2010-01-2267

Lean Gasoline Engine Reductant Chemistry During Lean NOx Trap Regeneration

Jim Parks, Vitaly Prikhodko, Bill Partridge, Jae-Soon Choi, Kevin Norman, Paul Chambon, John Thomas, Shean Huff
Oak Ridge National Laboratory

ABSTRACT

Lean NOx Trap (LNT) catalysts can effectively reduce NOx from lean engine exhaust. Significant research for LNTs in diesel engine applications has been performed and has led to commercialization of the technology. For lean gasoline engine applications, advanced direct injection engines have led to a renewed interest in the potential for lean gasoline vehicles and, thereby, a renewed demand for lean NOx control. To understand the gasoline-based reductant chemistry during regeneration, a BMW lean gasoline vehicle has been studied on a chassis dynamometer. Exhaust samples were collected and analyzed for key reductant species such as H_2, CO, NH_3, and hydrocarbons during transient drive cycles. The relation of the reductant species to LNT performance will be discussed. Furthermore, the challenges of NOx storage in the lean gasoline application are reviewed.

INTRODUCTION

Engines that operate at lean air-to-fuel ratios ("lean engines") offer the potential to reduce fuel consumption and, thereby, lower greenhouse gas emissions.[1] A difficult problem to address when commercializing vehicles with lean engines is the control of oxides of nitrogen (NOx) emissions. For stoichiometric combustion, the three-way catalyst technology commonly found on gasoline-engine vehicles controls emissions of NOx as well as carbon monoxide (CO) and hydrocarbon (HC) emissions; however, the three-way function is only effective in the low-oxygen exhaust conditions associated with stoichiometric combustion. Lean combustion results in oxygen-rich exhaust where the reduction of NOx is difficult.

Recently, diesel engine vehicles have been commercialized for the U.S. market that meet NOx emissions regulations by employing catalysts for lean NOx control.[2] Two catalytic approaches have been used: urea-based selective catalytic reduction (urea-SCR) and lean NOx trap (LNT) catalysts. The urea-SCR approach requires the on-board storage of urea which is introduced into the exhaust upstream of the SCR catalyst, converted to NH_3 via hydrolysis reactions, and interacts with NOx on the SCR catalyst. In contrast, the LNT technology utilizes fuel from the vehicle and advanced engine controls to enable periodic operation of the engine at rich air-to-fuel ratios which produces oxygen-depleted exhaust suitable for reducing NOx stored on the LNT catalyst surface. Both technical approaches have been proven effective in controlling NOx from diesel engines.

Despite the commercialization of diesel vehicles in the U.S. with lean NOx control, the U.S. passenger market is dominated by gasoline-engine vehicles. Gasoline engines can be operated lean, and direct injection gasoline engines show promise for significant fuel economy gains from lean operation. However, gasoline engines do not typically operate as lean as diesel engines, and portions of the load and speed map would likely be handled with stoichiometric operation. Thus, NOx control for lean gasoline engines would be required for both lean and stoichiometric conditions. The ability to operate gasoline engines with a wide range of air-to-fuel ratios offers advantages for the LNT catalyst approach for controlling NOx emissions since LNTs require rich air-to-fuel operation for reducing the NOx stored during lean operation. In this study, a lean gasoline engine in a BMW vehicle has been studied on a chassis dynamometer to evaluate the exhaust conditions during lean and rich air-to-fuel operation to better understand the chemistry of lean gasoline engine exhaust as related to the LNT technology.

EXPERIMENTAL METHODS

Experiments were conducted on a MY2008 BMW 1-series 120i lean gasoline engine vehicle. The engine was a model N43B20 2.0-liter, 4-cylinder engine with direct injection. The vehicle was operated on a chassis dynamometer with ultra-low sulfur certification gasoline fuel. The vehicle had previously accumulated sufficient mileage during use to degreen the catalysts.

The vehicle's exhaust system is composed of two three-way catalysts (TWCs) which were located in two exhaust manifolds (one for each pair of cylinders: 1-4 and 2-3) close coupled to the engine. Downstream of the merge point for the two exhaust manifolds, the LNT was located in an underfloor position. The muffler was located downstream of the LNT, and the tailpipe was connected to the dilution system of the chassis dynamometer emissions measurement system.

Several transient drive cycles were driven with the vehicle; the drive cycles included: US Federal Test Procedure-75 (FTP), US06 Supplemental Federal Test Procedure (US06), and Highway Fuel Economy Test (HFET). In addition to the transient drive cycle operation, the vehicle was operated at various speed and load conditions at near steady-state conditions for the purpose of collecting emissions data. During the steady-state operation, the vehicle speed remained constant and the vehicle load was changed in a stepwise fashion.

Emissions from the engine and the subsequent catalytic-induced emissions changes were measured with a variety of analytical techniques. Two sets of emission analyzers were used to measure engine out emissions upstream of the TWCs from exhaust pulled from each manifold. The emission analyzers included: heated chemiluminescence for NOx (California Analytical Instruments Model 400), non-dispersive infrared for CO and CO_2 and paramagnetic for O_2 (all three gases covered by California Analytical Instruments Model 300) on chilled exhaust, and heated flame ionization detector for hydrocarbons (California Analytical Instruments Model HFID). Another set of the same instruments (with different scale ranges) were used to characterize tailpipe emissions diluted by the dilution tunnel. Detailed measurements relative to the LNT regeneration were made with a FTIR (MKS Multi Gas 2030HS) and a capillary-based magnetic-sector mass spectrometry technique called SpaciMS.[3] The FTIR and SpaciMS measurements were primarily made in exhaust downstream of the TWCs and upstream of the LNT; however, some measurements were also made at engine out and tailpipe positions. The FTIR allowed measurement of NO, NO_2, NH_3, N_2O, CO, CO_2, and hydrocarbons. To complement the FTIR data, the SpaciMS was configured to measure H_2 and O_2. In addition to the exhaust analyzers, thermocouples and universal exhaust gas oxygen (UEGO) sensors were mounted at various positions in the exhaust as well.

The average of the two UEGO sensors mounted in the engine out positions of both exhaust manifolds served as the master timing signal for aligning the data from the analyzers. Since various analyzers have different delay times in exhaust transfer and measurement, a common signal was needed to time align measurements of exhaust species from different analyzers. The UEGO air-to-fuel signal was converted to exhaust concentrations for O_2,

CO_2, and H_2O using a simple model based on the fuel hydrogen to carbon ratio of 1.837. Then the O_2, CO_2, and H_2O signals were matched to appropriate signals for analyzers to achieve time alignment.

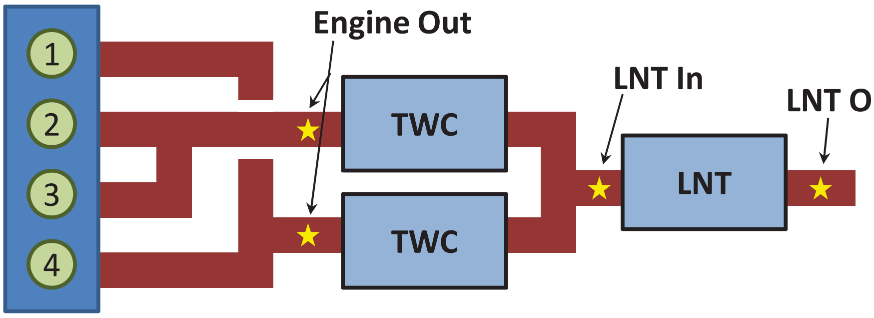

Figure 1. Schematic of BMW 120i exhaust system; yellow stars note exhaust sample positions.

RESULTS AND DISCUSSION

DRIVE CYCLE FUEL ECONOMY AND EMISSIONS

The benefits of lean operation on vehicle fuel economy were characterized by comparing vehicle performance over drive cycles with stoichiometric only and lean plus stoichiometric operation. The default operation of the vehicle is to operate lean at low loads and speeds and operate with stoichiometric combustion at higher loads and speeds. There are also two other fuel savings technologies employed by the vehicle: start-stop operation and an intelligent alternator that allows for micro hybridization. Based on information from the OEM service manual, these fuel saving technologies were turned off for the experiments presented here by manually shorting or bypassing sensors that control those functionalities. Stoichiometric only operation was more challenging to implement but was performed during cases where the vehicle was locked in stoichiometric mode. Thus, drive cycles were conducted with and without lean operation to define the benefit of lean combustion. Fuel economy results from three different drive cycles are shown in Table 1. For all three drive cycles, the fuel economy with lean operation was better than for stoichiometric only operation; however, the amount of improvement was dependent on the drive cycle with the lowest improvement occurring for the most aggressive drive cycle (US06) which relied more on stoichiometric operation for the more aggressive accelerations. Overall, fuel economy improvements of 4-15% were observed.

Table 1. Fuel Economy as a Function of Vehicle Mode and Drive Cycle

Drive Cycle	Stoichiometric Only Operation	Lean and Stoichiometric Operation	Fuel Economy Improvement from Lean Operation
FTP	26.8 mpg	29.5 mpg	10.0%
HFET	40.5 mpg	46.4 mpg	14.6%
US06	30.2 mpg	31.6 mpg	4.4%

While fuel economy improved with lean operation, the NOx emissions became worse with the addition of lean operation. Table 2 summarizes the tailpipe NOx emissions on a g/mile basis for the same data shown in Table

1. The increase in NOx emissions is quite notable for lean operation with the highest NOx emissions being observed for the most aggressive driving cycle (US06). All NOx emissions from lean plus stoichiometric operation were found to be above the 0.05 g/mile NOx level associated with the U.S. Tier II Bin 5 (at 50,000 miles) regulation. While this vehicle is not sold in the U.S. and was not designed to meet the U.S. emissions, the emissions relative to this regulation highlight the need for emissions reduction for the lean gasoline engine technology. Note that the values are rounded to the nearest hundredths of g/mile emissions.

Table 2. NOx Emissions in g/mile as a Function of Vehicle Mode and Drive Cycle

Drive Cycle	Stoichiometric Only Operation	Lean and Stoichiometric Operation
FTP	0.03 g/mile NOx	0.11 g/mile NOx
HFET	0.00 g/mile NOx	0.11 g/mile NOx
US06	0.03 g/mile NOx	0.35 g/mile NOx

LNT STORAGE AND REGENERATION CONDITIONS

During steady-state operation of the vehicle, data was acquired to understand the exhaust conditions experienced by the LNT catalyst. At lower loads, the engine operated at lean air-to-fuel ratios (AFR) with periodic operation at rich AFR for the purpose of regenerating the LNT. At higher engine loads (>60%), the engine operated at stiochiometric AFR. Figure 2 shows the average engine out AFR recorded by the two UEGO sensors in the exhaust manifold upstream of the TWC. The AFR plot is bifurcated with lean-rich cycling operation below 60% engine load and stoichiometric operation above 60% engine load. The engine speed did not affect the controlled AFR. LNT regeneration was performed at an AFR of 12 consistently over the load range; however, during lean operation the AFR varied with engine load and spanned from 19-28 with the lower AFRs occurring at higher loads.

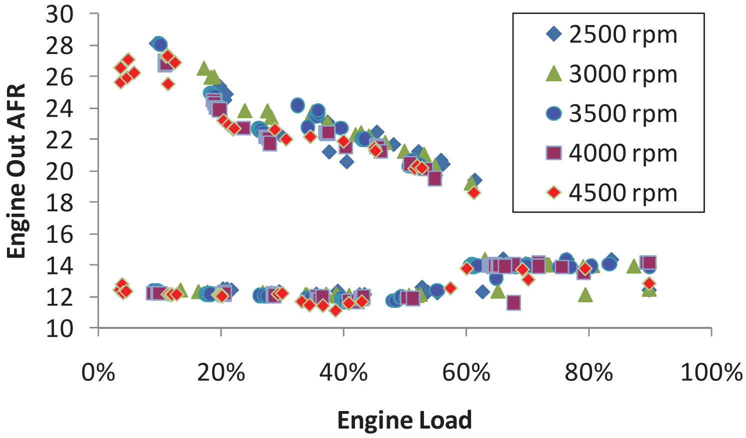

Figure 2. Air-to-fuel ratio as a function of load for different engine speeds.

Temperatures in the exhaust system varied as expected with AFR. Under lean conditions, the engine out exhaust generally ranged from 450-700°C, but at stoichiometric conditions associated with higher engine loads, engine out exhaust temperatures reached 700-800°C. There was a significant drop in exhaust temperatures from the engine out to the LNT positions. The LNT temperature generally ranged from 350-500°C during lean operation and varied between 400 and 600°C during stiochiometric operation. A comparison of the TWC and LNT temperatures as a function of engine load are shown in Figure 3 for data obtained at 3500 rpm engine speed (which will be presented as a representative speed for presenting exhaust chemistry data). Space velocity for the LNT was estimated to vary between 40,000/hr and 72,000/hr for the 2500 to 4500 rpm engine speed range based on the catalyst can dimensions.

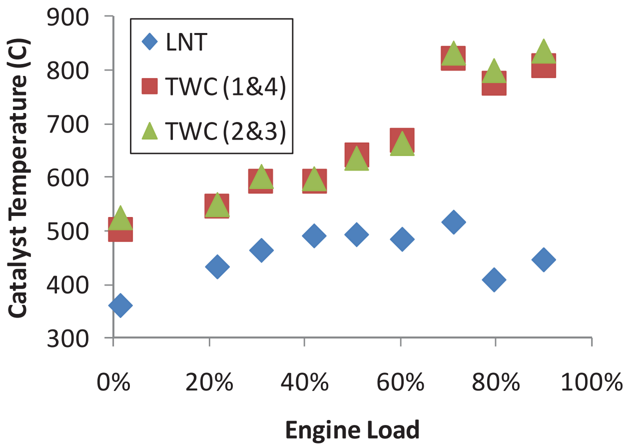

Figure 3. Catalyst temperatures as a function of load at 3500 rpm.

TWC AND LNT NOX REDUCTION

A major challenge for the LNT technology in lean gasoline engine applications is the high amount of NOx emissions during lean operation. Figure 4 shows the NOx concentration at various positions along the catalyst system as a function of engine load; all data is from 3500 rpm. Open data icons represent concentrations during the rich AFRs used for LNT regeneration; solid data icons represent lean and stoichiometric AFR operation. Engine out NOx levels range from 700 to 1800 ppm for lean operation which greatly challenges the LNT. The NOx was predominantly NO, but $NO:NO_2$ ratios at the LNT inlet position ranged from 6 to 27 with the lower $NO:NO_2$ ratios occurring at lower loads and moderate catalyst temperatures (350-400°C) where the TWC could shift the $NO:NO_2$ ratio towards NO_2 which is thermodynamically preferred at lower temperatures. The LNT is able to significantly decrease these high levels of NOx emissions, but LNT out data shows that significant slip of NOx occurs downstream of the LNT as the NOx emissions exceed the NOx storage capacity of the LNT. In contrast, at stoichimetric conditions at the higher engine loads, the TWC is very effective at reducing the high NOx emissions to low levels; note that the LNT serves to aid in NOx reduction as TWC chemistry occurs over the LNT during stoichiometric operation as well.

Significant NOx emissions occur during the rich regeneration event as well as NOx is released unreduced by the LNT. Figure 5 shows temporal profiles of NOx downstream of the LNT and at the engine out position to illustrate the slip of NOx past the LNT catalyst; data is shown for a 22% engine load and 3500 rpm engine speed. NOx downstream of the LNT occurs due to both NOx slip during the lean phase of operation (from insufficient storage capacity of the LNT) and NOx release during LNT regeneration. Note that the NOx emission peaks downstream of the LNT during LNT regeneration are declining as successive regenerations are altering the NOx storage in the LNT. Due to the high levels of NOx emitted by the engine and relatively lower storage capacity of the LNT, the LNT is regenerated quite frequently with lean periods ranging from 15 to 35 seconds typically. Regeneration periods were typically 3 seconds of duration at an AFR of 12.

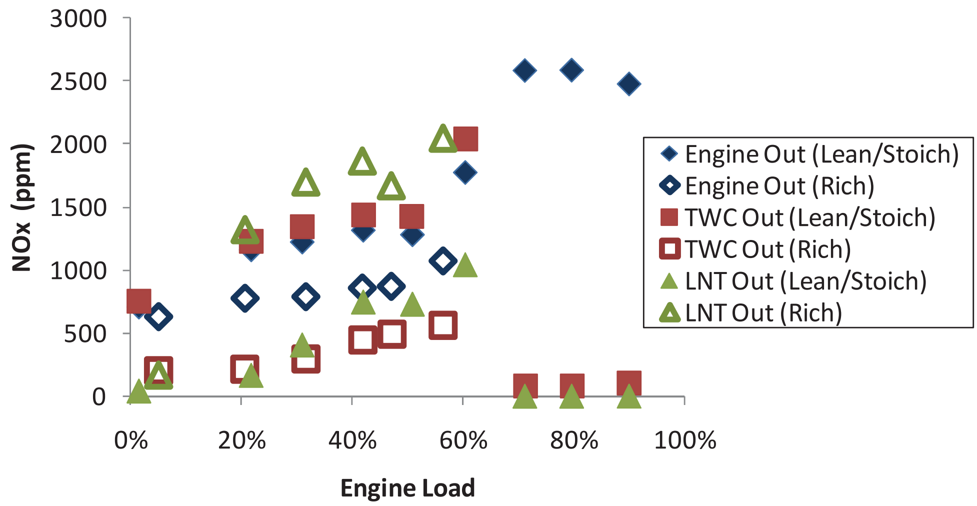

Figure 4. NOx concentration along catalyst system as a function of load at 3500 rpm.

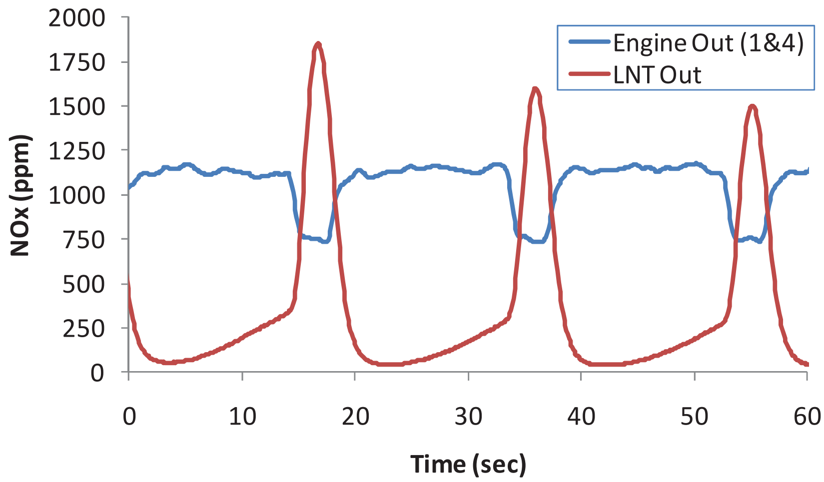

Figure 5. NOx as a function of time at the engine out and LNT out positions at 3500 rpm and 22% load.

REGENERATION CHEMISTRY

Effective regeneration of the LNT catalyst is dependent on several factors, and reductant chemistry is an important factor. Primary reductants known to be effective in regenerating LNTs were measured at the LNT inlet position. Figure 6 shows results for the reductants H_2, CO, and NH_3 as a function of engine load at 3500 rpm; the data represents the average exhaust concentration over the approximate 3-second regeneration event. H_2 was found at 1.7-2.7% levels and was present at higher levels than CO and NH_3. CO levels were between 1 and 1.8% and together with H_2 was a major reductant species. NH_3 was detected at levels a couple of orders of magnitude smaller than H_2 and CO on a concentration basis; note that the data icons in Figure 6 show the NH_3 data at ten times the raw magnitude for visualizing the NH_3 against the lean data close to the 0% range on the y-axis. The production of the reductants by the engine operating at rich AFRs and the upstream TWC was uniform over the rich period. Figure 7 shows the temporal profile of the H_2, CO, and NH_3 reductants at 32% engine load and 3500 rpm. The temporal shape of reductants produced is mostly Gaussian in shape and consistent from one regeneration event to another.

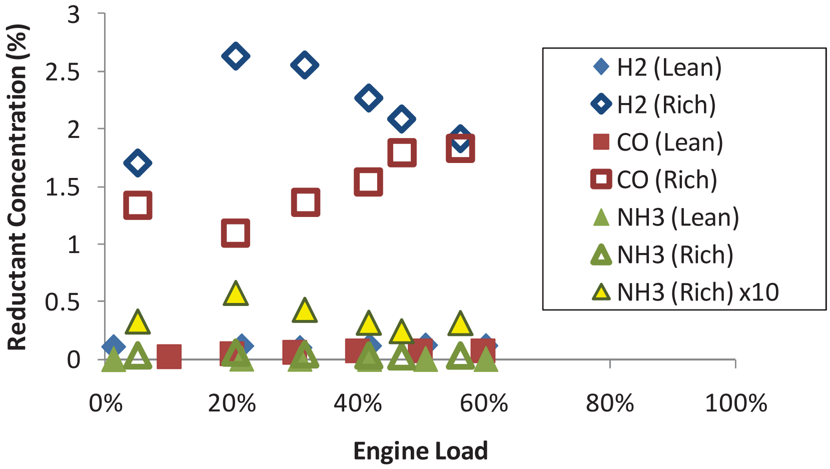

Figure 6. H_2, CO, and NH_3 reductants as a function of engine load at 3500 rpm.

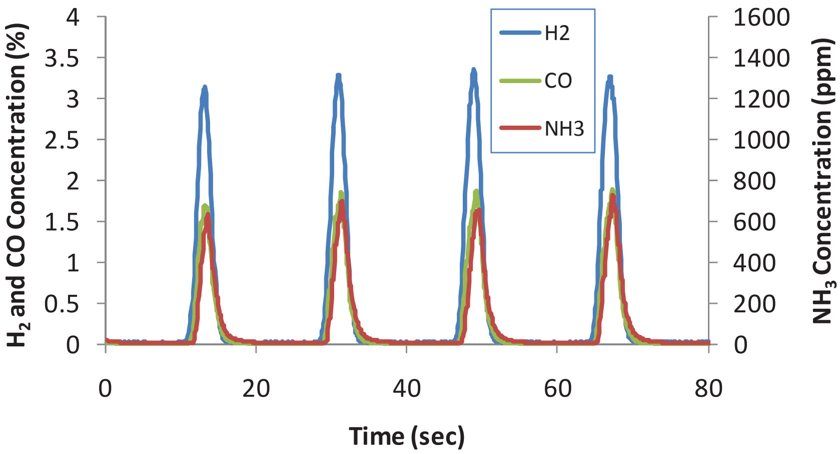

Figure 7. Reductants as a function of time at LNT inlet position at 3500 rpm and 32% load.

The upstream TWCs have a significant impact on the exhaust chemistry produced for the LNT during the rich regeneration event. Figure 8 shows reductant concentration upstream and downstream of the TWC during the rich LNT regeneration event; results are shown for 3500 rpm as a function of engine load. Results at the Engine Out or TWC In position represent the average level of reductants from both manifold legs. A sharp reduction in the CO concentration occurs over the TWC, and conversely, the H_2 concentration increases across the TWC. These CO and H_2 reductant levels indicate that CO is used to form more H_2 over the TWC via the water-gas-shift reaction. Note that in order to plot the data shown in Fig. 8, H_2 collected from two different experiments was used because only one H_2 analysis tool was available. Despite the small differences that occurred from using data from two different data sets, a calculation of the amount of H_2 generated based on the drop in CO and the 1:1 stoichiometry of the water-gas shift reaction shows that the H_2 at the TWC Out position is within 20% of the H_2 level measured for all points except the 10% load point. The lower temperature associated with the catalyst at the 10% load point likely causes less H_2 in that case.

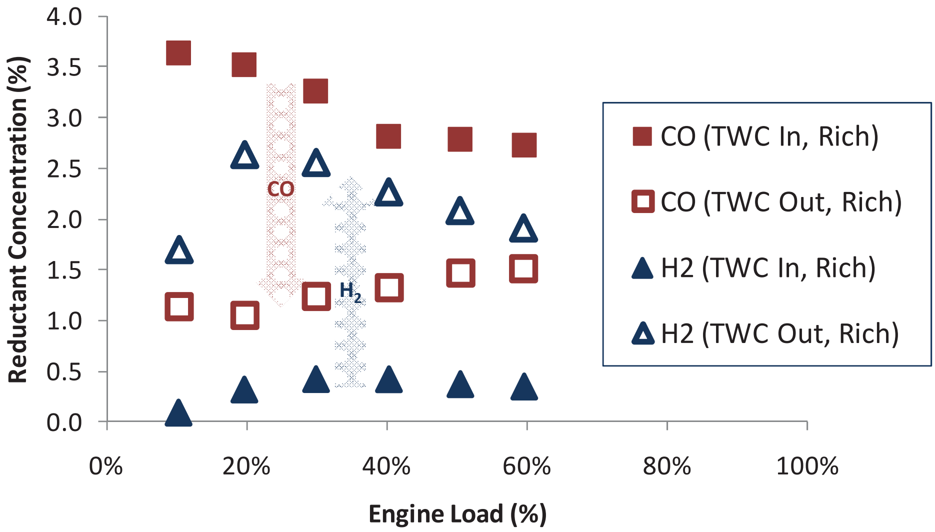

Figure 8. Changes in reductant chemistry over the TWC as a function of engine load at 3500 rpm.

Analysis of hydrocarbons that could serve as reductant species for the LNT was performed with the FTIR analyzer; however, only small amounts of HCs were observed. Ethane, ethylene, and propylene were only observed at trace levels. Methane was observed at levels between 30 and 120 ppm during the rich LNT regeneration event, but these levels are not significant enough to impact LNT regeneration.

The mixture of reductants observed at the LNT inlet position was different than previous observations of reductants present for LNT regeneration in diesel applications where the diesel engine is operated at rich AFRs.[4] Notable differences include the lack of significant levels of HCs for the lean gasoline engine case and differences in the relative level of CO and H_2 reductants. Observations of diesel exhaust during rich operation have shown higher amounts of CO relative to H_2 in contrast to the higher H_2 levels observed here for the lean gasoline engine. Higher exhaust temperatures combined with the TWC effects play important roles in the reductant chemistry resulting from the rich operation of the gasoline engine. Unfortunately, the higher H_2 levels would be more beneficial for the diesel application where much lower exhaust and catalyst temperatures (<250ºC) are common for light-duty vehicles.[5,6] The higher exhaust temperatures for the lean gasoline engine case provide better LNT performance, but the higher NOx levels in the lean gasoline case present a significant challenge.

CONCLUSIONS

A commercial lean gasoline engine vehicle (BMW 120i) with a LNT catalyst was characterized on a chassis dynamometer. Improvements in fuel economy due to the lean operation were between 4 and 15% over the stoichiometric fuel economy performance and varied according to the drive cycle used for the experiment; more aggressive drive cycles showed less benefit from lean operation. Characterization of the exhaust from the vehicle under steady-state conditions showed that the vehicle operates lean at lower engine loads (<60%) and operates at the stoichiometric AFR at higher engine loads (>60%). The lean-rich cycles employed to operate the LNT for lean NOx control were short (15-35 second period) due to the high NOx levels associated with the lean AFRs. Reductants produced during the rich regeneration event at an AFR of 12 were primarily H_2 and CO with smaller levels of NH_3 also present. The TWC had a significant impact on the reductant chemistry produced by effectively converting CO to H_2 by the water-gas-shift reaction.

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CONTACT INFORMATION

Jim Parks, parksjeii@ornl.gov

DISCLAIMER

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy (DOE), Vehicle Technologies Program. The authors gratefully acknowledge the support and guidance of program managers Ken Howden and Gurpreet Singh at DOE.