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

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ABSTRACT

Lean NOx Trap (LNT) catalysts are capable of reducing NOx in lean exhaust from diesel engines. NOx is stored on the catalyst during lean operation; then, under rich exhaust conditions, the NOx is released from and reduced by the catalyst. The process of NOx release and reduction is called regeneration. One method of obtaining the rich conditions for regeneration is to inject additional fuel into the engine cylinders while throttling the engine intake air flow to effectively run the engine at rich air:fuel ratios; this method is called "in-cylinder" regeneration. In-cylinder regeneration of LNT catalysts has been demonstrated and is a candidate emission control technique for commercialization of light-duty diesel vehicles to meet future emission regulations. In the study presented here, a 1.7-liter diesel engine with a LNT catalyst system was used to evaluate in-cylinder regeneration techniques. Characterization of the exhaust reductant chemistry during in-cylinder regeneration was performed. The effects of various injection strategies and fuels and the resulting exhaust chemistry on the performance of the LNT catalyst were analyzed. In addition, exhaust species measurement of NOx and select reductants were performed inside of the catalyst cells with a capillary-based mass spectrometry technique. The effect of various injection parameters on exhaust chemistry species and LNT performance are discussed. Results indicate that fuel chemistry does affect engine-out hydrocarbon (HC) species, but not engine-out carbon monoxide (CO) or hydrogen (H_2) generation. Higher engine-out CO and H_2 correlate to improved NOx reduction, irrespective of HCs.

INTRODUCTION

The highly effective three-way catalyst in widespread use in many modern vehicles with spark ignition engines simultaneously reduces nitrogen oxides (NOx) while also oxidizing carbon monoxide (CO) and hydrocarbons (HC). This catalyst function is enabled by tight control of exhaust air:fuel ratio (AFR); dithering the AFR slightly lean and slightly rich of stoichiometric operation allows the simultaneous control of these three pollutants. The excess oxygen present in lean diesel engine exhaust precludes the use of the three-way catalyst. The Lean NOx trap (LNT, also NOx adsorber or NOx Storage and Reduction (NSR) catalyst) is receiving considerable attention as a possible means to enable light- and heavy-duty diesel engines to meet future emissions standards. The LNT functions by storing NOx during normal lean operation (when excess oxygen in the exhaust hinders the chemical reduction of NOx). The LNT must be regenerated periodically by a rich excursion, a brief event in which the exhaust AFR is driven rich to achieve overall reducing conditions. The excess-fuel derived reductants (HCs, CO, hydrogen (H_2)) cause the release and subsequent reduction of the stored NOx.

Several approaches to achieving this momentary rich excursion are being researched. In some cases raw fuel is sprayed into the exhaust ("in-pipe injection") to enable regeneration.[1-4*] Synthesis gas has been shown to be a very effective reductant in both bench and full-scale laboratory experiments.[5-7] As such, on-board fuel reformers are being researched as a potential means to provide CO and H_2 for catalyst regeneration.[8] In addition, in-cylinder injection of excess fuel, or rich combustion, is a common approach,[9-10] and the approach addressed in this paper. All of these approaches have unique advantages and disadvantages and are being considered as strategies for various diesel vehicle applications either individually or as coupled technologies.[10-11]

In this paper, exhaust species generated by in-cylinder injection of excess fuel will be characterized. By combining intake throttling, exhaust gas recirculation (EGR) control, and manipulation of the timing and duration of in-cylinder fuel injection events, the exhaust can be driven into the rich regime required for LNT

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* Superscripted numbers denote references at the end of the paper.

regeneration. We will discuss several approaches for achieving rich exhaust conditions, and characterize the different species produced by the various techniques. The objective of this work is to characterize the reductant species generated via in-cylinder regeneration, and correlate these species with LNT performance. Through this study we improve our understanding of the LNT function, and provide key data to enable development of a variety of regeneration strategies and LNT systems. In addition, providing data to groups working to model the LNT function (for example, Cross-Cut Lean Exhaust Emissions Reduction Simulation, or CLEERS) can improve models to help guide engine research and catalyst development.

EXPERIMENTAL SETUP

ENGINE TEST CELL - This work was conducted at Oak Ridge National Laboratory, in the Fuels, Engines, and Emissions Research Center. A Mercedes OM668 1.7 liter common-rail diesel engine is coupled to a motoring DC dynamometer. The engine is a 1999 model used in the Mercedes A170 in Europe. Modifications to the engine include the addition of an electronic intake throttle, an electronically controlled EGR valve (in lieu of the stock vacuum-operated valve), and an EGR cooler. Additionally, the factory engine control module was replaced with a rapid development engine controller based on a dSpace® MicroAutoBox. This rapid development system (RDS) provides complete control over all engine electronics, including timing, duration, and number of fuel injection events, intake throttle, EGR valve, and turbocharger wastegate.

CATALYSTS – A diesel oxidation catalyst (DOC) and a lean NOx trap (LNT) catalyst were mounted in the exhaust system in the configuration shown in Figure 1. Both catalysts were supplied by a member company of the Manufacturers of Emission Controls Association (MECA); catalyst details are provided in Appendix A. The LNT formulation is identical to that being used in the aging phase of the Advanced Petroleum-Based Fuels – Diesel Emission Control (APBF-DEC) passenger car project, and the DOC is similar to the DOC used during the development in that same project.[9] Both catalysts had significant exposure to engine exhaust and sulfur prior to the experiments described. The catalysts were degreened in air then operated approximately 700 hours in engine exhaust from ultra-low sulfur fuel (<15 ppm S) during development and characterization of the regeneration strategies.

GAS ANALYSIS – Dual conventional emissions benches are used for raw exhaust sampling. Benches use California Analytical Instruments® (CAI) non-dispersive infrared analyzers for CO and carbon dioxide (CO_2), heated chemiluminescent detectors (HCLD) for NOx, and heated flame ionization detectors (HFID) for total hydrocarbons. In addition, ECM wide-range universal exhaust gas oxygen (UEGO) sensors and NGK NOx sensors are positioned at various locations in the exhaust, as shown in Figure 1.

EMISSIONS SPECIATION – A Nicolet Rega 7000 Fourier Transform InfraRed (FTIR) analyzer is used for quantifying several species, including ammonia (NH_3), nitrous oxide (N_2O), light hydrocarbons (e.g., methane, ethene, ethyne, propene, 1,3 butadiene, isobutylene), formaldehyde and acetaldehyde. Florisil® solid-phase extraction cartridges are used to collect a wide range of nitro-organic species (e.g., nitromethane, nitrophenol), using a method developed at ORNL. A Hewlett-Packard gas chromatograph mass spectrometer (GC/MS) with Entek Preconcentrator is used for identification and quantification of dozens of other HC species from diluted samples collected in Tedlar® bags.

PARTICULATE MATTER – Particulate matter (PM) emissions are measured using a micro-dilution tunnel and a tapered element oscillating microbalance (TEOM). The TEOM provides near real-time PM mass emissions information. In addition, a Celesco model 107 opacity meter provides real-time "smoke" measurement. The Celesco meter uses purge air to keep the optical windows clean. Since this air dilutes the raw exhaust the instrument is installed in the exhaust line downstream of all catalysts and sample points.
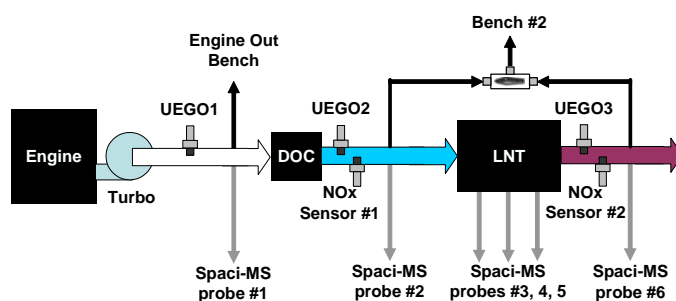

Figure 1. Exhaust sampling locations

IN-SITU AND HYDROGEN MEASUREMENT – A capillary inlet mass-spectrometer is used for measuring H_2 in the exhaust as well as at various locations within the LNT catalyst bed. The Spatially-resolved capillary inlet mass spectrometer (SpaciMS) was developed at ORNL, and has been described previously.[12] The original SpaciMS used a quadrupole mass spectrometer, while the new H2-SpaciMS uses a magnetic sector mass spectrometer to allow quantification of hydrogen. The instrument is also able to measure NOx, CO_2, oxygen, hydrogen sulfide, sulfur dioxide, and other species.

SAMPLING LOCATIONS – Figure 1 schematically shows the relative location of the engine, catalysts, sample locations and sensors. As only two emissions benches are available, all experiments are repeated with

sample location switching of bench 2. Also, experiments are repeated multiple times to allow sampling from each of the SpaciMS probes.

REGENERATION STRATEGIES

There are numerous possible approaches for achieving rich exhaust conditions using engine control. This paper will discuss two approaches, selected for their distinctly different emissions. Both strategies employ intake throttling to lower exhaust oxygen concentration, then excess fueling is used to transition rich.

In general, a "production-like" calibration would strive for the lowest practical engine-out NOx emissions and the highest practical LNT performance. In early experiments, there were a variety of strategies explored that achieved 95-99% NOx reduction with the fresh catalysts. However, with such high conversion efficiencies there was little performance difference between the strategies. As such, engine conditions and regeneration parameters were selected to accentuate the differences in performance due to the differences in exhaust chemistry.

For the strategies discussed here, no EGR was used during LNT loading or during regeneration to allow for rapid LNT loading and to prevent intake fouling. In addition, a three second rich pulse with a 57 second lean period was selected to generate considerable NOx and reductant slip from the LNT. These conditions produced the desired cycle averaged NOx reduction efficiencies in the range of 50-80%. Thus, challenging conditions were chosen for LNT evaluation to increase sensitivity to performance differences and to differentiate the relative effect of the different exhaust species.

DELAYED EXTENDED MAIN (DEM) - This strategy uses intake throttling to lower AFR. The main injection duration is extended to achieve rich conditions, and retarded a few crank angle degrees to reduce the torque increase associated with excess fueling. Figure 2 shows several oscilloscope trace snapshots in time that illustrate the approach. The traces show injector current versus time.

POST INJECTION – Post injection involves adding an injection event after the main injection event to achieve rich operation. The strategy studied here uses a throttle strategy identical to that of the DEM strategy, and excess fuel injection at select times after the main injection, as shown in Figure 3. Note that the pilot is disabled during the post injection. While the RDS and injector drive units are capable of commanding up to 8 injections per combustion event per cylinder, concerns about injector durability led to the strategy shown in the figure. The timing of the post injection event was studied and 80 degrees after top dead center (ATDC) was selected for detailed catalyst study as a notable change in the HC species was observed beyond about 75 degrees. Figure 4 indicates that the lighter HC species produced in-cylinder increase dramatically

beyond about 75 degrees ATDC. Post injection 80°ATDC (Post80) is compared to DEM in this paper. The minimum indicated AFR at LNT inlet and average fuel use for both strategies are the same throughout all experiments.
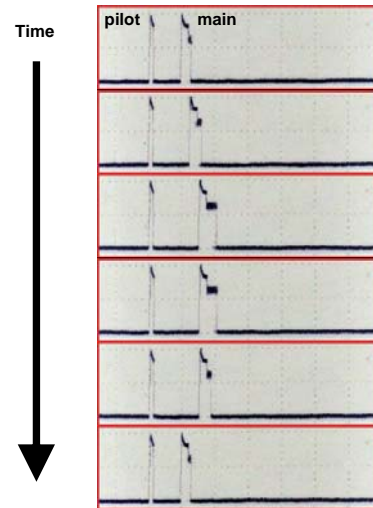

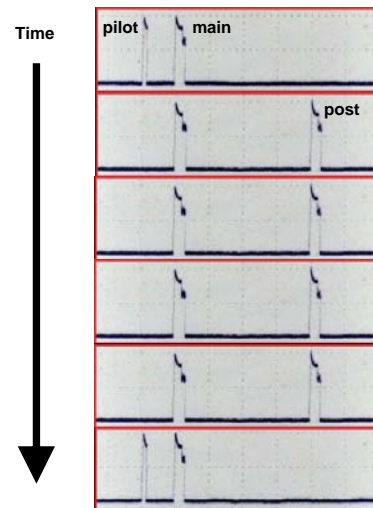**Figure 2. Oscilloscope traces showing DEM fuel injection strategy**

Figure 3. Oscilloscope traces showing Post80 fuel injection strategy

RESULTS

This section will discuss effects of strategy and AFR on exhaust species, effects of fuel chemistry on exhaust species, and finally effects of these species on catalyst performance. Unless otherwise noted, all reported experiments were run at a nominal 1500 rpm, 50 ft-lb

torque setting, at a minimum indicated AFR of 14:1 during regeneration. LNT inlet temperature for this load with a 57 second lean/3 s rich strategy averages about 300°C, with catalyst core temperatures of about 320°C.

- Lighter compounds increase between 70 & 80 deg
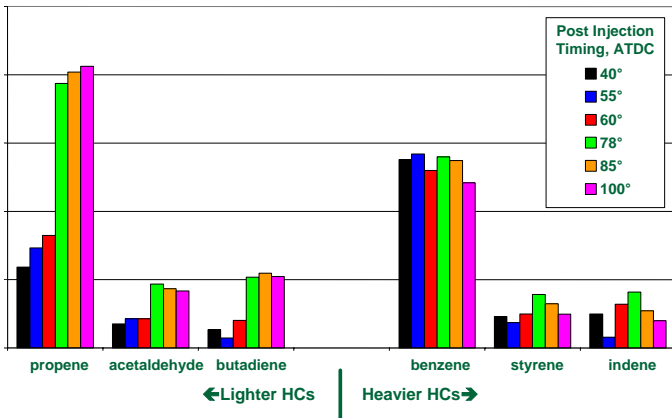- Heavier compounds remain flat throughout timing sweep

Figure 4. Relative concentration of selected HC species for post-timing sweep

REGENERATION STRATEGY EFFECTS ON EXHAUST HCS – Figure 5 shows the peak engine-out hydrogen, CO, and total HC concentrations for the DEM and Post80 strategies at several AFR. Note that all three exhaust components (H_2, CO, HC) decrease with increasing AFR for the DEM strategy while only HC follows this trend for the Post80 strategy. Hydrogen and CO remain relatively flat across the Post80 AFR sweep.
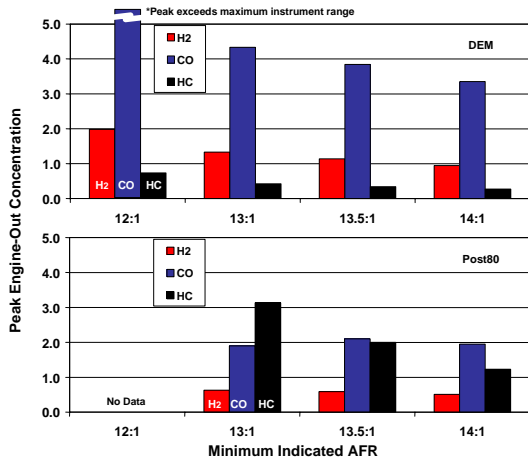

Figure 5. Engine-out H_2, CO, and HC for AFR sweep, DEM and Post80 strategy, BP15 fuel

Figure 6 shows how several light HC species are affected by both AFR and DEM or Post80 strategies, contrasted with normal lean engine-out levels ("EO Lean"). Note that increasing AFR lowers the concentration of these lighter species for the DEM strategy, while the levels are relatively flat for the Post80 strategy. None of these light HC compounds are

present in raw diesel fuel, they have been created by in-cylinder fuel cracking. Considering Figures 5 and 6 together indicates that the increased fuel delivered at richer AFR in the Post80 strategy is not cracking into any of the species presented, and is likely simply adding raw diesel fuel HCs to the exhaust.

With the exception of methane, the light HC species presented in Figure 6 have been shown to be more reactive than other HC species in HC lean NOx catalysis[13-15] and are often used in bench-scale catalyst research.[5,7,13-15] It is important to note that for all FTIR data shown, the average molecular concentration in the sample cell is made up of 57 seconds of lean operation and 3 seconds of rich operation. As the lean engine conditions produce very little exhaust HC, the actual peak levels during regeneration are believed to be on the order of 20 times higher than those shown in the figure.
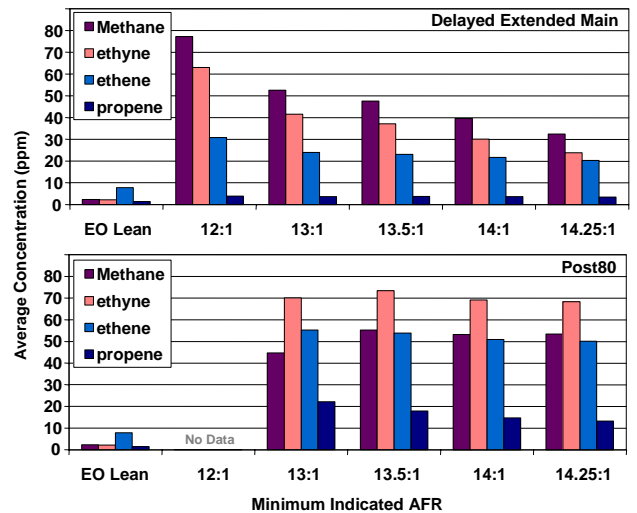

Figure 6. Engine-out light HC species for AFR sweep, DEM and Post80 strategy, BP15 fuel

Hydrocarbon species that were detected but are not reported here include 1,3 butadiene and iso-butylene. These compounds were detected in normal lean engine-out exhaust in the 1-2 ppm range, and higher during rich/lean cycling. Tailpipe (LNT-out) emissions of these compounds were below the detection limit of the instrument. Nitro-organics were also measured using Florisil® solid-phase extraction cartridges. Nitromethane, nitro-phenol, and some unknown nitro-organics were collected in part-per-billion concentrations. Quantification of some of these compounds will be discussed in a subsequent publication.

Figure 7 shows the partial oxidation product acetaldehyde for the same conditions presented in Figures 5 and 6. Note that normal lean exhaust contains considerably more acetaldehyde than the light HCs presented earlier. Also note that the acetaldehyde is

fairly constant for the DEM AFR sweep while decreasing with increasing AFR for the Post80 strategy. Aldehydes are important as they are reactive organic compounds and indicators of extensive fuel cracking and partial oxidation. Note that the engine also produced single-digit ppm-levels of formaldehyde under normal lean conditions and 1-2 orders of magnitude more under rich conditions. While the FTIR can detect and quantify formaldehyde, the slow transient response of this gas through the sample system prohibited reliably reporting these data.

Figure 9 shows the real-time CO, H_2, and HC concentration (engine-out) and mass air flow for the typical DEM strategy. A 30 second window is shown although the strategy was repeated every 60 seconds. The traces shown are the average of 10 consecutive regeneration events. Figure 10 shows similar information for a typical Post80 strategy. These real-time data are shown to highlight the differences in the strategies, and to show the relative temporal response of the various instruments.

Figure 7. Engine-out acetaldehyde emissions for AFR sweep, DEM vs. Post80 strategy, BP15 fuel

Figure 8 shows some selected HC species measured by GCMS (BP15 fuel), showing that the Post80 strategy produces a wider array of compounds than the DEM strategy. Note that of all the compounds in figures 6-8, only tridecane is present in raw diesel fuel. All other species have been created in the combustion process. The Post80 strategy produces a much broader array of HC cracking products.
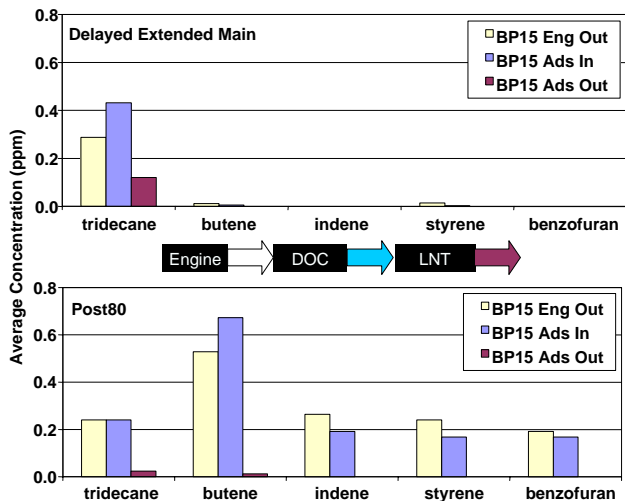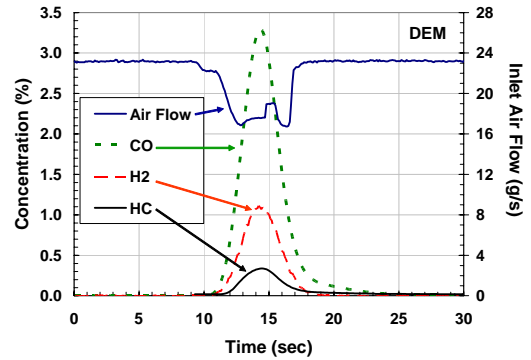
Figure 8. Selected HC emissions for DEM vs. Post80 strategy (14:1 minimum indicated AFR)

Figure 9. Real-time engine-out CO, HC, and H_2 emissions and mass air rate for DEM strategy (average of 10 consecutive regeneration events, 14:1 AFR, BP15 fuel, 3s rich/ 57s lean)
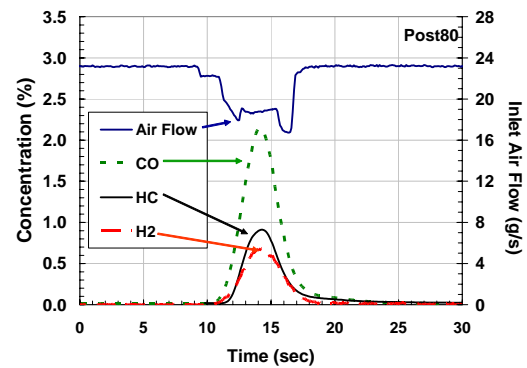
Figure 10. Real-time engine-out CO, HC, and H_2 emissions and mass air rate for Post80 strategy (average of 10 consecutive regeneration events, 14:1 AFR, BP15 fuel, 3s rich/ 57s lean)

Figure 11 compares the peak total HC for the two strategies for 14:1 AFR. (These data are on a C_1 basis. That is, molecular concentrations of species from FTIR or GC/MS analysis have been multiplied by the number of carbon atoms in each particular compound and the

respective FID response factor to roughly equate various species concentrations to total FID response). Note that the bulk of the DEM HCs are accounted for in only a small number of compounds, in particular methane, ethyne, ethene, and propene. For the Post80 strategy the sum of these five selected compounds is 40% higher than with DEM. Moreover, the Post80 strategy contains an additional 5000 ppm of as yet unquantified HC species (C_1 basis) beyond that of DEM. This "other" category in the chart is made up of unburned fuel and heavier cracking products that were detected via GC/MS but not quantified due to the vast number (>100) of species.
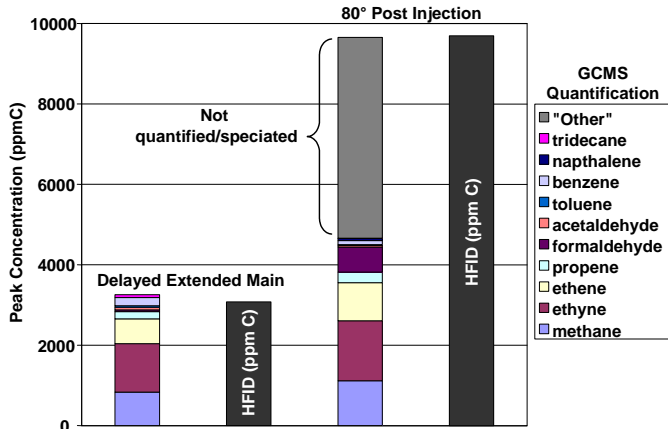

Figure 11. Peak engine-out HC species during regeneration, DEM vs Post80 (14:1 minimum indicated AFR, BP15 fuel)

FUEL CHEMISTRY EFFECTS ON EXHAUST HCS – Ultra-low sulfur fuels were used in this study, with sulfur (S) contents at or below the 15 part per million (ppm) limit set by EPA for 2006. Selected properties of the fuels are shown in Table 1. Chromatograms of the 3 fuels are shown in Figure 12. The peaks labeled C_{10}–C_{25} are normal alkanes. The Diesel Emission Control Sulfur Effects (DECSE) program defined a fuel that has been widely used in diesel emission control research.[16] This fuel is a mix of refinery streams blended to yield properties representative of 1999 industry average fuel in all respects except for sulfur level. The initial batch of DECSE base fuel was around 3 ppm S, the DECSE fuel used in this study was less than 1 ppm S. The BP15 fuel is a much broader refinery cut, and as shown in the chromatogram, contains a much wider array of HC species than the DECSE fuel. BP15 is a one-time refinery run by BP to produce a "2007-like" fuel, with 15 ppm S (refined for the APBF-DEC Program).[17] The ECD-1 is a commercially available fuel that has been approved for use in California. As shown in Table 1 and Figure 12, ECD-1 and BP15 are very similar in their HC species, varying only in aromatics, cetane, and S level.

As expected, the different fuels produce different exhaust hydrocarbon species, shown in Figure 13. This data for the Post80 strategy shows higher engine out benzene with DECSE fuel than with BP15, and also shows complete oxidation (or reformation/utilization) of the benzene across the DOC and LNT. Similarly, Figure 14 shows the same compounds for the DEM strategy. Note again the complete benzene oxidation. Reasons for this higher benzene oxidation are unclear, but we suspect that benzene may be more reactive than other available compounds in the DECSE case, whereas the broader HC mix with BP15 yields a host of more preferred species, leaving the benzene unutilized. This hypothesis is partially supported by Figure 15, which shows tridecane plus several cracking products for these two fuels for the Post80 strategy. Note the higher concentrations of all of these compounds in the BP15 case.

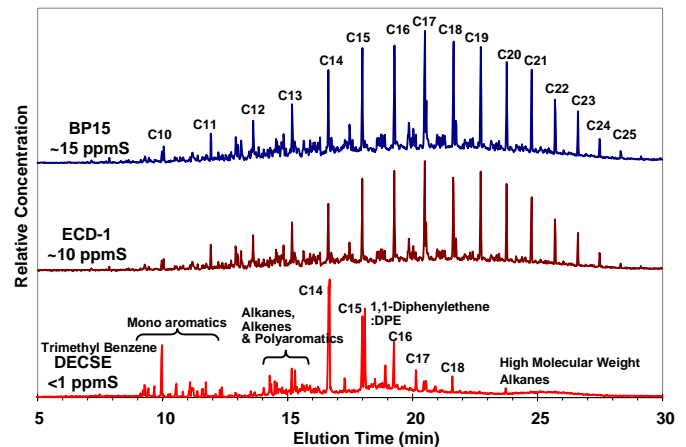| Table 1. Selected fuel Properties			
Fuel/ Property	**BP15**	**ECD-1**	**DECSE**
Cetane No.	50	54	44
Aromatics, % ASTM D1319	29	24	27
Sulfur, ppm ASTM D5453 (as tested)	14	9	<1
H/C ratio	1.86	1.87	1.84

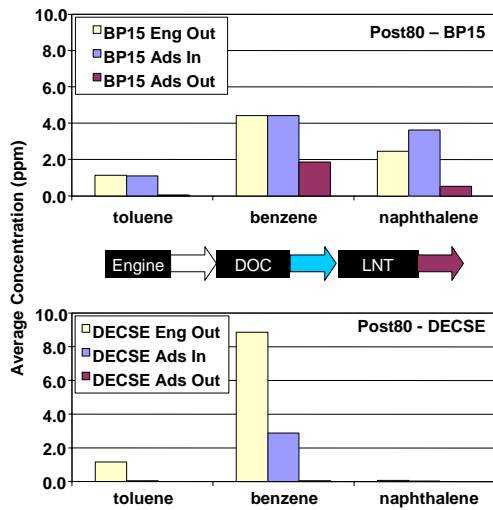**Figure 12. GCMS chromatograms showing raw fuel HC species**

Figure 13. Selected aromatic HCs, BP15 vs. DECSE fuel, Post80 strategy (14:1 minimum indicated AFR)
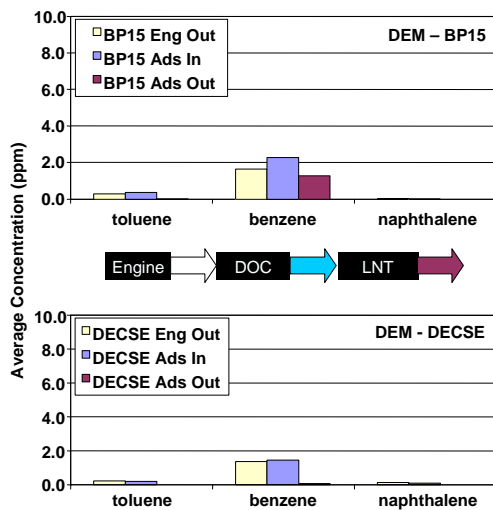

Figure 14. Selected aromatic HCs, BP15 vs. DECSE fuel, DEM strategy (14:1 minimum indicated AFR)
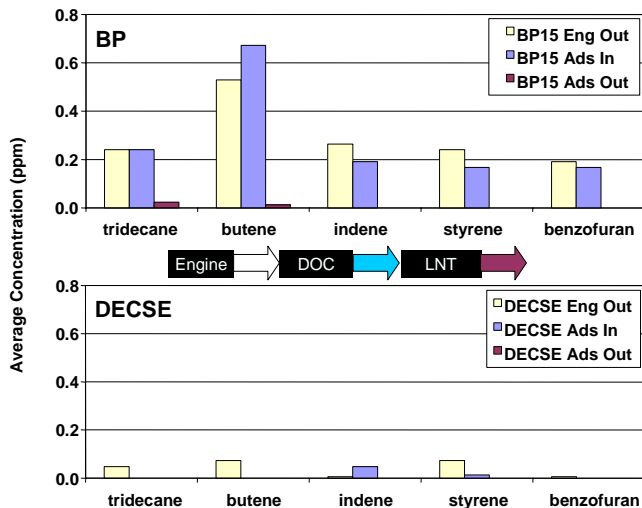

Figure 15. Selected HC species for BP15 vs. DECSE fuel, Post80 strategy

REGENERATION STRATEGY EFFECTS ON PM EMISSIONS – Figure 16 shows the dramatic difference in PM produced by these two strategies for two AFR. Both TEOM mass rate and Celesco opacity are shown. The two measurements are offset in time for clarity. The DEM strategy causes nearly an order of magnitude increase in PM over the normal lean operation, and as expected, the richer AFR (13:1) produces more PM (than 14:1). The Post80 strategy produces an almost imperceptible increase in PM for either AFR.
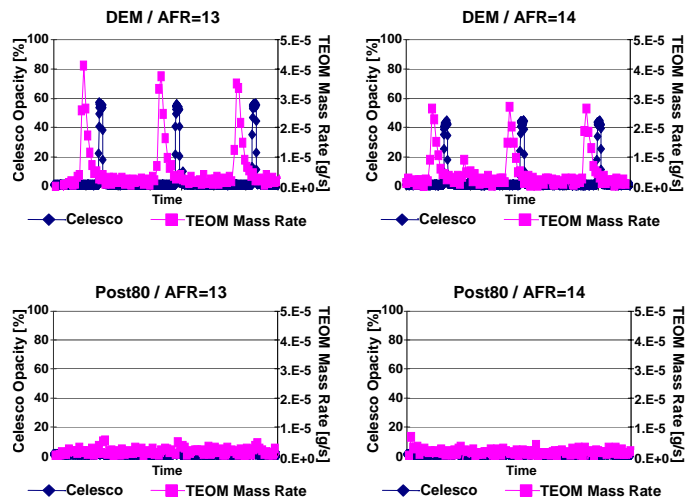

Figure 16. PM emissions for DEM and Post80 strategies at two AFR with BP15 fuel (Celesco and TEOM traces offset in time)

SUMMARY OF FUEL AND STRATEGY EFFECTS – Figures 17a and 17b 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 17c. 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 17d 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.[7]
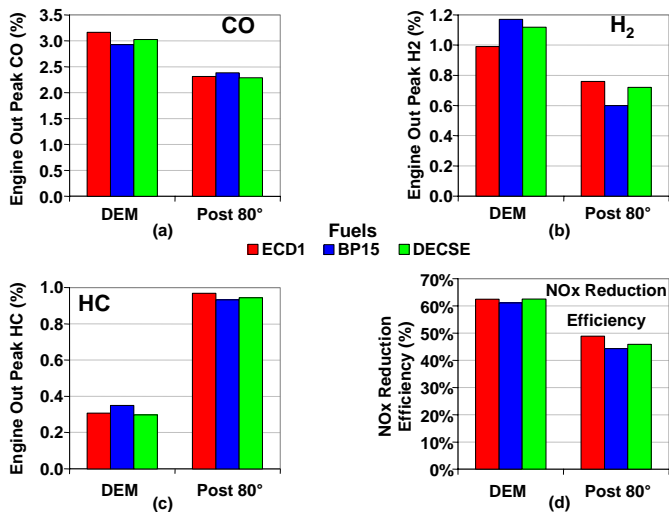
Figure 17. Summary of fuel and strategy effects on CO, H₂, and HC emissions and average NOx reduction

Figure 18. In-situ measurements through the catalyst system for DEM strategy, BP15 fuel

Figure 19. In-situ measurements through the catalyst system for Post80 strategy, BP15 fuel

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 18 and 19 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 18) 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.
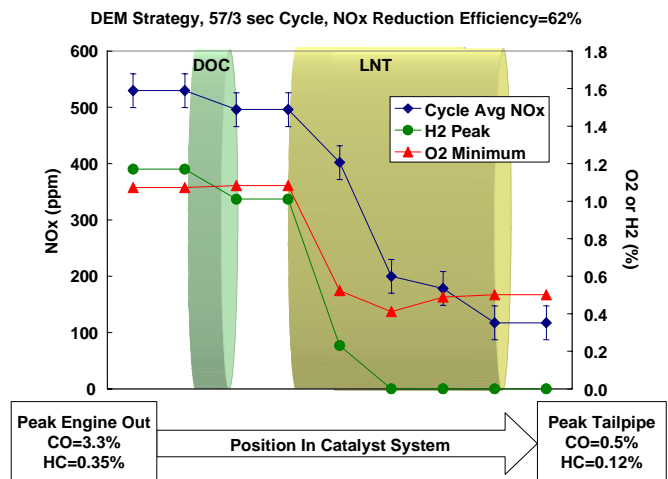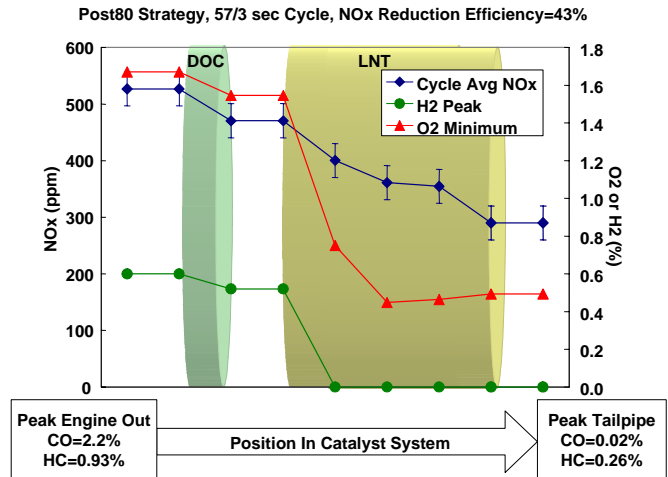
The Post80 strategy data (Figure 19) is similar to the DEM strategy data in terms of O_2 depletion; however, a higher engine out O_2 level (1.7%) is indicated. Hydrogen depletion occurs earlier in the Post80 case with H_2 fully consumed by the ¼ length position. The lower available LNT-in H_2 concentration with the Post80 strategy corresponds with lower NOx reduction efficiency shown in Figure 17d. 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.

During regeneration, reductants perform generally three functions: 1) depletion of oxygen (in exhaust or stored on catalysts), 2) chemical release of NOx from storage sites, and 3) chemical reduction of NOx. For the case of in-cylinder regeneration presented here, the bulk oxygen depletion of the exhaust occurs during in-cylinder combustion processes; however, significant levels of engine-out reductants must be consumed to catalytically complete the depletion of the remaining ~1-2% oxygen in the exhaust. Table 2 shows an inventory of the quantity of reductants typically produced during the DEM and Post80 strategies relative to the reductant consuming processes of O_2 depletion and NOx reduction (release and reduction combined). Depletion of stored oxygen or chemical reduction of catalyst materials have been ignored in this simple analysis. By integrating real-time gas concentrations for the regeneration cycle, total moles of each constituent have been estimated. "Total reductants" is defined as the sum of CO, H_2, and HC, where HC is expressed in moles of equivalent reduction to CO (2.925 times the $CH_{1.85}$ concentration, as measured by the FID, based on 2 moles of CO-equivalent reductant required to consume 1 mole of O_2). "Remaining reductants" represents the fraction of reductants remaining for NOx reduction purposes after the O_2 is depleted from the exhaust; here the amount of O_2 required to be depleted is based on SpaciMS measurement of engine-out O_2. Finally, the molar ratio of the remaining reductants available to the NOx reduced is 7.6 and 13.5, respectively, for the DEM and Post80 strategies. Thus, the overall efficiency of the DEM reductant species pool (more CO and H_2, less HC) is more efficient than the Post80 reductant species pool (less CO and H_2, more HC). It is important to note that lower HC utilization results in higher tailpipe HC emissions as shown in Figures 18 and 19.

Table 2. Reductant, Oxygen, and NOx Inventory (per regeneration)		
(milli-moles)	DEM	Post80
CO	80	53
H_2	27	18
HC (as $CH_{1.85}$)	20	37
Total Reductants (CO-equivalent)	165	180
Reductant needed to consume Engine-out O_2 During Regeneration (CO-equivalent)	39.6	65
Remaining Reductants (after O_2 depletion, CO-equivalent)	125	115
NOx Reduced	16.4	8.5
Available Reductants:NOx Reduced	7.6	13.5

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.

FUTURE WORK

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.

ACKNOWLEDGMENTS

REFERENCES

1. Jim Parks, Aaron Watson, Greg Campbell, and Bill Epling, "Durability of NOx Absorbers: Effects of Repetitive Sulfur Loading and Desulfation", *Society of Automotive Engineers Technical Series* 2002-01-2880 (2002).

2. John H. Stang, David E. Koeberlein, and Michael J. Ruth, "Cummins Light Truck Diesel Engine Progress Report", *Society of Automotive Engineers Technical Series* 2001-01-2065 (2001).

3. Yoshinori Takahashi, Yoshinaka Takeda, Nobuhiro Kondo, and Minehiro Murata, "Development of NOx Trap System for Commercial Vehicle – NOx Regeneration by Diesel Fuel and Phenomenon of Sulfur Poisoning and Regeneration", *Society of Automotive Engineers Technical Series* 2004-01-0580 (2004).

4. Cynthia C. Webb, Phillip A. Weber, and Matthew Thornton, "Achieving Tier 2 Bin 5 Emission Levels with a Medium Duty Diesel Pick-Up and a NOx Adsorber, Diesel Particulate Filter Emissions System—NOx Adsorber Management," *Society of Automotive Engineers Technical Series* 2004-01-0585 (2004).

5. Philip G. Blakeman, Paul J. Andersen, Hai-Ying Chen, J. David Jonsson, Paul R. Phillips, and Martyn V. Twigg, "Performance of NOx Adsorber Emissions Control Systems for Diesel Engines", *Society of Automotive Engineers Technical Series* 2003-01-0045 (2003).

6. C. Scott Sluder and Brian H. West, "Effects of Regeneration Conditions on NOx Adsorber Performance", *Society of Automotive Engineers Technical Series* 2002-01-2876 (2002).

7. Stephen Poulston and Raj R. Rajaram, "Regeneration of NOx Trap Catalysts," *Catalysis Today,* 81 (2003) 603-610.

8. Yougen Kong, Sam Crane, Palak Patel, and Bill Taylor, "NOx Trap Regeneration with an On-Board Hydrogen Generation Device", *Society of Automotive Engineers Technical Series* 2004-01-0582 (2004).

9. Dean Tomazic, Marek M. Tatur, and Matthew J. Thornton, "Development of a Diesel Passenger Car Meeting Tier 2 Emissions Legislation", *Society of Automotive Engineers Technical Series* 2004-01-0581 (2004).

10. Koichiro Nakatani, Shinya Hirota, Shinichi Takeshima, Kazuhiro Itoh, and Toshiaki Tanaka, "Simultaneous PM and NOx Reduction System for Diesel Engines", *Society of Automotive Engineers Technical Series* 2002-01-0957 (2002).

11. Shawn D. Whitacre, Brad J. Adelman, Mike May, and Joseph G. McManus, "Systems Approach to Meeting EPA 2010 Heavy-Duty Emission Standards Using a NOx Adsorber Catalyst and Diesel Particle Filter on a 15L Engine", *Society of Automotive Engineers Technical Series* 2004-01-0587 (2004).

12. Partridge, W.P., Storey, J.M.E., Lewis, S.A., Smithwick, R.W., DeVault, G.L., Cunningham, M.J., Currier, N.W. and Yonushonis, T.M. (2000). "Time-Resolved Measurements of Emission Transients By Mass Spectrometry," *SAE Transactions - Journal of Fuels & Lubricants* **109**, p. 2992, paper no. 2000-01-2952.

13. John W. Hoard, Alexander Panov, "Products and Intermediates in Plasma-Catalyst Treatment of Simulated Diesel Exhaust," *Society of Automotive Engineers Technical Series* 2001-01-3512 (2001).

14. Steven J. Schmieg, Byong K. Cho, and Se H. Oh, "Hydrocarbon Reactivity in a Plasma-Catalyst System: Thermal Versus Plasma-Assisted Lean NOx Reduction," *Society of Automotive Engineers Technical Series* 2001-01-3565 (2001).

15. Yisen Cheng, John V. Cavataio, William D. Belanger, John W. Hoard, and Robert H. Hammerle, "Factors Affecting Diesel LNT Durability in Lab Reactor Studies," *Society of Automotive Engineers Technical Series* 2004-01-0156 (2004).

16. Diesel Emission Control – Sulfur Effects (DECSE) Program: NOx Adsorber Catalysts; Phase II Summary Report; U.S. Department of Energy, Office of Transportation Technologies, U.S. Government Printing Office: Washington, DC, October 2000.

17. Ralph McGill, Magdi K. Khair, and Christopher A. Sharp, "Demonstration of Potential for Selective Catalytic Reduction and Diesel Particulate Filters," Proceedings of the 9th Diesel Engine Emissions Reduction Conference, 2003, DOE Office of Scientific and Technical Information.

DEFINITIONS, ACRONYMS, ABBREVIATIONS

ASTM: American Society for Testing and Materials

ATDC: After Top Dead Center

BP15: Diesel fuel from BP with 15 ppm sulfur, refined for the Advanced Petroleum-Based Fuels – Diesel Emission Control Program

CLEERS: Cross-Cut Lean Exhaust Emissions Reduction Simulation, an industry-government R&D focus project of the Diesel Cross-Cut Team with the objective of promoting development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.

CO: Carbon monoxide

CO_2: Carbon dioxide

DECSE: Diesel Emission Control Sulfur Effects, an industry government program c. 1999 that specified a near-zero sulfur diesel fuel for research purposes

DEM: Delayed extended main, a regeneration strategy in which the main injection event is broadened to effect rich operation and delayed to minimize torque fluctuation

ECD-1: Emission-Control Diesel, a commercially-available Arco/BP diesel fuel

HC: Hydrocarbons

HCLD: Heated chemiluminescent detector (for NOx)

HFID: Heated Flame Ionization Detector (for HC)

MECA: Manufacturers of Emission Controls Association

NDIR: Non-dispersive infra-red, detector for CO and CO_2

NOx: Nitrogen oxides (NO and NO_2)

ORNL: Oak Ridge National Laboratory

Post80: Regeneration strategy using post injection at 80° ATDC

APPENDIX A

The catalysts used in this study were provided by a member company of the Manufacturers of Emission Control Association (MECA). Available catalyst information is shown in table A-1.

Table A-1. Catalyst Specifications		
Catalyst	DOC	LNT
Cells/in^2	400	400
(Cells/cm^2)	(62)	(62)
Diameter x length, inches	4.16x3	5.66x6
(mm)	(106x76)	(144x152)
Volume, in^3	41	151
(liter)	(0.67)	(2.5)
Precious metal,g/ft^3	70	120
(g/liter)	(2.5)	(4.2)
Formulation	Pt	Ba-based Pt/Pd/Rh
Space Velocity (1/hr) Normal lean/ Regeneration	97,000/ 77,000	26,000/ 21,000