Assessing Reductant Chemistry During In-Cylinder Regeneration Of Diesel Lean NOx Traps

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Objectives

- Characterize H2, CO, and HC's generated by the engine
  - FTIR, GC/MS, SpaciMS to characterize engine strategies
- Characterize candidate Lean NOx Traps (LNT) for performance and degradation
  - Correlate various reductants with catalyst performance
- Develop stronger link between bench and full-scale system evaluations
  - Provide data through CLEERS to improve models. Use models to guide engine research

Approach

- Establish a relationship between exhaust species and various regeneration strategies on a fully controlled engine
- Characterize effectiveness of in-cylinder regeneration strategies
- Develop and execute rapid sulfation/desulfation experiments
- Develop experiments for bench-scale work to further characterize LNT monoliths, wafers, and/or powders

Accomplishments

- Received full-size MECA catalysts (DOC and NOx Ads) in August 2003
  - LNT cores for bench flow (same formulation)
- Defined and procured 2 "model catalysts" (via CLEERS & Emerachem)
  - Engine and bench samples
- Diagnosed engine problem, replaced engine (unplanned)
- Investigate Effects of
  - fuel chemistry and regeneration strategy on exhaust species
  - exhaust species on LNT performance
  - regeneration strategy on PM
- Examined 3 fuels, 2 strategies with full speciation, SpaciMS
  - Further examine other temperatures
  - Examine Regeneration in the midst of LTC operation
- Developed desulfation strategy, desulfurized LNT
- Coordinating experimental plans with CLEERS and bench reactor teams

Future Directions

- Similar experiments with catalysts in fresh, heavily sulfated, and desulfated conditions and across a wider temperature range are planned to understand if the conclusions hold for broader cases.
- Further investigate regeneration during "LTC"
- Rapid sulfation/desulfation with speciation and SpaciMS
- Examine model catalysts and other MECA catalysts
- Share results and coordinate research plans through CLEERS LNT focus group

Introduction

As part of the Department of Energy's strategy to reduce imported petroleum and enhance energy security, OFCVT has been researching enabling technologies for more efficient diesel engines. NOx emissions from diesel engines are very problematic and the U.S. Environmental Protection Agency (EPA) emissions regulations require ~90% reduction in NOx from light- and heavy-duty diese engines in the 2004-2010 timeframe. An active research and development focus for lean burn NOx control is in the area of LNT catalysts. LNT catalysts adsorb NOx very efficiently in the form of a nitrate during lean operation, but must be regenerated periodically by way of a momentary exposure to a fuel-rich environment. This rich excursion causes the NOx to desorb and then be converted by more conventional three-way catalysis to N_2. The momentary fuel-rich environment in the exhaust can be created by injecting excess fuel into the cylinder or exhaust and/or throttling the intake air and/or increasing the amount of Exhaust Gas Recirculation (EGR). The controls methodology for LNTs is very complex, and there is no clear understanding of the regeneration mechanisms. NOx regeneration is normally a 2-4 second event and must be completed approximately every 30-90 seconds (duration and interval dependent on many factors; e.g., load, speed, and temperature).

While LNTs are effective at adsorbing NOx, they also have a high affinity for sulfur. As such, sulfur from the fuel and possibly engine lubricant (as SO_2) can adsorb to NOx adsorbent sites (as sulfates). Similar to NOx regeneration, sulfur removal (desulfation) also requires rich operation, but for several minutes, at much higher temperatures. Desulfation intervals are much longer, on the order of hundreds or thousands of miles, but the conditions are more difficult to achieve and are potentially harmful to the catalyst function. Nonetheless, desulfation must be accomplished periodically to maintain effective NOx performance. There is much to be learned with regard to LNT performance, durability, and sulfur tolerance.

Different strategies for introducing the excess fuel for regeneration can produce a wide variety of hydrocarbon and other species. One focus of this work is to examine the effectiveness of various regeneration strategies in light of the species formed and the LNT formulation. Another focus is to examine the desulfation process and examine catalyst performance after numerous sulfation/desulfation cycles. Both regeneration and desulfation will be studied using advanced diagnostic tools.

Approach

A 1.7-L Mercedes common rail engine and motoring dynamometer have been dedicated to this activity (Figure 1). The engine is equipped with an electronic engine control system that provides full-bypass of the OEM engine controller. The controller is capable of monitoring and controlling all the electronic devices associated with the engine (i.e., fuel injection timing/duration/number of injections, fuel rail pressure, turbo wastegate, electronic throttle, and electronic EGR).

Two regeneration strategies (Delayed Extended Main (DEM) and Post80) and three fuel compositions (ECD1, BP15, and DECSE) have been studied with the goal of introducing a broad range of species to the LNT catalysts. Advanced tools such as H_2-SpaciMS and GC/MS are being used to characterize the species produced in the engine or in upstream catalysts. The H_2-SpaciMS is being used for both in-pipe and in-situ measurements within the catalyst monoliths. In addition, catalysts and exhaust species will be characterized after rapid sulfation and during desulfation. LNT catalysts have been provided by some MECA members. "Model" catalysts will also be characterized. Catalysts are being studied under quasi-steady conditions, that is steady load and speed but with periodic regeneration, as shown in Figure 2.

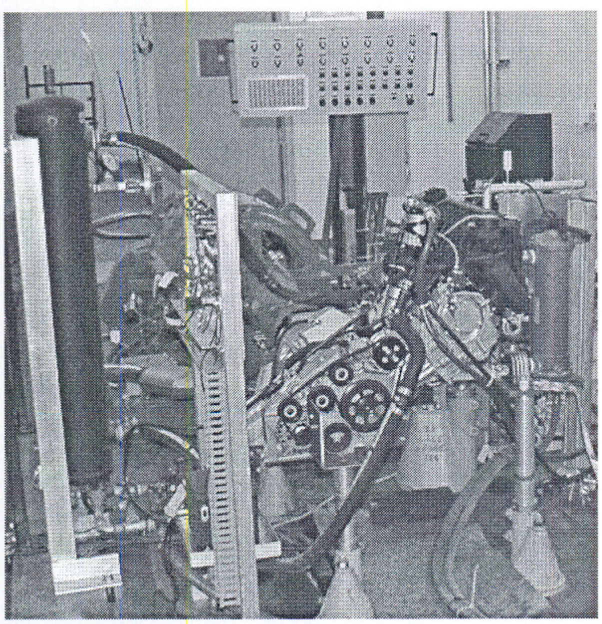

Figure 1. [Experimental setup including engine, control system, motoring dyno, and exhaust system]

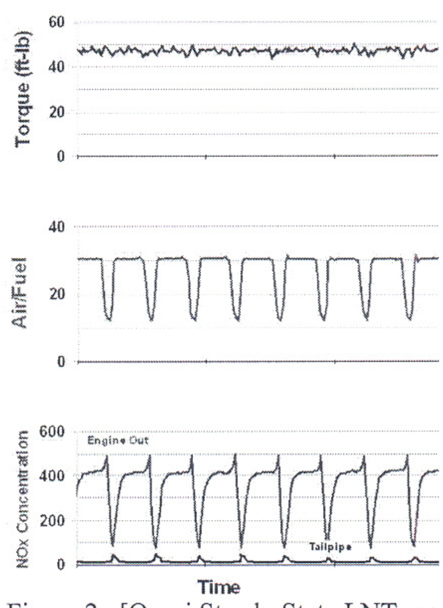

Figure 2. [Quasi Steady State LNT regeneration trace]

Finally, bench-scale work will be used to further characterize LNT monoliths, wafers, and/or powders using our bench-scale reactor and the DRIFTS reactor. Results and characteristics of the engine experiments will be used to help define more meaningful bench scale studies. In some cases, the exact same catalyst formulation we are characterizing on the engine stand is also being examined in the bench studies.

Results

SUMMARY OF FUEL AND STRATEGY EFFECTS – Figures 3a and 3b show the differences in CO and H_2 production for the DEM and Post80 strategies for all three fuels evaluated at the same nominal 1500 RPM, 50 ft-lb_f, 300°C exhaust temperature condition. The DEM strategy produces consistently more CO and H_2 than the Post80, regardless of fuel. The total HC emissions for each strategy and fuel are summarized in Figure 3c. It is interesting to note that while we observed differences in the detailed HC species produced by the strategies and fuels, there appears to be no significant fuel effect on total CO, HC, or H_2 for any given strategy. Figure 3d indicates that DEM consistently produces better NOx reduction than the Post80 strategy for all fuels. Moreover, the strategy-dependent LNT efficiency correlates with that of CO and H_2 concentration, but not HC. This result suggests that for the conditions reported here H_2 and CO have a greater effect on LNT efficiency than do all other HCs present. These results are consistent with bench scale experiments in the literature that have shown H_2 to be the preferred reductant, followed by CO, then propene.

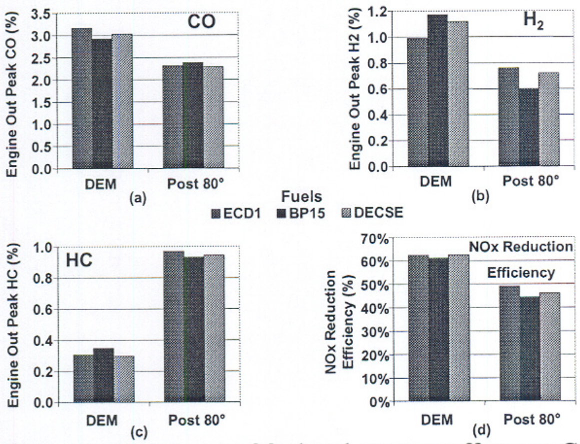

Figure 3. [Summary of fuel and strategy effects on CO, H_2, and HC emissions and average NOx reduction]

IN SITU ANALYSIS OF H_2 UTILIZATION – In-situ intra-catalyst speciation was used to further investigate the role of reductants in the LNT regeneration process. The H2-SpaciMS was used to measure transient total NOx, O_2, and H_2 concentrations at ¼, ½, and ¾ catalyst-length locations within the LNT. These results are combined with conventional LNT-in and -out CO and HC measurements from standard bench analyzers and are shown in Figures 4 and 5 for the DEM and Post80 regeneration strategies, respectively. The figures show peak H_2, CO, and HC levels and minimum O_2 during regeneration as well as average NOx levels over the sorption cycle; similar results were obtained for each fuel studied (data from BP15 fuel is shown).

The data from the DEM strategy (Figure 4) shows little change in exhaust chemistry across the DOC during regeneration. Some decrease in the reductant levels occurs, but the primary decrease in reductant concentration occurs in the LNT catalyst. The strategy is effective in consuming oxygen since engine-out O_2 levels drop to 1.1%; however, the DOC is not effective in completely removing the remaining O_2 since the 1.1% level remains downstream of the DOC. Measured O_2 levels drop to 0.5% at ¼ length inside the LNT and remain at that level throughout the LNT. Oxygen levels of 0% are difficult to measure considering the fact that O_2 levels drop for 2-3 seconds intermittently between lean exhaust O_2 levels of 12.6%; thus, it is assumed that the 0.5% level is representative of O_2 depletion in the catalyst. Note that any remaining O_2 going into the LNT catalyst may influence regeneration since reductants must be consumed to complete the O_2 depletion process. The measured H_2 level drops inside the LNT during the first ½ of the catalyst which corresponds with the largest drop in NOx level. Once H_2 is depleted (during the downstream ½ of the catalyst), little NOx reduction occurs despite the fact that both CO and HCs are plentiful in the catalyst as evident from measurements at the LNT outlet.

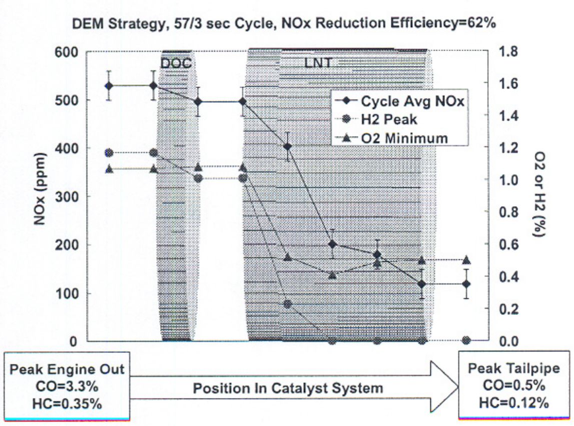

Figure 4. [In-situ measurements through the catalyst system for DEM strategy, BP15 fuel]

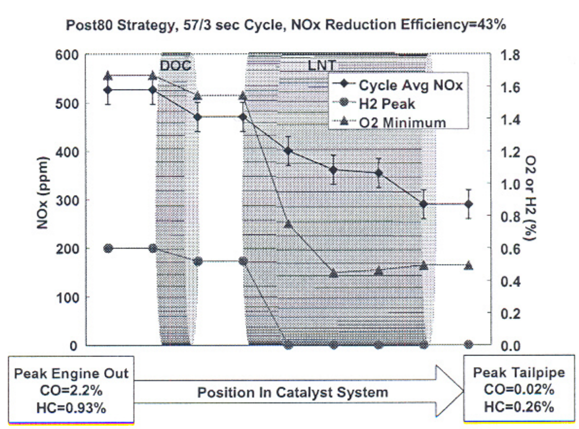

Figure 5. [In-situ measurements through the catalyst system for Post80 strategy, BP15 fuel]

The Post80 strategy data (Figure 5) is similar to the DEM strategy data in terms of O_2 depletion; however, a higher engine out O_2 level (1.7%) is indicated. Hydrogen depletion occurs earlier in the Post80 case with H_2 fully consumed by the ¼ length position. The lower available LNT-in H_2 concentration with the Post80 strategy corresponds with lower NOx reduction efficiency shown in Figure 3d. The lower H_2 and CO levels combined with the higher O_2 level at LNT-in may contribute to the degraded regeneration efficiency for the Post80 strategy; less of the apparently preferable reductants are available and more of these are required for O_2 depletion. Note that in the Post80 case, CO is fully depleted across the LNT. HC levels are greater at both the engine-out and LNT-out positions for the Post80 strategy. The consumption of HCs inside the LNT catalyst may contribute to some NOx reduction since both CO and H_2 are consumed in the LNT; however, the HCs appear less effective for NOx reduction since no large drop in NOx levels was observed in the LNT after the H_2 was consumed.

Conclusions

Two strategies for in-cylinder regeneration have been developed for studying reductant chemistry effects on LNTs. Each strategy was evaluated with three fuels, BP15, ECD-1, and DECSE.
Notable conclusions are the following:

- Fuel chemistry has a definite effect on exhaust HC speciation, but negligible effect on engine-out CO and H_2 emissions for the fuels evaluated.
- For 14:1 minimum indicated AFR, the Post80 strategy produces 3 times the HCs, with a much broader mix of HC species than DEM
- The DEM strategy produces higher engine-out CO and H_2, and lower HC emissions than Post80
- The DEM strategy produces much higher PM emissions than the Post80 strategy
- For the conditions studied with a minimum AFR of 14:1:
  - DEM yields higher NOx conversion than the Post80 strategy, implying that CO and H_2 are the key reductants, and that HC effects on regeneration are secondary.
  - The correlation between hydrogen depletion and NOx reduction inside the LNT catalyst indicates H_2 may be the most reactive reductant for LNT regeneration.
  - Although both the DEM and Post80 strategies yield engine-out O_2 levels below 2%, the higher O_2 concentrations for the Post80 strategy may contribute to poorer regeneration performance as reductant supply is consumed to complete depletion of O_2 in the exhaust.

Acronyms

NOx	Oxides of Nitrogen (i.e., NO, NO_2, and NO_3)
H_2	Molecular hydrogen
O_2	Molecular oxygen
CO	Carbon monoxide
HC	Hydrocarbons
CRADA	Cooperative Research and Development Agreement
MECA	Manufacturers of Emission Controls Association
GC/MS	Gas Chromatograph / Mass Spectrometer
PM	Particulate Mater
H_2-SpaciMS	Hydrogen calibrated Spatially Resolved Capillary Inlet Mass Spectrometer
OEM	Original Equipment Manufacturer
EGR	Exhaust Gas Recirculation
DRIFTS	Diffuse Reflectance Fourier Transform Infrared Spectroscopy
DEM	Delayed and Extended Main
Post80	Late Cycle Injection after the Main Fuel Pulse at 80° After Top Dead Center
RPM	Revolutions per minute
Ft-lb	Unit of torque – foot-pound
°C	Unit of temperature – degrees Celsius
LNT	Lean NOx Trap