nitrates decompose, releasing the NO_x which reacts with the reductants in the rich exhaust [e.g., HC, CO, and hydrogen (H₂)] to produce N₂ and carbon dioxide (CO₂) and/or H₂O. Another promising aftertreatment system for lean NO_x control combines the LNT and SCR technologies, where NH₃ produced by the LNT during the rich periods is stored on the downstream SCR catalyst and used to reduce NO_x that slips past the LNT during the lean periods [3,4,5,6,7,8,9,10,11,12,13,14]. Theis et al. [14] showed that a 4-zoned or 8-zoned catalyst system with alternating segments of LNT and SCR catalyst provided similar NO_x conversion and reduced NH₃ slip

during lean/rich cycling relative to a conventional 2-zone LNT/SCR configuration, where a single LNT catalyst is placed upstream of a single SCR catalyst. The lower NH_3 slip was attributed to an improved balance of NO_x and NH_3 in the SCR zones of the multi-zone configurations. The multi-zoned approach also reduced the N_2O formation and HC slip.

A fourth lean NO_x aftertreatment system is the passive TWC+SCR approach [15]. Here the TWC generates NH_3 from the feedgas NO_x during rich periods, and the NH_3 is stored on the downstream SCR catalyst. The SCR catalyst then uses the stored NH_3 to reduce NO_x during lean operation.

One issue with the LNT, passive SCR, or LNT/SCR approach is that the rich periods used to purge the LNT and/or to create NH_3 for the SCR catalyst reduce the fuel economy by 1 to 2%. Nevertheless, the overall fuel economy improvement from lean/rich cycling is significantly positive.

In 2011, Ford began a 4.5-year demonstration project under joint funding with the DOE to achieve a 25% improvement in fuel economy while achieving Tier 2, Bin 2 emission levels (later modified to Tier 3, Bin 30 emission levels) on a 2.3 L gasoline turbocharged direct-injection (GTDI) engine in a Ford Taurus [16]. For assessing the fuel economy improvement, the baseline vehicle was a Ford Taurus powered by a 3.5 L port-fuel-injected (PFI) naturally-aspirated (NA) engine with independent variable cam timing (iVCT). Several engine technologies were investigated to achieve the 25% improvement in fuel economy, including turbocharging, downsizing the engine displacement, the use of direct-injection, cooled EGR, and stop-start technology. As an optional action, lean operation during cruises was investigated. To provide NO_x control during the lean periods, two passive approaches were investigated that did not require customer maintenance: the TWC+LNT/SCR system and the TWC+SCR system. This paper summarizes the work on the TWC+LNT/SCR system. A companion paper describes the work on the TWC+SCR approach [17]. For both systems, high emphasis was placed on achieving the HC targets as well as the NO_x targets due to the very low emissions levels allowed for the Tier 2, Bin 2 standards.

EXPERIMENTAL

Catalysts

The TWC, LNT, and SCR catalyst samples used in this work were core samples with a length and diameter of 2.54 cm that were extracted from full-size cordierite bricks. It was assumed that the washcoat loadings and PGM distributions within the catalyst bricks were uniform. Therefore, the brick locations from where the cores were collected were not recorded.

TWC Samples

Several TWC technologies were used containing various levels of oxygen storage capacity (OSC) and platinum group metal (PGM) loadings that are listed in Table 1. The high OSC catalyst was a production formulation containing 96 grams per cubic foot (gpcf) Pd and 4 gpcf Rh (i.e., 1.57 g/L Pd and 0.066 g/L Rh) on a 900 cell per

square inch (CPSI) substrate with 2 mil walls (i.e., 900/2). This formulation will be referred to as “hi-OSC-100” in this paper. Samples of another production catalyst with a moderate level of OSC on 400/4 substrates were used with two PGM loadings. One contained 38 gpcf Pd and 2 gpcf Rh (0.62 g/L Pd and 0.033 Rh), while the other contained 196 gpcf Pd and 4 gpcf Rh (i.e., 3.21 g/L Pd and 0.066 g/L Rh). These catalysts will be referred to “mod-OSC-40” and “mod-OSC-200”, respectively. Finally, samples of two non-OSC formulations were used containing either 116 gpcf (1.90 g/L) Pd or 200 gpcf (3.28 g/L) Pd on 400/4 substrates. These will be referred to as “no-OSC-116” and “no-OSC-200”, respectively.

TWC Aging

Table 1 also lists the durability schedules used to age the TWC samples prior to testing. The rich/stoich/lean schedule was a proprietary schedule that cycled between rich, stoichiometric, and lean conditions every 60 seconds. The inlet temperature was 800°C, and the maximum bed temperature was 960°C. A full size converter with the hi-OSC-100 formulation was aged on the schedule to the equivalent of 120K miles on an engine/dynamometer, and a 1” by 1” core sample was extracted from the brick for laboratory testing. For the samples aged on the pulse-flame combustion reactor (a.k.a. pulsator) [18], core samples of 1” diameter were aged with the same rich/stoich/lean schedule at an inlet temperature of 800°C for 50 hours. The no-OSC-116 catalyst was degreened on the flow reactor for 2 hours at 800°C under lean conditions with 10% O_2 , 5% H_2O , 5% CO_2 , and the balance N_2 .

Table 1. TWC Catalyst Formulations, PGM Loadings, Aging Schedules

Catalyst Designation	OSC Level	PGM loading (gpcf Pt/Pd/Rh)	Aging Protocol
Hi-OSC-100	High	0/96/4	Engine - rich/stoich/lean 120K miles equiv
Mod-OSC-40	Moderate	0/38/2	Pulsator – rich/stoich/lean 800°C inlet 50 hours
Mod-OSC-200	Moderate	0/196/4	Pulsator – rich/stoich/lean 800°C inlet 50 hours
No-OSC-200	None	0/200/0	Pulsator – rich/stoich/lean 800°C inlet 50 hours
No-OSC-116	None	0/116/0	Flow reactor - lean 800°C inlet 2 hours

LNT & SCR Samples

The LNT used in this work was a formulation containing barium and cerium and catalyzed with 85 gpcf of PGM (73/7.5/4.5 gpcf Pt/Pd/Rh) on 400/6 substrates. The SCR catalyst was a copper/chabazite formulation on 400/4 substrates. This SCR formulation is used in production on the Ford medium duty diesel truck. No further details about the LNT or SCR formulations will be provided out of respect for the supplier.

LNT & SCR Aging

Some of the early work for this project was performed with LNT and SCR samples that had been previously aged in the flow reactor for another project [14], where a 1” diameter LNT core sample was placed ahead of a 1” long SCR core sample in the flow reactor. One set was

aged for 25 hours at an inlet temperature of 800°C with continuously lean exhaust (10% O₂, 5% CO₂, 5% H₂O, balance N₂), while a second set was aged for 20 hours under the same conditions. The aging temperature of 800°C was intended to expose the LNTs and SCR catalysts to the maximum temperature that could be expected in the U/B location and was not intended to represent a certain mileage or full-useful-life (FUL) conditions. After aging, both LNT samples and the SCR catalyst from set 2 were cut into four 0.25" (0.64 cm) long pieces so various configurations of LNT and SCR catalyst could be investigated during the performance evaluations. Later experiments for this project were performed with multi-zone LNT/SCR catalyst systems that were aged downstream of a TWC while the TWC samples were aging on the pulsator with the rich/stoich/lean cycle as described above. Here six 0.5" core samples with alternating LNT and SCR zones were aged with inlet temperatures of 600, 700, or 800°C to determine if the LNT/SCR performance could be improved with a reduced aging temperature. For all of the LNT and SCR samples, small holes were drilled axially through the pieces so that a 1.6 mm thermocouple could be inserted through the samples for measuring the inlet temperature or the catalyst bed temperature during the aging and performance evaluations.

Performance Evaluations

The flow reactor used for the performance evaluations contained 2 ovens, as shown in Figure 1. The TWC was placed toward the rear of the first oven, and the LNT or LNT/SCR system was placed toward the rear of the second oven. The 2 ovens were operated at different temperatures to represent the close-coupled position and the underbody position. The total length of the TWC was usually 1", and it consisted of either one catalyst formulation or two 0.5" pieces with different catalyst formulations butted together. When one TWC washcoat formulation was used, the PGM loading was uniform; when two different washcoat formulations were used, the total PGM loading was either uniform (e.g., 200 gpcf/200 gpcf) or zoned (e.g., 200 gpcf/40 gpcf). The total length of the LNT or LNT/SCR system was varied during the different experiments. The total flow rate was maintained at 6.4 L/min for all experiments, resulting in a space velocity of 30,000 hr⁻¹ for a 1" long catalyst. While it is recognized that an U/B TWC would be needed on the vehicle to supplement the CC TWC and satisfy the Tier 2, Bin 2 emission standards during the FTP and US06 test cycles, the laboratory testing neglected the U/B TWC and involved samples representing only the CC TWC and U/B LNT/SCR catalyst.

Most tests consisted of alternating lean and rich periods (e.g., 60 seconds lean and 5 seconds rich, referred to as a "60/5" cycle). Tests where the lean duration was held constant and the rich purge time was varied are referred to as "purge tests" in this paper. Mass flow controllers were used to control the flow rates of the different gases, and two electronically-controlled three-way solenoid valves were used to switch between the lean condition (i.e., O₂) and the rich condition (i.e., CO/H₂). The oxygen level was always 10% during the lean periods (λ =A/F ratio/14.6=2.0) and 0% during the rich periods. The H₂O and CO₂ concentrations were always 5% during the lean and rich periods. Many of the experiments were performed with 2500 ppm C₂H₄ (i.e., 5000 ppm on a C1 basis) during both the lean and rich periods, although some early tests included the C₂H₄ only during the

rich periods. For most tests, different NO levels were used during the lean and rich periods. While these NO levels were varied throughout the project depending on the type of test, the NO concentration during the lean periods was usually 200 ppm NO. During the rich periods, the NO level was increased to either 500 or 1000 ppm to more accurately simulate engine operation. The CO concentration during the rich periods was set at 4.0, 2.5, 1.5, or 0.5% to provide rich lambdas of 0.81, 0.86, 0.91, or 0.95 when 2500 ppm C₂H₄ was used; the H₂ level was always 1/3 the CO level. To provide a rich lambda of 0.99, the CO and H₂ levels were maintained at 0.5% and 0.17% while the C₂H₄ concentration was lowered to 800 ppm. Due to the many different catalyst configurations and test conditions used during this project, the specific details of each experiment will be provided in the section where the results of that experiment are discussed.

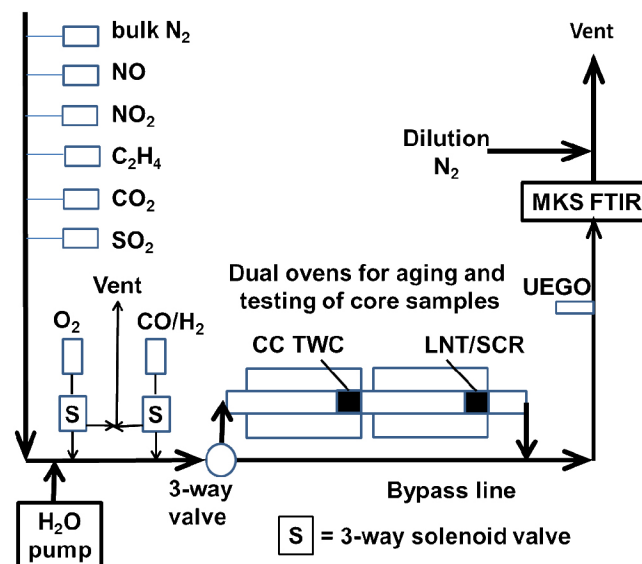


Figure 1. Experimental apparatus

For all tests, the average concentrations of the feedgas NO_x, HC, and CO were determined over several lean/rich cycles while the exhaust was bypassed around the reactor. With the exhaust flowing through the catalyst bed, testing was continued until the performance of the catalyst stabilized. The concentrations of the NO_x, HC, and CO at the reactor exit were then averaged over several lean/rich cycles. The average HC, CO, and NO_x conversions were calculated from the average feedgas concentrations and the average concentrations in the reactor exit according to:

$$\text{Ave \% conversion} = 100 * [1 - (\text{ave exit level}) / (\text{ave FG level})] \quad (1)$$

The average yield of NH₃ was calculated as a percentage of the feedgas NO level according to:

$$\text{Ave \% NH}_3 \text{ yield} = 100 * [(\text{ave NH}_3 \text{ level}) / \text{ave FG NO level}] \quad (2)$$

The average yield of N₂O was calculated as a percentage of the feedgas NO level from:

$$\text{Ave \% N}_2\text{O yield} = 100 * [2 * (\text{ave N}_2\text{O level}) / \text{ave FG NO level}] \quad (3)$$

where the factor of 2 accounts for the fact that two molecules of NO are required to produce one molecule of N₂O.

The feedgas and the exhaust from the reactor were analyzed with a 1 Hz MKS Fourier transform infrared (FTIR) analyzer equipped with a sample line heated to 191°C.

RESULTS AND DISCUSSION

Emission Budgeting

Emission budgeting was performed to determine the maximum allowable levels of HC, CO, and NO_x during lean/rich cycling on cruises that still allowed the Tier 2, Bin 2 standards to be met. The limits for HC, CO, and NO_x on the FTP are 10 mg/mile, 2.1 g/mile, and 20 mg/mile, respectively, after 120,000 miles of driving. Estimates were made for the emissions during the cold-start portion of the FTP and during warmed-up operation at stoichiometry. When possible, data from other vehicles were used to approximate these levels. Table 2 shows these estimates along with the desired engineering tolerances for HC, CO, and NO_x during the FTP. This left target emission levels during lean/rich cycling of 1 mg/mile, 1.3 gm/mile, and 5 mg/mile for HC, CO, and NO_x, respectively. The particulate matter standard for Tier 2, Bin 2 is 10 mg/mile; it was assumed that the engine-out level of PM would satisfy this limit, so a gasoline particulate filter (GPF) was not considered for this project.

Table 2. Emission Budgeting to Satisfy Tier 2, Bin 2 Emission Standards

Tier 2, Bin 2 Standards	HC	NOx	CO
Emission Requirement	10 mg/mile	20 mg/mile	2.1 g/mile
Engineering tolerance	1.7	5	0.5
Cold-start emissions	~7	7	0.3
Stoichiometric emissions (Post-lightoff)	~0	3	~0
Lean/rich cycling emissions	1	5	1.3

Multi-Zone LNT/SCR Design

Previously, it was shown that a LNT/SCR system provided similar NO_x conversion during lean/rich cycling as an all-LNT with the same total volume [14]. Since there is no PGM in the SCR catalyst, the LNT/SCR system uses 50% less PGM than the all-LNT approach and is therefore significantly lower in cost. In addition, it was shown that 4 or 8 alternating zones of LNT and SCR catalyst provided similar NO_x conversion and lower NH₃ slip relative to a sequential or 2-zone LNT/SCR design, where a single LNT is followed by a single SCR catalyst. This was attributed to a better balance of NO_x and NH₃ within the SCR zones of the multi-zone systems, resulting in better consumption of the stored NH₃. Also, the multi-zone configurations produced less N₂O than the all-LNT or 2-zone LNT/SCR designs. This was attributed to the fact that a significant portion of the NO_x

conversion occurred in the SCR zones of the multi-zone designs, and the copper/zeolite SCR catalyst is less prone for generating N₂O than the platinum-containing LNT. The 4-zone and 8-zone LNT/SCR designs produced similar NH₃ yields, so the 4-zone design was initially selected for the DOE project because it would be easier to manufacture in production.

LNT/SCR Volume Optimization

An experiment was performed to determine the minimum volume of LNT/SCR required to satisfy the NO_x slip target of 5 mg/mile. The hi-OSC-100 TWC sample aged on an engine/dynamometer was placed in the first oven, heated to 500°C to represent the close-coupled location, and tested alone using a 60 s lean/10 s rich cycle (i.e., 60/10 test). The rich lambda was 0.86, the C₂H₄ level was 2500 ppm during lean and rich operation, and the NO levels were 200 ppm lean and 500 ppm rich. A LNT/SCR catalyst was installed in a second oven downstream and operated at 300°C to simulate the underbody location, and similar 60/10 tests were performed. To vary the volume of the LNT/SCR catalyst, the LNT/SCR contained from one up to six 0.50" long zones with alternating LNT and SCR catalysts. The exhaust flow rate was held at 6.4 L/min for these tests, so the space velocity (accounting for both the TWC and the LNT/SCR volumes) ranged from 30K hr⁻¹ for the 1" TWC by itself down to 7.5K hr⁻¹ for the 1" TWC + 3" LNT/SCR system.

It was desired to convert the NO_x concentrations from the reactor (measured in ppm) into the weighted mg/mile NO_x during lean/rich cycling on the intended DOE vehicle in order to allow easier comparison with the 5.0 mg/mi target from Table 2. Estimates were made for the total weighted exhaust flow on the vehicle during lean operation on the FTP. Using the mileage for Bags 1 and 2 of the FTP (i.e., 7.5 miles) and assuming that all of the NO_x is emitted as NO₂ (46 g/mole) per EPA protocol, the ppm NO_x from the reactor and the lean exhaust flow from the vehicle were used to project the weighted mg/mile NO_x during lean/rich cycling on the vehicle. Figure 2 is a semilog plot showing the weighted mg/mile NO_x as a function of the total catalyst length, accounting for the TWC and LNT/SCR system. The TWC alone reduced the feedgas NO_x of 230 mg/mile to 194 mg/mile, thereby providing approximately 16% NO_x conversion during the 60/10 cycle. This was attributed to nearly 100% NO_x conversion during the rich periods and essentially no NO_x conversion during the lean periods. After the first LNT/SCR zone, the NO_x slip was reduced to 26.0 mg/mile, corresponding to an overall NO_x conversion of 88.7%. The second LNT/SCR zone further reduced the NO_x to 17.4 mg/mile with an overall NO_x conversion of 92.4%, and the third LNT/SCR zone reduced the NO_x slip to 4.4 mg/mile, corresponding to an overall NO_x conversion of 98.1%. Thus, the NO_x slip target of 5 mg/mile was successfully met on the lab reactor. However, a relatively large volume of LNT/SCR was required, resulting in the relatively low space velocity of 7.5K hr⁻¹. Using the average flow rate during lean operation on the vehicle, this translated into a total catalyst volume of 6.8 L on the intended application. Assuming a 1.8 L TWC, this suggested a 5.0 L LNT/SCR would be needed to meet the target NO_x level. This testing was performed without an U/B TWC; however, since an U/B TWC would provide little or no NO_x conversion during lean operation, it was assumed that an additional 5.0 L volume would still need to be 5.0 L.