Ultra Clean Transportation Fuels Initiative

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Final Project Report- Discovery of Novel NOx Catalysts for CIDI Applications by High-throughput Methods

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Public Abstract

DOE project DE-PS26-00NT40758 has developed very active, lean exhaust, NOx reduction catalysts that have been tested on the discovery system, laboratory reactors and engine dynamometer systems. The goal of this project is the development of effective, affordable NOx reduction catalysts for lean combustion engines in the US light duty vehicle market which can meet Tier II emission standards with hydrocarbons based reductants for reducing NOx. General Motors (prime contractor) along with subcontractors BASF (Engelhard) (a catalytic converter developer) and ACCELRYS (an informatics supplier) carried out this project which began in August of 2002. BASF (Engelhard) has run over 16,000 tests of 6100 possible catalytic materials on a high throughput discovery system suitable for automotive catalytic materials. Accelrys developed a new database informatics system which allowed material tracking and data mining. A program catalyst was identified and evaluated at all levels of the program. Dynamometer evaluations of the program catalyst both with and without additives show 92% NOx conversions on the HWFET, 76% on the US06, 60% on the cold FTP and 65% on the Set 13 heavy duty test using diesel fuel. Conversions of over 92% on the heavy duty FTP using ethanol as a second fluid reductant have been measured. These can be competitive with both of the alternative lean NOx reduction technologies presently in the market. Conversions of about 80% were measured on the EUDC for lean gasoline applications without using active dosing to adjust the C:N ratio for optimum NOx reduction at all points in the certification cycle. A feasibility analysis has been completed and demonstrates the advantages and disadvantages of the technology using these materials compared with other potential technologies. The teaming agreements among the partners contain no obstacles to commercialization of new technologies to any potential catalyst customers.

Introduction

Using high-throughput techniques, this program has identified NOx reduction catalysts with conversion rates over 90% that use diesel fuel as well as alternative fuels as the reductant. Previous catalyst development was characterized by sequential, iterative examination of candidate catalyst materials, which can be painstaking and slow. High-throughput chemistry was used in this catalyst discovery because of advances in automation, robotics, analysis and miniaturization which allow rapid catalyst assays.

Automotive catalysis is a very challenging application for high-throughput methods because of the large number of species in the feed gas, large range of operating conditions, catalyst degradation and complex functional behavior of the NOx catalysts. Our approach integrated three levels of materials evaluation: high-throughput testing, laboratory synthetic exhaust testing, and diesel and lean gasoline dynamometer testing to allow us to cover the discovery phase space in a reasonable time. The systematic multiscale approach allowed new materials evaluation at rates as high as 200 materials per week. This program is unique in combining high-throughput materials discovery and traditional gram sample reactor testing in a concurrent, parallel method to accelerate the development of new materials for NOx reduction in diesel exhaust. The development approach allows requirements necessary for automotive applications to direct the three levels of testing of the catalyst discovery process where materials flow up through increasingly realistic and detailed testing to identify commercially viable catalysts. First pass screening of materials at the high-throughput level was limited to coarse scales of the variables. These scales were chosen to minimize the possibility that active catalysts will be missed. Data mining identified the materials and/or material families that show NOx reduction activity which would then be comprehensively evaluated in the laboratory reactor with synthetic exhaust gases. Results of synthetic exhaust tests were used to refine the high-throughput evaluation of these material families so that further high-throughput screening could identify the optimum NOx reduction material in that family of materials. Optimized materials were then transferred to the GM reactor in monolith core form to evaluate their performance in a realistic operating environment and with proposed alternative fuels.

In the final phase of the program materials for possible commercial development were selected. Conversion efficiencies for these materials were evaluated on a dynamometer for the HWFET, US06, EUDC, SET 13 and the heavy duty FTP cycle. An engine control strategy for diesel applications has been identified. Fuel economy penalties were estimated for various fuels and system architectures.

Approach

This catalyst discovery team included GM (world's largest automotive manufacturer, CIDI engine manufacturer and emission control system integrator), BASF (formerly Engelhard) (major company for the supply of automotive catalysts, chemical catalysts and refinery catalysts and Accelrys (developer of advanced discovery informatics tools). This program was formulated to allow CIDI engines to meet Tier II emission standards (see table 1) with standard and/or ultra-clean fuels without significant use of precious metals.

Table 1. Anticipated future U.S. emission standards (gm/mi). Bin 5 abstracted from the compilation of Emissions Standards Passenger Cars WorldWide, January 2000, Delphi Energy and Engine Management Systems.

HC	NOx	CO	PM
0.09	0.07	4.2	0.01

The greater fuel economy of CIDI and GDI engines makes them a definite benefit for the US consumer.

Automotive Catalyst Development Program

Using high-throughput synthesis and evaluation methods for materials screening, the approach mapped out NOx reduction behavior in material families of interest and explored a wide range of materials parameters

High-throughput materials discovery has faced several technical challenges. Key among the difficulties is:

- rapid synthesis of representative materials on a small-scale,
- implementation of relevant high-throughput testing,
- high-throughput materials characterization,
- informatics to systemize the large volume of data
- efficient conduction of a discovery campaign,
- scale-up requirements in moving from high-throughput studies to full size catalyst brick testing.

The BASF (Engelhard) screening equipment has been specifically designed for evaluation of automotive catalysts. It:

- incorporates gas flows and space velocities necessary for automotive catalytic converters
- is compatible with “washcoated” catalysts
- is designed for automotive operating temperatures (up to 650-700 °C)
- incorporates water vapor in the feed stream
- is designed to include hydrocarbon injection and volatilization

This system has been benchmarked against BASF (Engelhard) standard synthetic gas reactors and correlates well.

This system detects reactants and products so that each library element is examined as a function of test conditions (e.g., temperature, hydrocarbons, and NOx).

Testing with synthetic gases at GM has been carefully designed to yield trends, which represent catalyst response under vehicle conditions and was used to test scaled up monolith cores. This synthetic exhaust reactor at GM was designed to simulate a wide variety of CIDI exhaust compositions anticipated in present or advanced diesel engines. These results were used as feedback to refine the high-throughput synthesis/rapid screening process. The GM reactor is used to investigate in detail the effects of exhaust gas composition, the temperature dependence, adsorption versus reduction, aging due to exhaust components and the dependence of the catalytic activity on space velocity. The hydrocarbon component has been varied in the synthetic exhaust reactor to determine the effect of alternative fuels components and the correct level of hydrocarbon for reduction.

Data Management and Informatics

The data that has been generated at the various laboratories participating in the experimental program was uploaded over the Internet (ANX) lines to a central (GM) database server where it was accessible to all researchers. A unique database was developed for this project so that the samples could be tracked and the synthesis method and testing results could be directly correlated. Consequently, the system tracks samples from the time that they are synthesized through the screening measurements, materials characterization and on to final storage or disposal. A GUI has been developed at Accelrys handles this wide range of data to access the database.

Project Plan

The technical effort on the project was organized into three phases of activity:

- tool development (adaptation of existing subsystems) ;
- catalyst discovery program (catalytic materials discovery and evaluation); and,
- a feasibility analysis (evaluation of the new catalytic materials for commercial feasibility).

Tool Development

During the first 6 months, the team adapted and developed the tools necessary for high throughput discovery of new NOx reduction catalysts. BASF (Engelhard) catalysts were mounted on this unit and tested for several catalytic reactions relevant to BASF (Engelhard) technology. Similar studies were carried out, one catalyst at a time, on a traditional reactor. The results obtained by these two methods agreed quite well. The two testing systems were validated against each other using a benchmark catalyst that reflected prior HC-SCR NOx reduction performance. Database design and user interfaces were extended and modified to accommodate the high-throughput assays and information from the synthetic exhaust tests. The automotive catalyst data management system was implemented and hosted on a dedicated server at GM Powertrain which ensured data integrity and security.

NOx Reduction Catalyst Discovery

The NOx reduction catalyst discovery program was integrated through three scales of synthesis and testing:

- first search for active catalytic materials (see figure 1 for an example of a high-throughput scan);
- data mining of the discovery results to select material compositions to upscale;
- characterization of promising materials by detailed experimental evaluation of one of the promising catalytic materials in the GM reactor (see figure 2 for an example of temperature scans of upscaled catalytic materials) ;
- second discovery search within a structural family for the optimum catalytic material;
- GM reactor evaluation of the best catalytic material of the family;
- evaluation of the effect of alternative fuels on the catalytic material on the GM reactor
- evaluation of the catalytic material in diesel or lean gasoline exhaust;

Evaluation of reductant identity and effectiveness, high temperature aging, sulfur poisoning, phosphorous poisoning, hydrocarbon poison and a refinement of the dependence of the activity on oxygen concentration is part of the GM reactor evaluation of downselected catalyst materials.

Several promising catalyst formulations have been tested in lean exhaust using either diesel engines or lean gasoline engines mounted on engine dynamometers.

Feasibility Analysis

The feasibility analysis (see appendix) has evaluated several the NOx reduction catalyst prototypes for engineering applicability. This includes conversion efficiencies for the heavy duty FTP cycle, the HWFEC, SET 13, EUDC (for lean gasoline) and the US06. A candidate control strategy for diesel applications has been developed.

Deliverables

Project deliverables to the Government are reports. The project team provided? all reports in accordance with requirements specified in the solicitation (Table 2).

Table 2. Reports to be delivered to the government.

Report Type	Report	Frequency
Project Management	Federal Assistance Program Status Report Financial Status Report Federal Cash Transactions Report	Quarterly Quarterly Quarterly
Technical	Technical Progress Report	Quarterly

	Final Report	90 days after project completion
Environmental	Hazardous Substance Report Hazardous Waste Report	At onset At project end
Property	Property in Contractor Custody High Risk Property Report of Termination Inventory	Yearly Yearly At project end

Project team members

BASF (Engelhard)

BASF (Engelhard) is an industry leader in emission control from mobile sources. Following the passage of the Clean Air Act, BASF supplied oxidation catalysts to the automotive industry and was a pioneer in commercialization of the first three way automotive catalysts. Today BASF is a leading supplier of emission control catalysts for gasoline and diesel vehicles. BASF has state of the art facilities for emissions control R&D, performance testing and manufacturing as well as the business and marketing skills to rapidly commercialize innovations that may result from this program.

General Motors (GM)

GM's Advanced Powertrain Emissions Control directorate and GM's R & D and Planning Center coordinated this project. Advanced Powertrain Emissions Control has the responsibility to develop and implement aftertreatment systems for planned new powertrain and the R & D Center is the central research and development organization for General Motors Corporation. General Motors Corporation was first registered in 1908. General Motors is the largest automotive company in the world. It designs, manufactures, assembles and sells automobiles and trucks including automotive systems and components, such as engine and engine management systems and emission control systems.

Accelrys (Molecular Simulations Incorporated)

Molecular Simulations Inc. (ACCELRYS) is a scientific software company. ACCELRYS has been producing quality software for almost 20 years in support of an international customer base engaged in pharmaceutical and materials research. These software applications include database systems for drug discovery, informatics and workflow software systems and services.

Results

One primary downselected material (program catalyst) at different loadings and with different additives was has been evaluated at all three levels for a wide range of properties crucial to application to automotive NOx reduction.

Range of materials explored

Over 16,000 tests of 6100 materials were achieved on the high throughput system. These included:

- single element materials
- binary element materials
- ternary element materials
- different processing and synthesis techniques
- different washcoats

If 60 possible elements were considered as potential catalytic materials, then would be over 3500 binary combinations, more than 200,000 ternary combinations and well over 11,000,000 quaternary combinations. The number of combinations goes up much faster if washcoat options and processing variations are considered. Consequently even with high throughput processing it was not possible to consider all combinations. The approach selected was to concentrate on elemental and binary washcoat mixtures. In the case of the binary mixtures, they were somewhat arbitrarily selected. When a sample shows activity which is at least 80% of the benchmark catalyst, that “hit” is confirmed by a scale up and testing in the GM core reactor. If the “hit” is confirmed, then binary combinations of that element were evaluated. With any given “hit”, a range of compositions around the hit are evaluated in order to refine the optimum composition and the best composition is scaled up to be evaluated in the GM core reactor. Some ternary elemental compositions were evaluated.

Fuels evaluation

N-octane was the reductant initially used for the discovery system evaluation. N-octane, propylene, ethanol and iso-octane were the reductants initially evaluated in the GM core reactor. It became apparent during the program that fuel mixtures behaved differently as reductants compared with the single component fuels. Consequently sim-diesel and sim-gasoline blends were introduced to more effectively define the fuel effects. These mixtures are:

sim-diesel
67 vol.% n-dodecane
33 vol.% m-xylene

sim-diesel #2
67 vol.% n-dodecane
23 vol.% m-xylene
10 vol.% naphthalene

sim-gasoline
33 vol% m-xylene
45 vol.% iso-octane

12 vol.% 1-octene
10 vol% n-octane

Sim-diesel and sim gasoline were also used in the discovery system. Sim-diesel #2 was used only infrequently, it basically gave the same result as the two component sim-diesel, but did include the effect of multi-ring aromatics. In addition to simulate ethanol blending of fuels ethanol was added to sim-diesel as volume percents.

Example of a discovery experiment

A discovery experiment includes experimental samples and one or more samples of the project reference. All samples were aged by hydrothermally treating the sample for 16 h in a gas flow of 10% steam in air at 650^{o}C. Since reactivity information from the discovery reactors is not as precise as a standard lab reactor a reference sample is used as a benchmark. In addition, measured values from the GM reactor can be used to provide values (eg; absolute NOx reduction activity, space velocity, etc.) for the discovery runs. Figure 1 shows the activity sweeps as a function of temperature for a range of samples in a single discovery run. The bright yellow curve is the reference material. Consequently any sample with a conversion above that curve could be considered a “hit”. As can be readily seen, there are quite a number of materials which exceed the reference sample in this run. This particular discovery system has the significant property of providing a full temperature scan for the materials, consequently activity curves which include light-off temperatures can be extracted from this experiment. As noted earlier, over 16,000 tests were run and evaluated using this technology.

Example of a GM reactor run

The complementary GM reactor runs are shown in figure 2 where the red curve is the equivalent curve to the yellow reference curve in figure 1. As can be seen, the reference conversion corresponds to an approximately 40% NOx conversion at a space velocity of 50,000 hr$^{-1.}$ Each one of the materials shown in this plot came from one of the higher conversion runs in a discovery run such as shown in figure 1. It is clear that the translation from a high throughput small sample synthesis to a scaled up core level synthesis does not always give a conversion on the GM reactor greater than the reference material; however, it is also clear that this approach does show some very significant HC-SCR conversion on the GM reactor. In this evaluation set, there are several materials which give NOx conversions in the 70% range for these conditions and one that gives almost a 90% NOx conversion.

Space velocity

The effect of space velocity on the program catalyst is shown in figure 3. This catalyst behaves in the classical manner in that the activity improves with lower space velocity. Lower space velocity physically corresponds to longer contact times with the catalytic material in the coated monolith. The conversions at lower space velocities(~12,000 hr^{-1})

are approaching 100% conversions which are similar to the conversions that can be attained by TWC technologies.

Thermal aging effects

Thermal aging can be categorized into two effects. One being pure lean thermal aging; the other being the effect of lean-rich cycling. The first aging cycle is characteristic of the aging that would occur for a purely lean application which would most likely occur for diesel engine aftertreatment requirements. The second with lean rich cycling is the situation that might occur for a lean burn gasoline application. Figure 4 shows the effect of both types of aging for the program catalyst in a laboratory environment. The loss in activity for 'steam" aging is not significant until over 750 °C. However the effect on the catalyst of redox aging is appreciable above 650 °C. To this point here has been no effort in this program to improve the catalyst durability.

Carbon Poisoning

Long term exposure of the catalyst to the hydrocarbon reductant at lower operating temperatures tends to cause a loss in activity. In figure 5, the NOx concentration is plotted versus time in a full size catalyst with external dosing of hydrocarbon into the diesel exhaust stream at a constant speed operation. In this particular case, the dosing is occurring at an exhaust temperature of slightly more than 300 °C, there is a monotonic loss in NOx reduction activity over about 60 minutes from approximately 76 % conversion down to approximately 12 % conversion. However, discontinuing dosing causes a return of essentially all the activity even at this relatively low exhaust temperature. Carbon poisoning regeneration strategies were identified. Additional evaluation of NOx reduction in diesel exhaust at higher temperatures shows that there is little carbon poisoning and that regeneration happens quickly at temperatures above 400 °C. The discovery system was used to develop materials that are resistant to carbon poisoning.

Sulfur effects

Sulfur does cause a loss of activity for the program catalyst. Figure 6 shows a monotonic loss of NOx reduction activity with SO_2 exposure. It goes from a 96% conversion to approximately 75% conversion over about a 50 minute exposure with a gas phase concentration of SO_2 which far exceeds the expected exposures from today's low sulfur fuels. Figure 7 shows that multiple sulfur regenerations do cause some long term loss of activity; however, the catalyst does retain high activity. Some discovery work was invested into improving the program catalyst resistant to sulfur poisoning.

Phosphorous effects

Phosphorous was not found to have a significant poisoning effect on this catalyst. A surface analysis of the catalyst after exposure to phosphorous shows clear evidence of surface phosphorous deposition; however, the phosphorous deposition amounts required to cause significant loss of activity are larger than would be expected for the 120,000 mile required lifetime of a light duty personal vehicle aftertreatment system (see figure 8). No effort was judged needed to identify a phosphorous resistant washcoat.

Gasoline discovery/reactor

Preliminary evaluation of the program catalyst for lean gasoline applications showed encouraging results when tested with passive dosing (i.e.; using the engine out hydrocarbons as the reductant). The application architectures for lean gasoline aftertreatment for lean engines are expected to be different than diesel applications because the lean gasoline engines spend an appreciable portion of the drive cycle in stoichiometric operation, the general hydrocarbon identity of the reductant is different (either engine out hydrocarbons or fuel injected hydrocarbons) and the operating engine out temperature for lean gasoline is characteristically higher than that of the diesel vehicle operating cycle. A reactor evaluation (figure 9) of the NOx reduction activity curves shows that this material can get equivalent conversions with simulated gasoline as the reductant; however, it's effectiveness occurs at higher exhaust gas temperatures.

Diesel Engine testing

The diesel aftertreatment architecture for engine testing (figure 10) has a diesel oxidation catalyst (DOC) as the first device in the exhaust stream. This configuration has the engine followed by a diesel oxidation catalyst, a hydrocarbon injector, a mixer to homogenize the injected fuel, the HC-SCR catalyst and a clean-up DOC. The other notations in the figure are various emission detection instruments. One of the reasons for the inclusion of the DOC just after the engine is to remove all engine out hydrocarbons which then allows for precise metering and control of the identity of the hydrocarbons into the HC-SCR catalyst using the HC-injection system. This architecture carries through almost all of the diesel engine studies., although one set of dynamometer experiments did use an architecture that did not include the upstream DOC. These engine studies are all accomplished with full size bricks, hand-coated by BASF.

The first set of dynamometer runs clearly shows engine conditions under which NOx conversions exceed 90% (figure 11). Early tests of the NOx emissions on the HWFET (figure 12) show repeatable NOx conversions of 92%.

Gasoline Engine testing

In the case of the majority of the lean gasoline studies, no DOC is included upstream of the HC-SCR catalyst and no HC injector system was in use. A few tests did use a configuration similar the diesel configuration (figure 10) where the DOC is replaced by a three-way catalyst (TWC). Consequently, the only hydrocarbons available for NOx reduction were those found in the normal engine exhaust. It was identified early on in the program that the optimum C1:N ratio for NOx reduction is approximately 8. By relying on only engine emitted hydrocarbons this ratio often fell below 8 and thereby limiting the NOx conversion. Testing of the lean gasoline engine was focused initially on steady state conditions. Six engine operating points were selected to test this aftertreatment technology (table 3).

Table 3. Lean gasoline engine operating points used for HC-SCR aftertreatment evaluation.

Test Point	RPM	Load	Comments
1	1500	1.0	Low NOx, low mass flow rate, low temp
2	1500	2.0	Low+ NOx, low mass flow rate, prime temp
3	1200	3.0	Mid NOx, low mass flow rate, prime temp
4	2500	4.0	High NOx, high mass flow rate, high temp
5	2000	2.0	Mid NOx, mid mass flow rate, prime temp
6	2800	2.0	Mid NOx, high mass flow rate, hi temp tail

Test point 5 was selected as the base point to which the engine would return between evaluating the other steady state points. All the NOx conversions from testing these steady state points exceeded 70% and three of these points exceeded 90% NOx conversions. This is an indication that this technology could be used in a lean burn gasoline application.

Evaluation of this material in lean gasoline exhaust (figure 11) shows NOx conversions of over 90% at some lean gasoline operating conditions. If a fuel injection scheme is used to add hydrocarbons in advance of the catalyst, then the reductant concentration can be kept in the optimum operation temperature range. However, if the catalyst is dependent on the engine out hydrocarbon concentration for NOx reduction, then that ratio can fall quite low and there is a serious loss of NOx reduction. As can be seen from the figure 13, the low NOx reduction levels occur at very low C;N ratios which is consistent with an insufficient exhaust hydrocarbon concentration to keep the NOx reduction activity at 90% levels. The discovery approach identified two additional catalytic materials that were more active NOx reduction materials and more resistant to carbon poisoning for use with gasoline as the reductant.

In addition, E85 and straight ethanol were evaluated and also found to be suitable reductants for this technology.

Stochastic process modeling (SPM)

This technique was used to develop a predictive model of the NOx conversion versus hydrocarbon inlet concentration in order to develop engine control strategies. This technology was primarily applied to evaluating control strategies for lean gasoline NOx aftertreatment on transient cycles. There is no underlying physical assumption of the functionality of the data points for SPM, the points are assumed to have a random behavior and the mathematical description of that is fundamentally an interpolative prediction with some limited extrapolation of the data. This approach was used primarily to develop dosing controls for gasoline applications. Figure 14 shows a comparison between the measured and the predicted NOx concentrations for a typical lean gasoline dynamometer measurement. As it can be seen the predictive results are quite accurate.

Technical Accomplishments

General Motors (GM), in collaboration with BASF (Engelhard) (E) and Accelrys, Inc were awarded DOE Solicitation DE-PS26-00NT40758 in August 2002.. DOE project DE-PS26-00NT40758 has developed very active, lean exhaust catalytic materials that have been tested on the discovery system, laboratory reactors and engine dynamometer systems. The goal of this project is the development of effective, affordable NOx reduction catalysts for lean combustion engines in the US light duty vehicle market which can meet Tier II emission standards using on board fuel as the NOx reductant. The technical accomplishments include:

- BASF (Engelhard) demonstrated a high-throughput discovery system that works effectively for evaluating HC-SCR catalyst materials
- BASF (Engelhard) has synthesized and evaluated over 6100 possible catalytic materials in 16,000 tests
- BASF (Engelhard) scaled up >150 catalysts and coated 32 full size pieces for engine testing
- Accelrys developed a special informatics system which tracked the materials tested on the discovery system, indexed all properties including the activity curves and allowed data mining.
- GM reactor system confirmed discovery predictions of high NOx conversions of over 90%
- GM reactor system identified control strategy approaches
- GM engine dynamometer testing confirmed reactor predictions of high NOx conversions
- A feasibility analysis (see appendix) has been completed and demonstrates the advantages and disadvantages of the technology using these materials compared with other potential technologies.
- 7 patents have been applied for based on the work in this program and at least one additional patent is in preparation.

The teaming agreements among the partners contain no obstacles to commercialization of new technologies to any potential customers.

Conclusions

This project has identified active, supported metal catalysts that have over 90% NOx conversion under actual engine operating conditions for both diesel engines and lean gasoline engines. These catalysts have been evaluated using a range of emission certification procedures with cycle NOx conversions as high as 92%. A feasibility analysis of these catalysts for diesel applications was completed**.**

Figures

Figure 1. Example of single discovery experiment shown for a range of synthesized materials. The yellow curve is the project reference material used in all the discovery catalyst performance determinations.

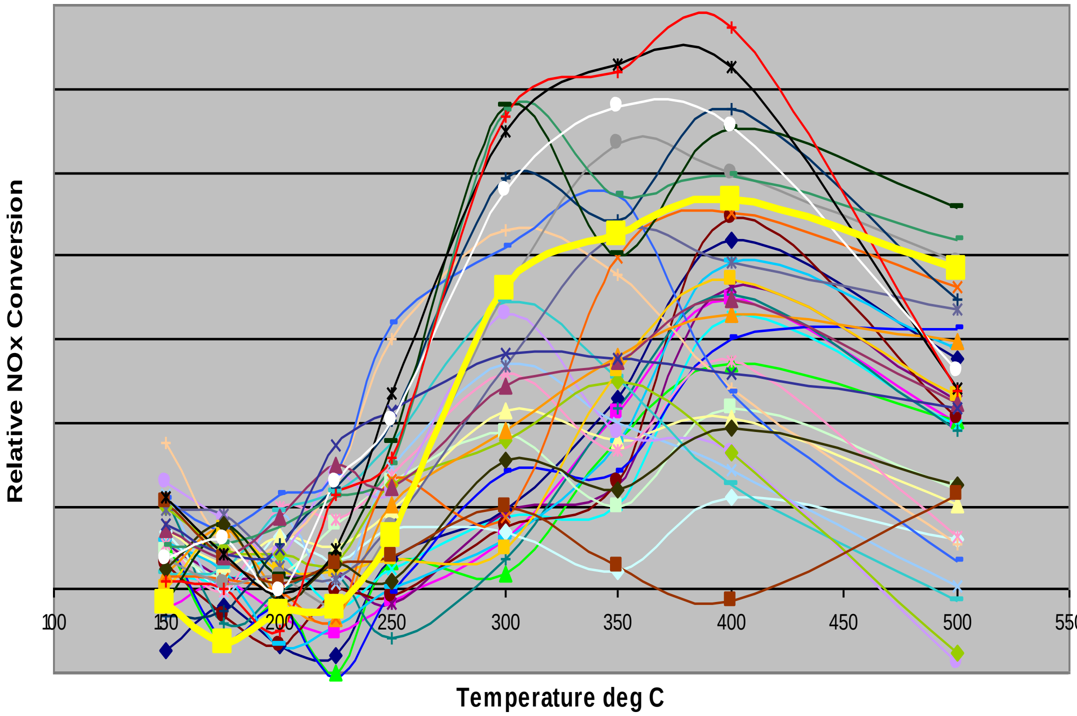


Figure 2. Example of a GM reactor run on a range of scaled up catalytic materials as identified as 'hits" from a discovery run. The red curve is the reference catalyst similar to the yellow curve in figure 1. The sample numbers are those used in the informatics database.

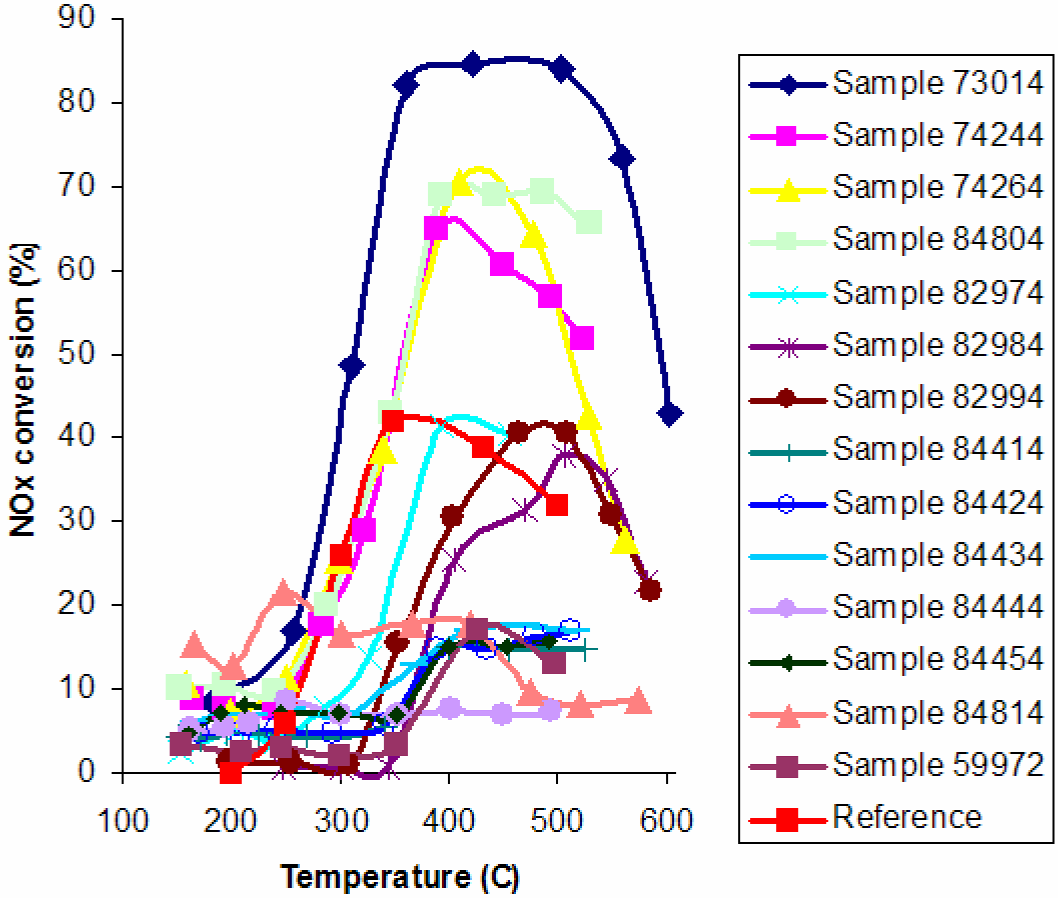


Figure 3. Program catalyst activity curves obtained from one of the GM reactor systems where the NOx reduction activity is shown as a function of space velocity for a single coated monolith. This figure clearly shows the increase in activity with space velocity decrease. SV ~ 12,500>25,000>50,000>75,000 h^{-1} where the black curve is the lowest space velocity

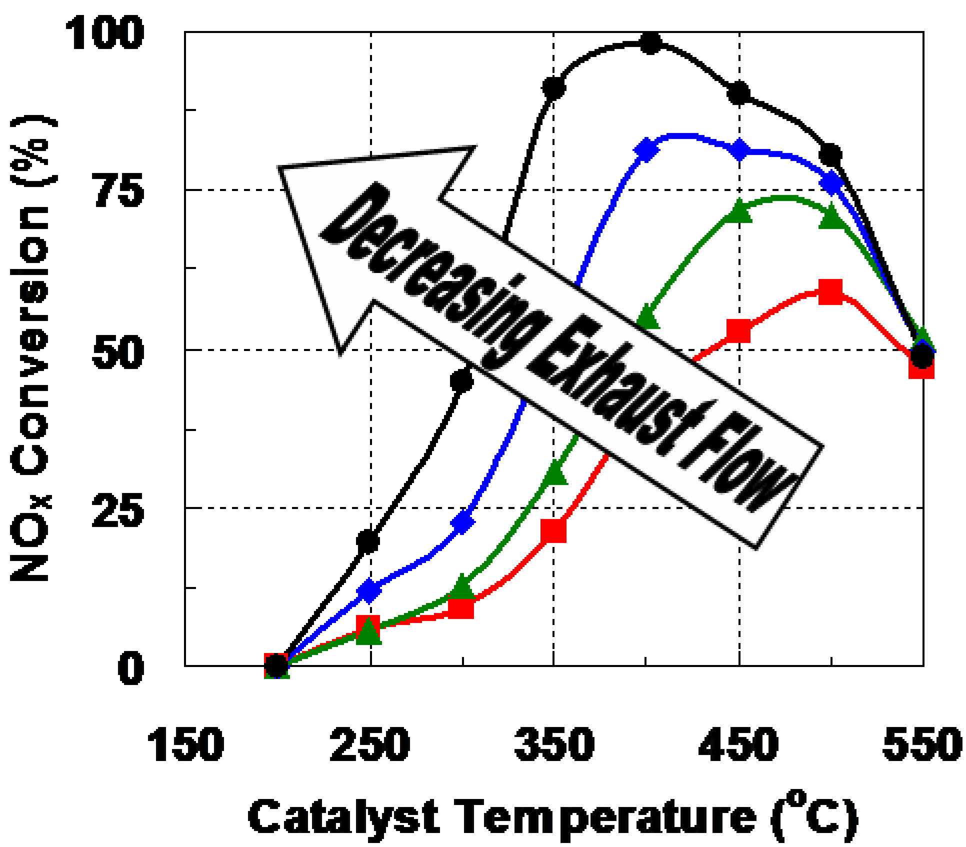


Figure 4. Effect of the two aging protocols on the program catalyst coated monolith core. The lean aging cycle is a 16 hour aging in steam at the listed temperature. The redox aging is a rich-lean aging cycle repeated many times. This rich-lean cycle was performed at the listed temperatures.

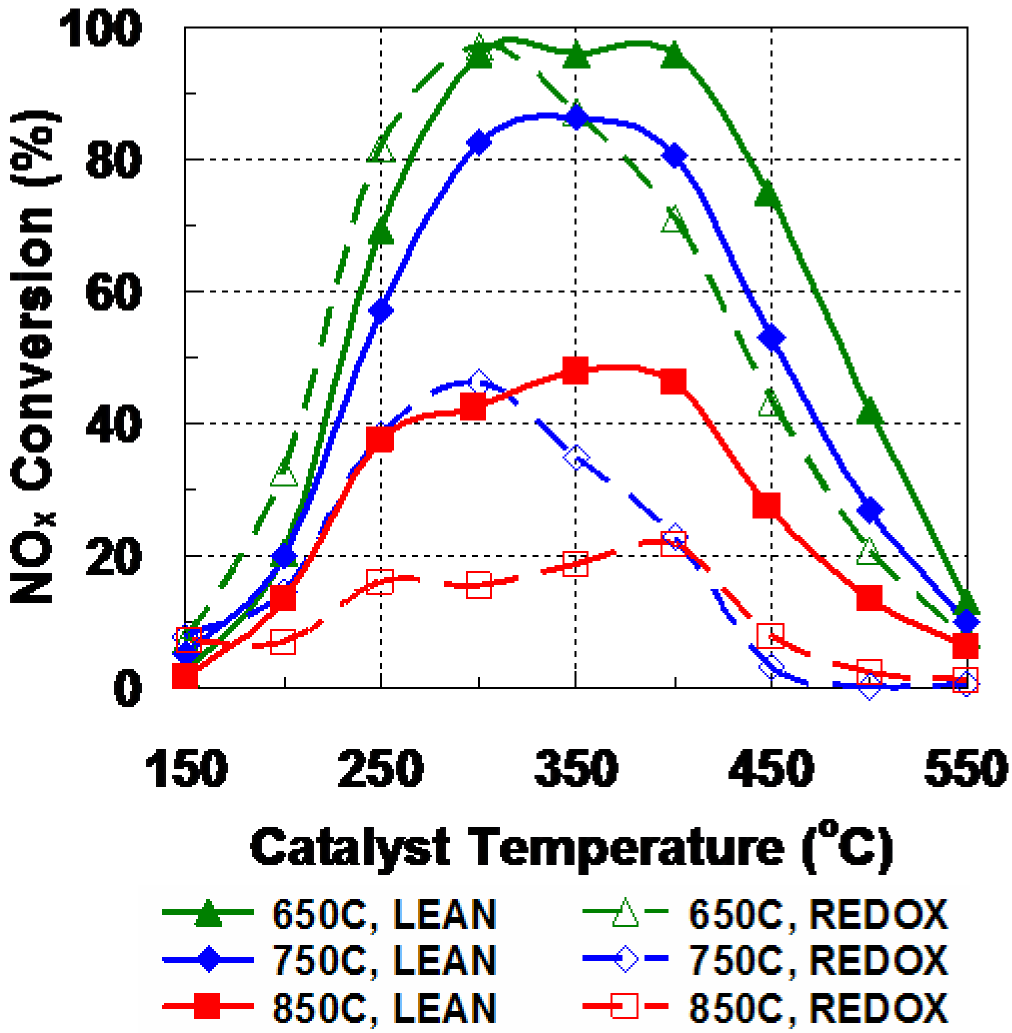


Figure 5. Carbon poisoning experiments using actual diesel exhaust and a separate hydrocarbon dosing system are performed with a full size set of monolith “bricks” coated with the program catalyst.

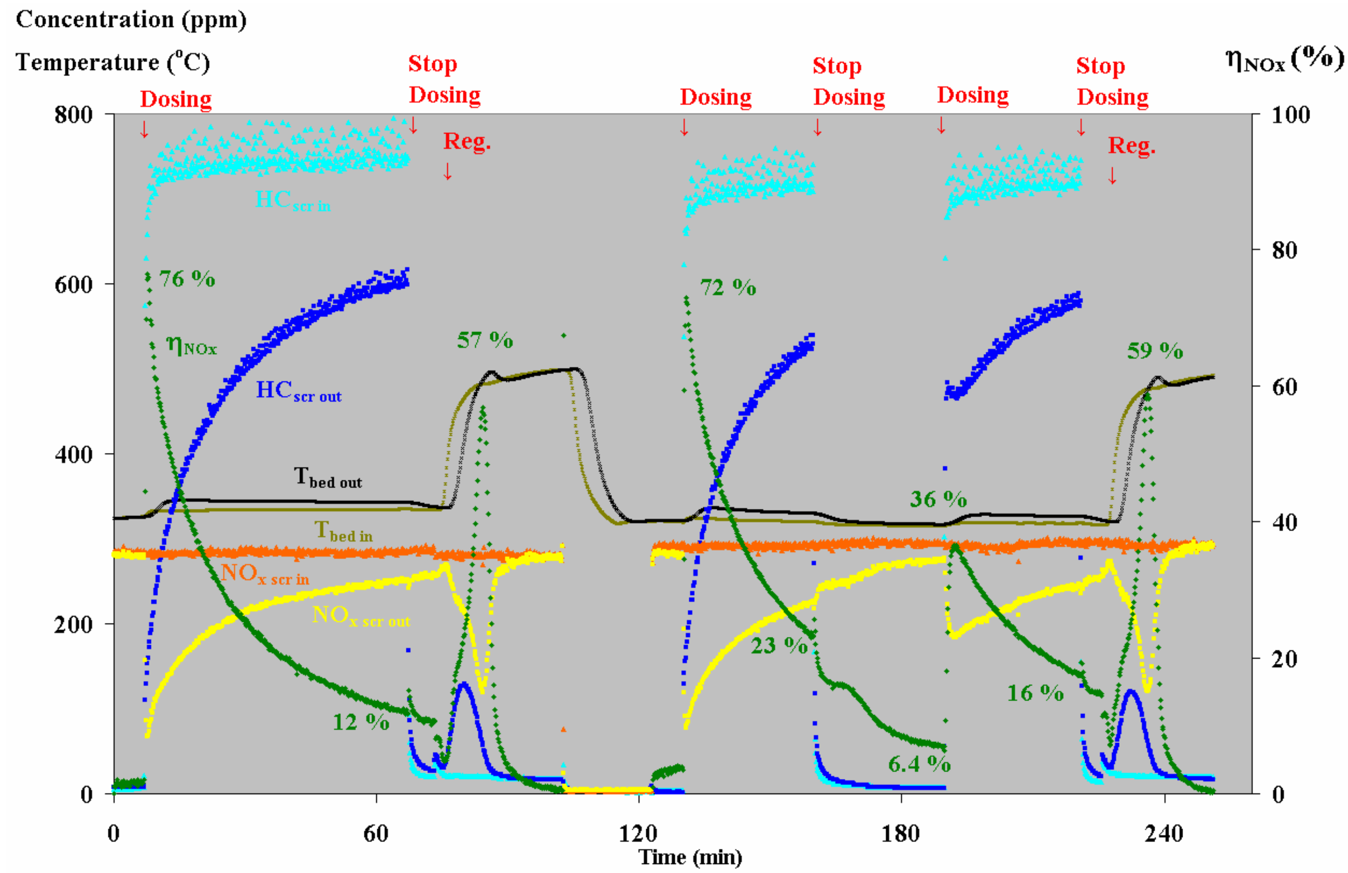


Figure 6. Sulfur exposure experiment using a GM reactor over approximately one hour. The sulfur exposure here is many times what would be expected from ultra-low sulfur (ULS) diesel fuel.

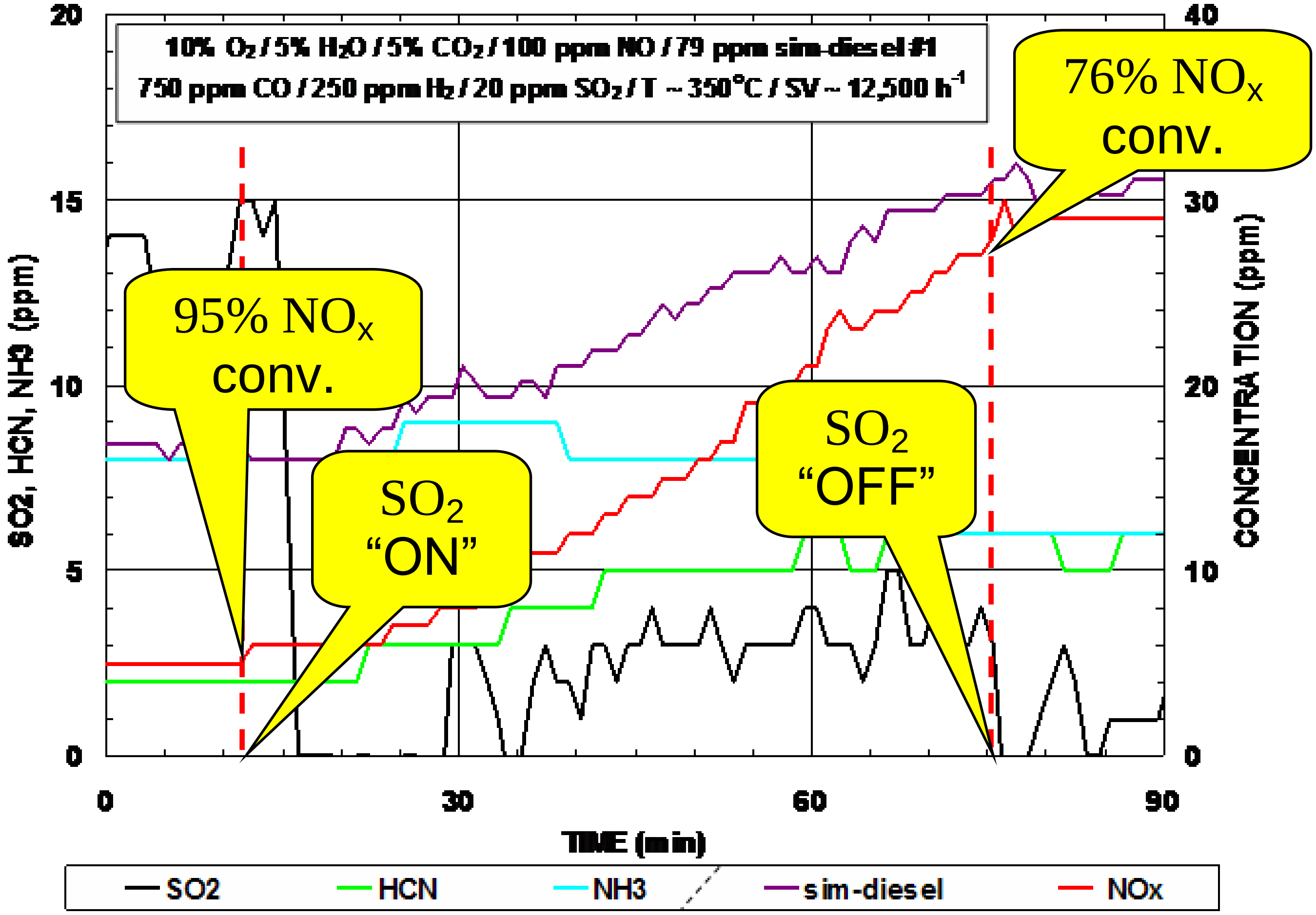
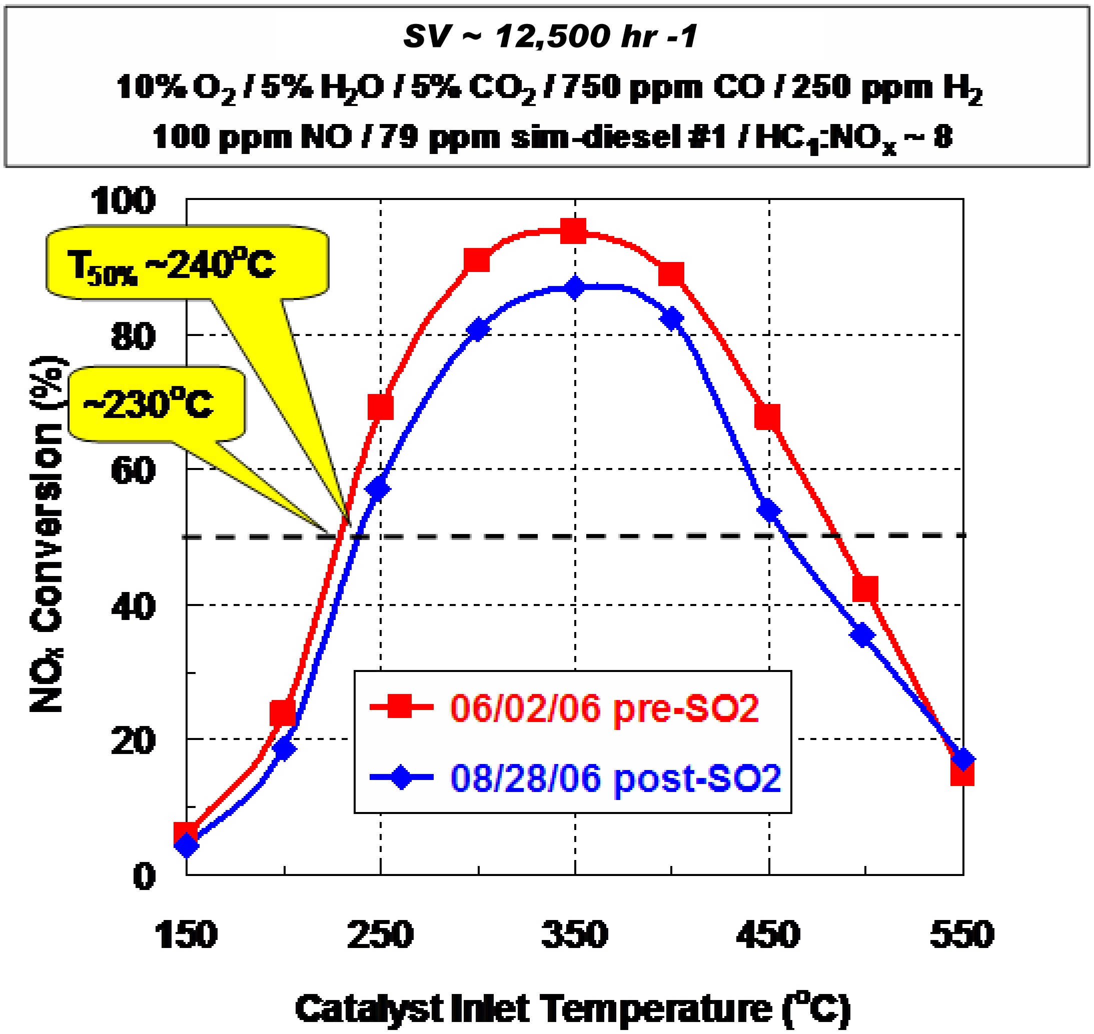


Figure 7. Multiple sulfur regenerations do cause some loss in the overall activity of the catalyst; however it is not appreciable.



SV ~ 12,500 hr -1
10% O2 / 5% H2O / 5% CO2 / 750 ppm CO / 250 ppm H2
100 ppm NO / 79 ppm sim-diesel #1 / HC1:NOx ~ 8
T50% ~240°C
~230°C
NOx Conversion (%)
100
80
60
40
20
0
150
250
350
450
550
Catalyst Inlet Temperature (°C)
06/02/06 pre-SO2
08/28/06 post-SO2

Figure 8. The effect of cumulative phosphorous poisoning is shown where there is a gradual loss in activity with exposure. ?% is an estimate of the phosphorous deposition over the regulated lifetime of the aftertreatment system.

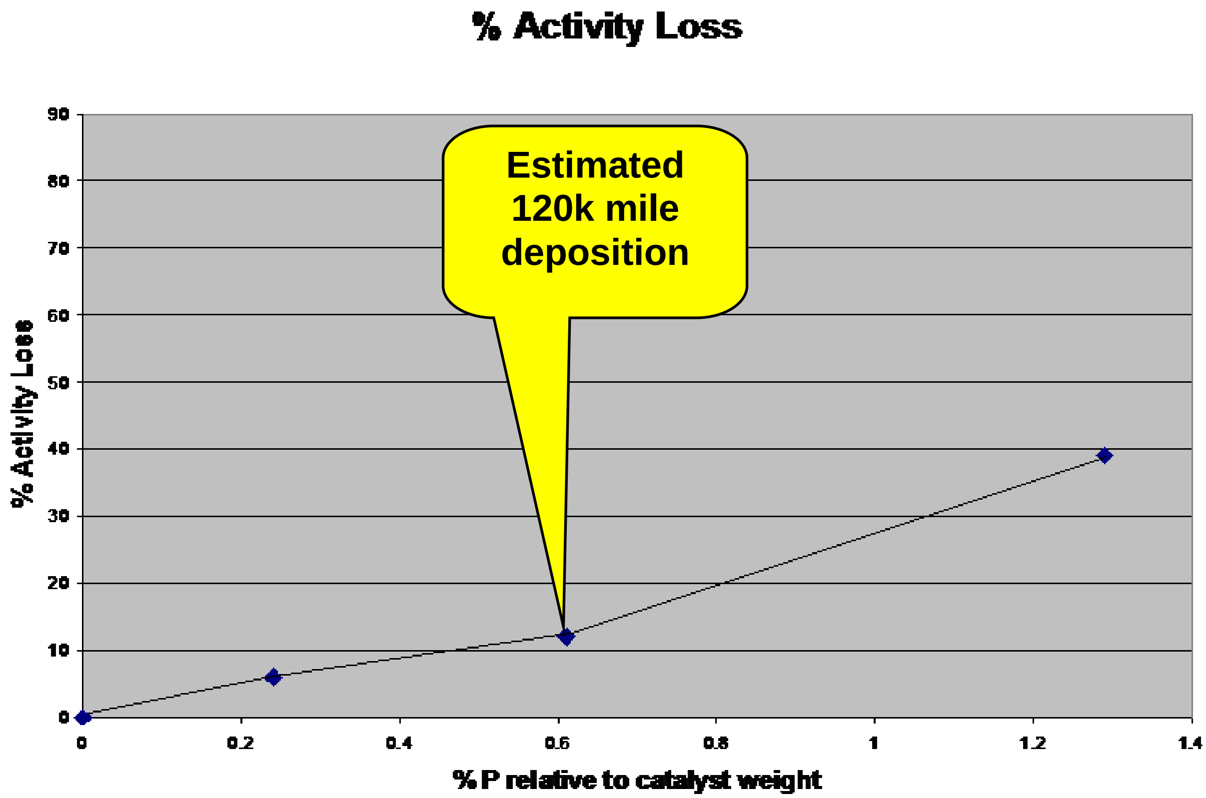


Figure 9. GM reactor activity curves comparing simulated gasoline and simulated diesel fuels on the program catalyst. Increasing the space velocity for the simulated diesel gives similar activity curves to the simulated gasoline activity curve.

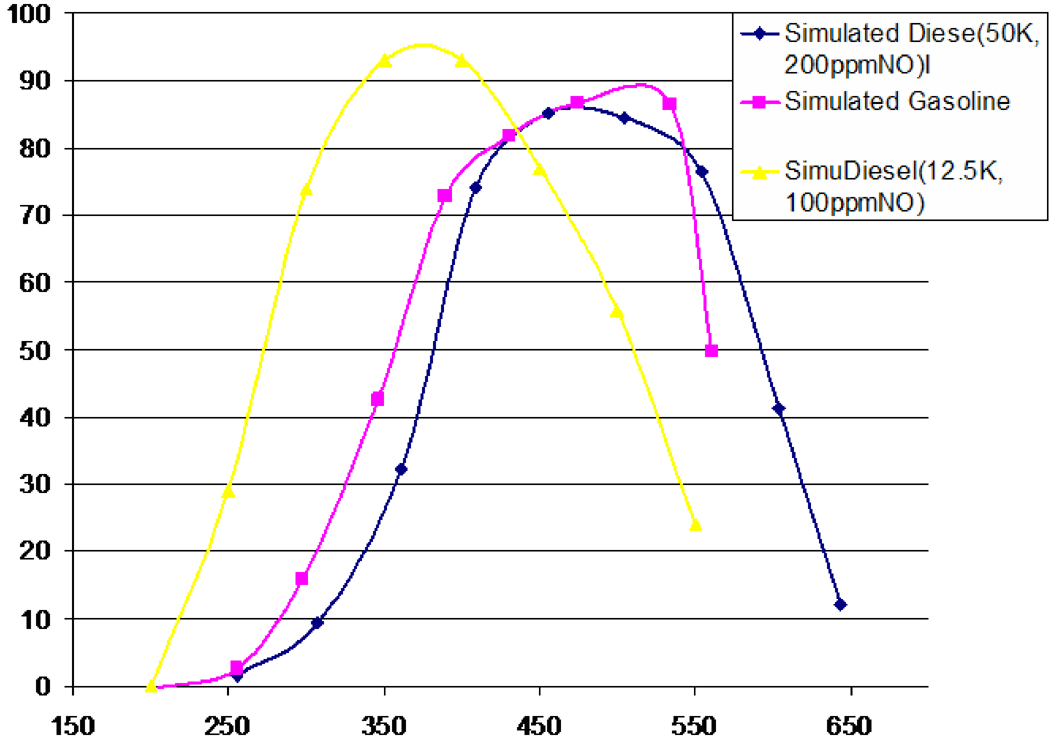


Figure 10. Schematic of the diesel exhaust treatment architecture shows the typical aftertreatment architecture that has been used to test these catalysts under actual operating conditions on a dynamometer.

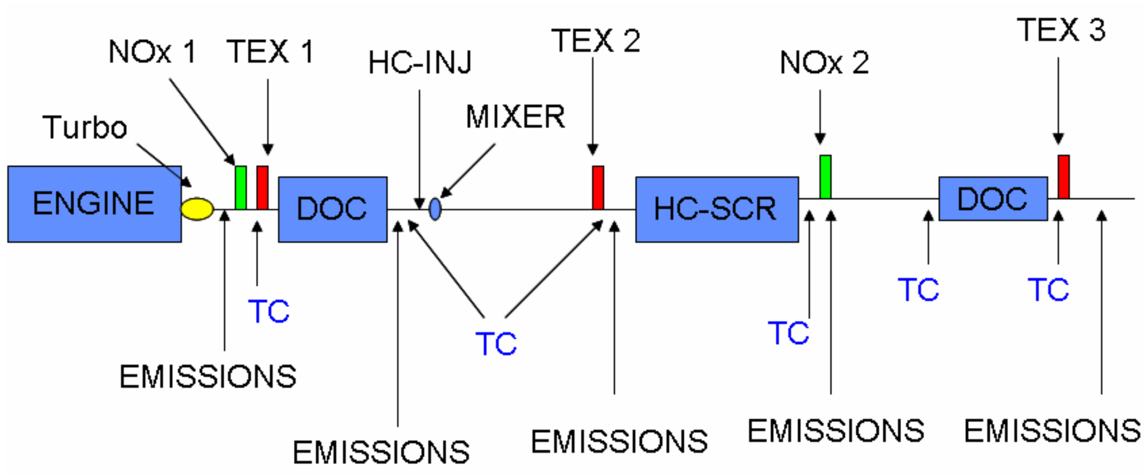


Figure 11. Emissions trace for NOx tailpipe emissions from an experimental 6 cylinder diesel engine using the aftertreatment architecture and the program catalyst shown in figure 10.

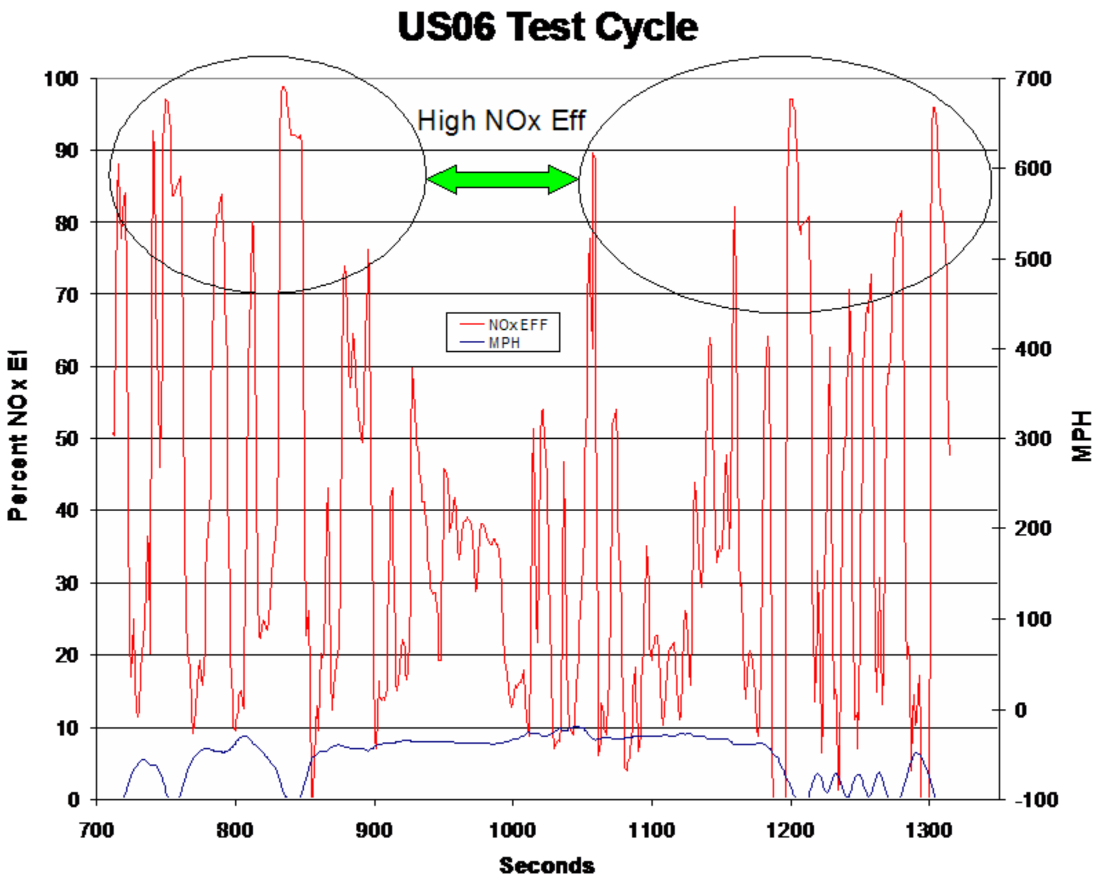


Figure 12. Emissions trace for NOx from HWFET on the same engine and aftertreatment architecture with the program catalyst described in figure 11. This test gives overall NOx conversions of 92%.

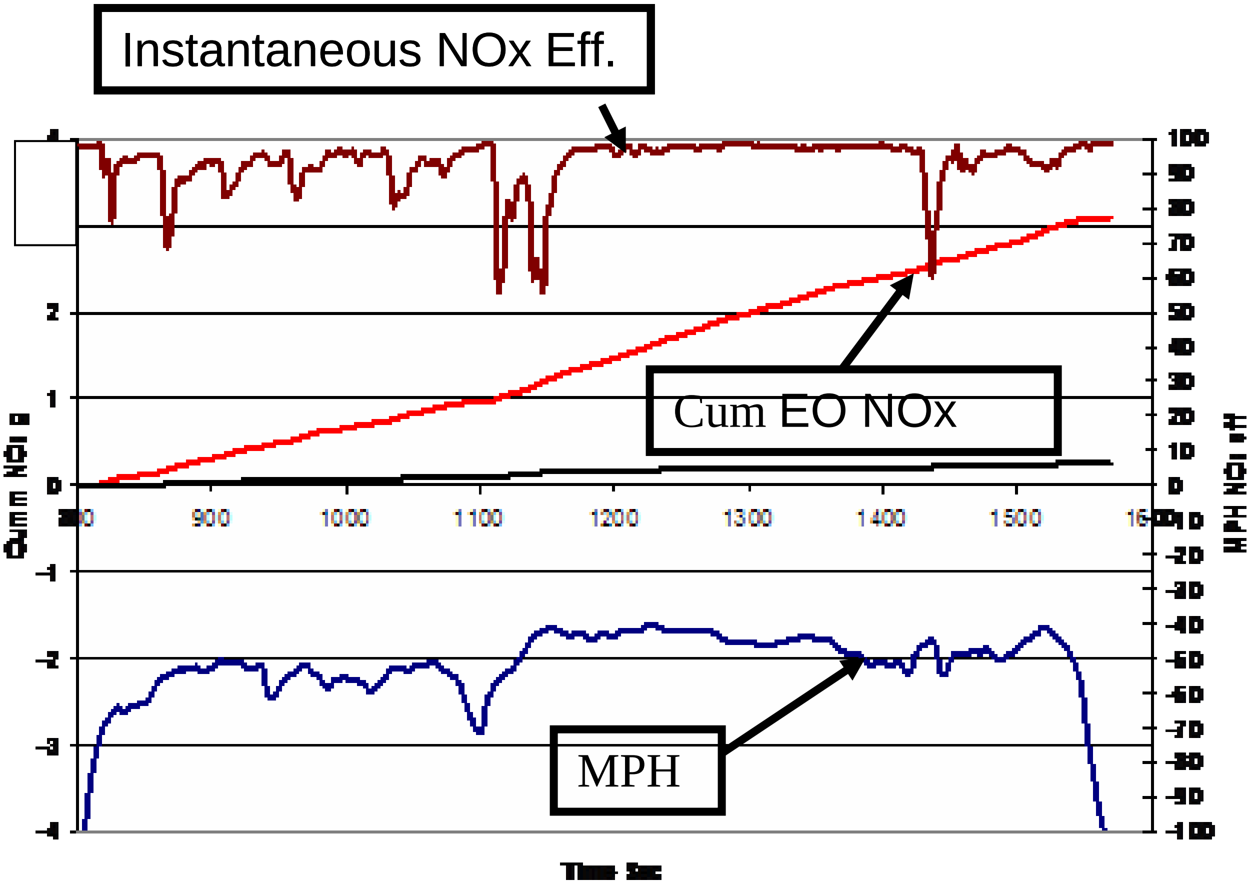


Figure 13. Dynamometer lean gasoline testing on a 2.2 liter 4 cylinder engine using a no DOC and no fuel injection ahead of the catalyst. The full size catalyst in this case was approximately two times the engine displacement and uses the same washcoating as the diesel catalyst measurements. The test points are those shown in table 3.

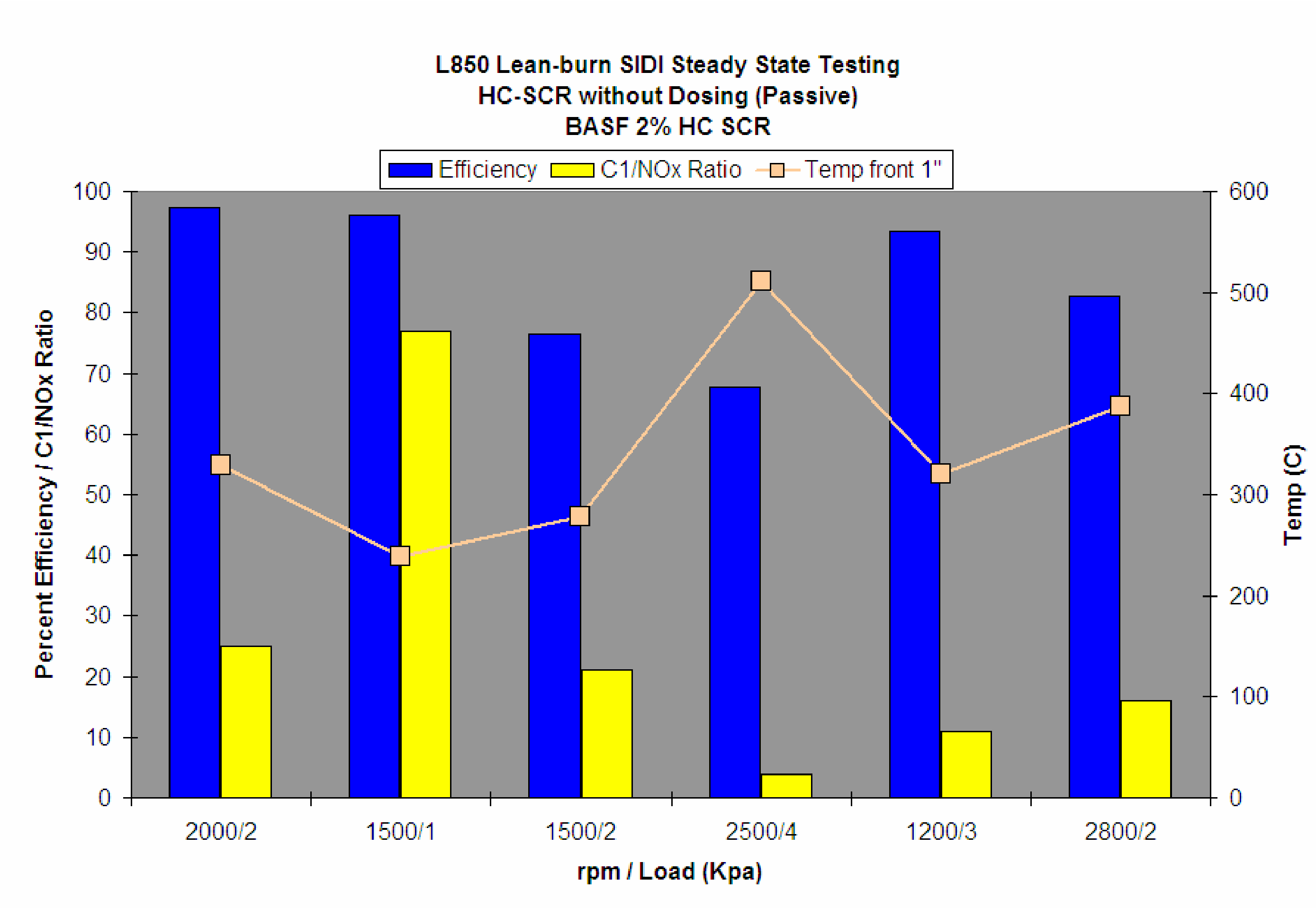
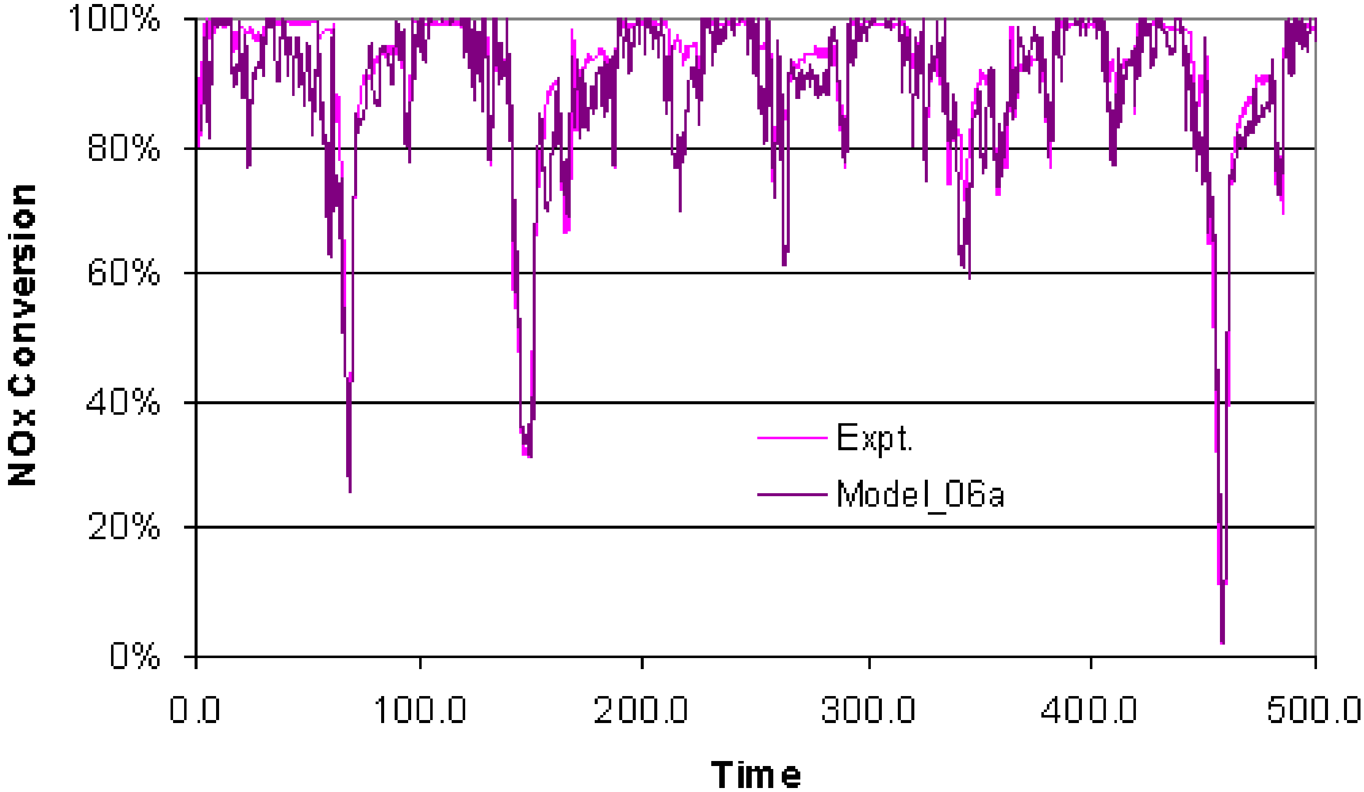


Figure 14. Lean gasoline dynamometer NOx measurements using the same aftertreatment architecture as in figure 13 and SPM predictions of NOx conversions over the same cycle. This SPM model was tuned using the steady state, lean gasoline dynamometer measurements.



Appendix

Feasibility Analysis

A feasibility analysis is comprised of three elements:

1. Can the technology satisfy the emission standards on practical engine/aftertreatment architecture?
2. Does it have properties that make utilizing it an advantage over present technologies
3. Is it economically acceptable?

HC-SCR with diesel fuel

Evaluating the program catalyst for diesel applications with onboard diesel fuel as the reductant, it was concluded that the most probable diesel application of this technology would be for heavy duty certification. This conclusion was reached based on the temperature versus activity curve that has been measured for this catalytic material. Effectively the optimum operating temperature is above 300 C which is more commonly observed in large displacement, heavy duty diesels that must satisfy the heavy duty certification standards. Consequently full size bricks using the program catalyst were coated and evaluated on a 6.6 Duramax diesel in a dynamometer running heavy duty loads and evaluated over the heavy duty certification cycle. This engine is/has been used in both heavy duty and light duty vehicle applications. The aftertreatment architecture for this system is the same as shown in figure 10 where ULS diesel fuel is injected just before the mixer. Since many components of diesel fuel have very high evaporation temperatures (T_c), diesel fuel was not injected into the exhaust stream until the exhaust temperature reached approximately 300 °C. For the heavy duty FTP this does not occur for this powertrain combination until almost 200 seconds into the cycle. With no injected hydrocarbons there is very little hydrocarbon available in the exhaust to reduce NOx. The results shown in figure A1 show that until the exhaust fuel injection is initiated, there is not much NOx reduction. After the initiation of injection, NOx reduction becomes quite active and for much of the cycle exceeds 90% NOx conversion. However, the NOx standard for this heavy duty chassis certification is 0.20 g/HP-hr and these measurements show this system exceeds that standard by three to four times depending on the catalyst volume used in the aftertreatment architecture.

The set 13 mode test (figure A2) is another test designed to evaluate the capability of an aftertreatment system to satisfy emission standards. This test is a set of steady state points the cover the range of conditions that an HD diesel engine will need to satisfy emission standards in order to be certified in Europe. It is clear from these points (figure A3) that increasing catalyst volume increases NOx conversion. This is typically true for all automotive catalysts. The conversion at idle is low which occurs because the exhaust temperature is below the 300 °C where hydrocarbon dosing occurs and consequently there are no hydrocarbons available to reduce NOx. This catalytic material tends to have a drop off in conversion at high space velocities and low oxygen concentrations. Points A100, B100, C100 and A75 all have relatively low oxygen concentrations and high space velocities. Points A100, B100 and C100 have the highest engine out NOx concentrations of all the set 13 points.

A comparison of the HC-SCR results using diesel fuel as the reductant to a common supplier produced urea SCR catalyst (see figure A4) on the set 13 test shows that even with the diesel reductant injection active the urea SCR typically shows higher NOx conversion than the HC-SCR. Considering this set of evaluation points shows a wide range of engine conditions, it is clear that the urea SCR tolerates a much wider range of engine conditions with high NOx conversion. The conditions needed to develop a control strategy for use of this program catalyst are described in table A1.

Feasibility conclusion for fuel HC-SCR for diesel applications: This technology cannot meet heavy duty diesel emission standards using diesel fuel as the reductant unless a technology is developed that enables diesel fuel injection and vaporization at temperatures from 200 °C to 300 °C. Also diesel fuel as a reductant is not as efficient as urea as a reductant for NOx control.

Evaluating the program catalyst for diesel applications with ethanol (or E85) as a second fluid reductant using the heavy duty certification cycle shows a greater cycle NOx reduction for the HDFTP (figure A5). Since ethanol (and E85) vaporizes at a much lower temperature than ULS diesel fuel, reductant injection can occur at 200 °C or lower. Re-evaluating the HDFTP (see figure A5) with ethanol injected effectively from the beginning of the HDFTP cycle, it can be shown that the net NOx emissions drop to 0.09 g/HP-hr which is well below the emission standards. An similar evaluation of the set 13 test shows equivalent results (figure A6) where in all but the idle operating condition and the C100 operating point have NOx conversions exceeding 90%. Using E85 as a second fluid reductant produces equivalent results to a large degree because the E85 can also be injected into the exhaust stream at temperatures as low as 200 °C. Comparing the conversions at the set 13 test points show that HC-SCR shows a consistent higher NOx conversion compared to urea SCR; however, the improvement over urea SCR is incremental. A qualitative comparison of the properties of using a second fluid ethanol or aqueous urea is detailed in table A2. There are advantages to using an ethanolic or E85 second fluid.

Feasibility conclusion for ethanol or E85 HC-SCR for diesel applications: These technologies can the meet heavy duty diesel emission standards using ethanol or E85 as a second fluid reductant. The technology is competitive or slightly superior to urea SCR. Material costs for this technology are not expected to be significantly greater than the costs for a urea SCR aftertreatment system.

Evaluating the program catalyst for lean gasoline applications has not undergone nearly as extensive evaluation as for the diesel applications. However as shown in figure 13 even passive dosing gives quite good NOx conversion results on a lean gasoline dynamometer test. Based on these results and the development of two gasoline specific formulations each of these formulations was evaluated on the passive dosing EUDC (figures A7 and A8). Each of these tests show substantial NOx conversions on the order of 80%. This is a rather encouraging result since the engine control strategy was not modified to improve the NOx conversion by tailoring the engine out hydrocarbons to improve the NOx conversion. Nor was a dosing system added to this aftertreatment architecture to enhance the NOx conversion.

Feasibility conclusion for gasoline, E85 or gasoline HC-SCR for lean gasoline applications: There is clear potential for these enhanced program catalysts to be used for lean gasoline NOx reduction. Insufficient testing has been completed to formalize a recommendation of the feasibility of this technology for lean gasoline applications.

Figure A1. Heavy duty FTP (HDFTP) cycle as defined for chassis certification shows the performance of the aftertreatment architecture as described in figure 10. Hydrocarbon injection was not started until the exhaust temperature just before the catalyst reached 280 °C which is approximately 200 seconds after light-off for this engine and exhaust manifold

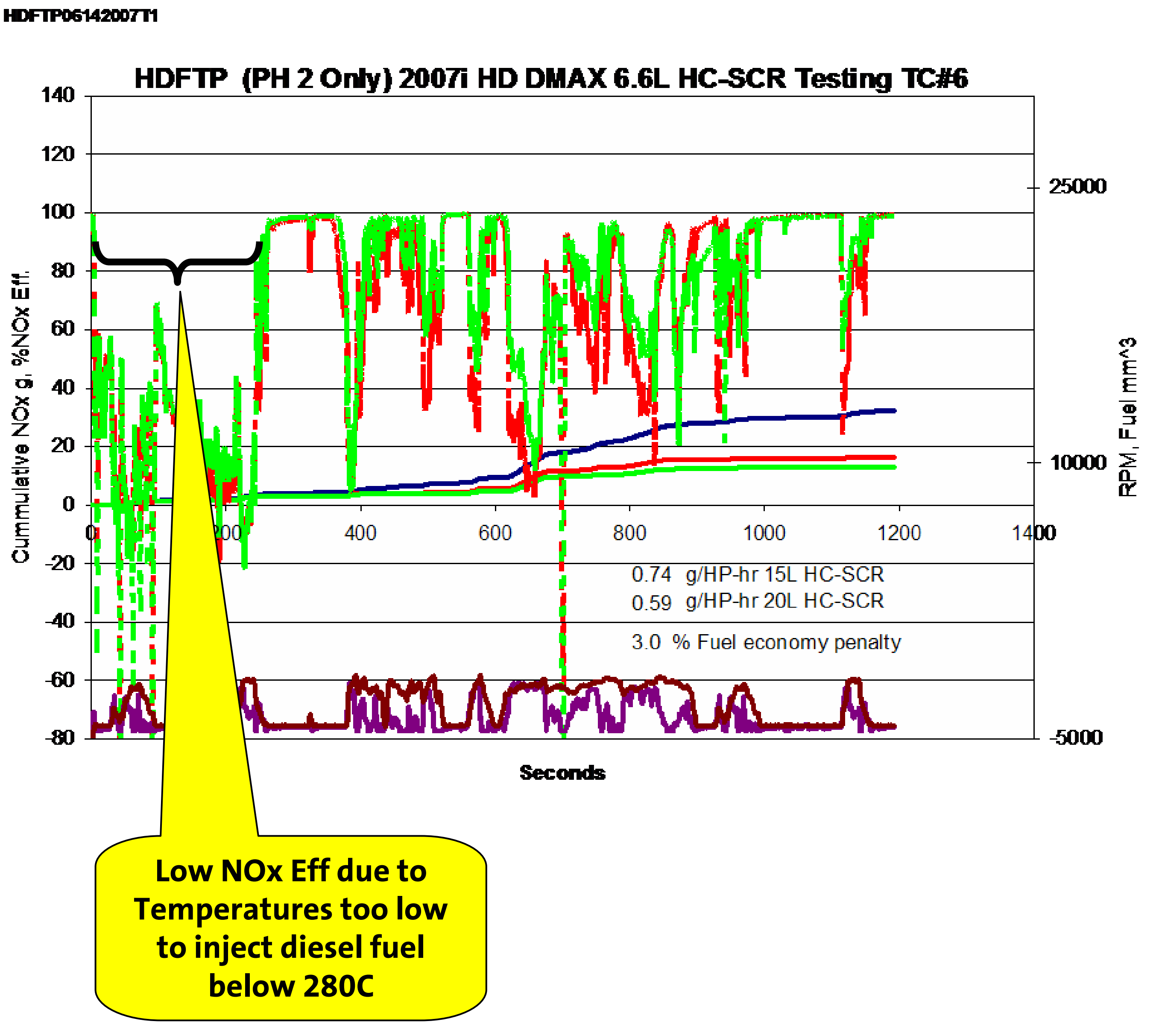


Figure A2. Supplemental Emission Test (SET) (aka Steady State Test / 13 Mode Test, Euro III - European Stationary Cycle used to evaluate heavy duty diesel emission for European heavy duty certification. These points are engine dependent.

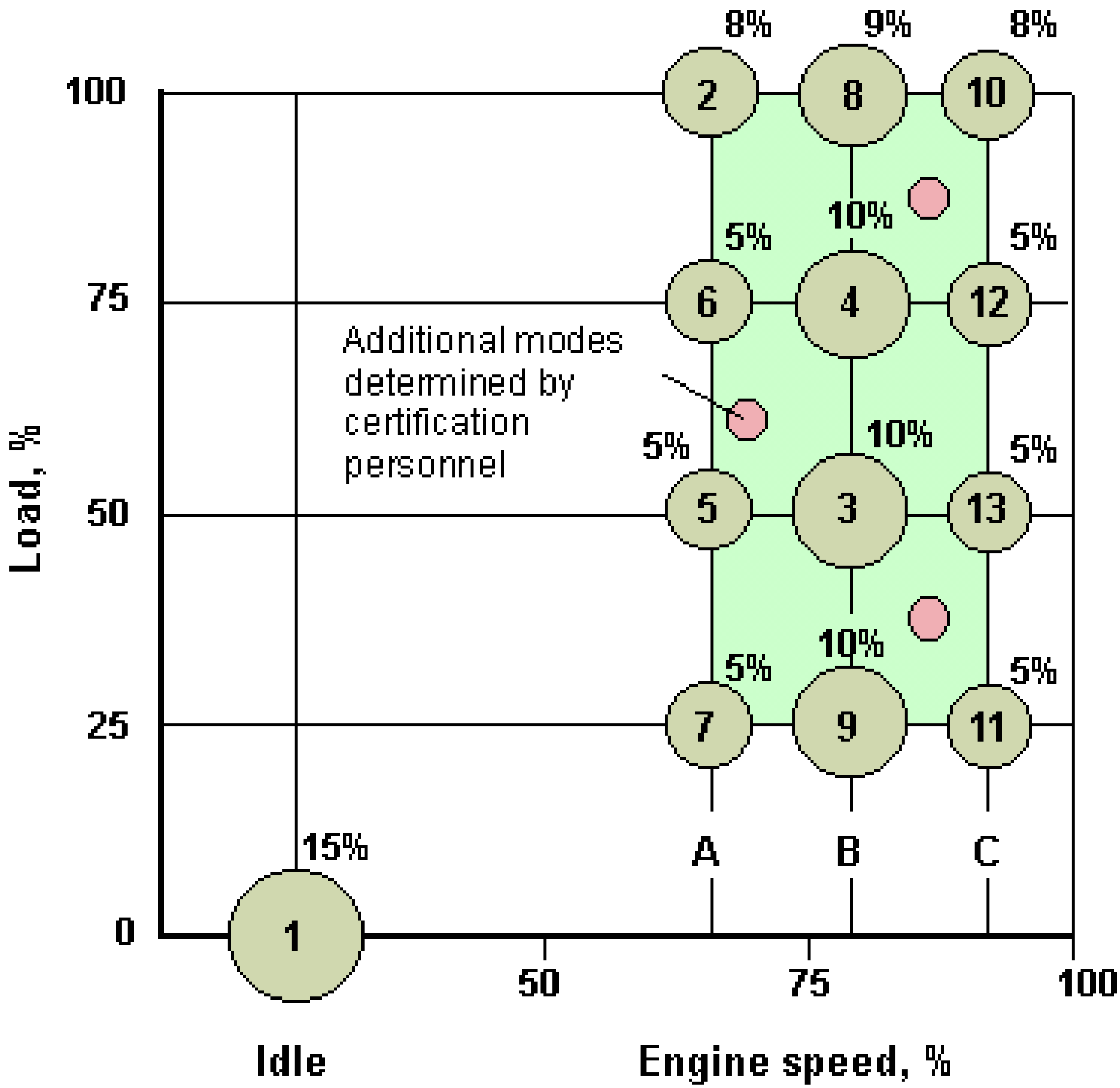


Figure A3. Bar chart of NOx conversion results for two different catalyst volumes using ULS diesel fuel as the reductant. This uses the aftertreatment architecture shown in figure 10 and uses GM's 6.6 liter Duramax diesel engine. The points on the chart are the Set 13 points as shown in figure A2.

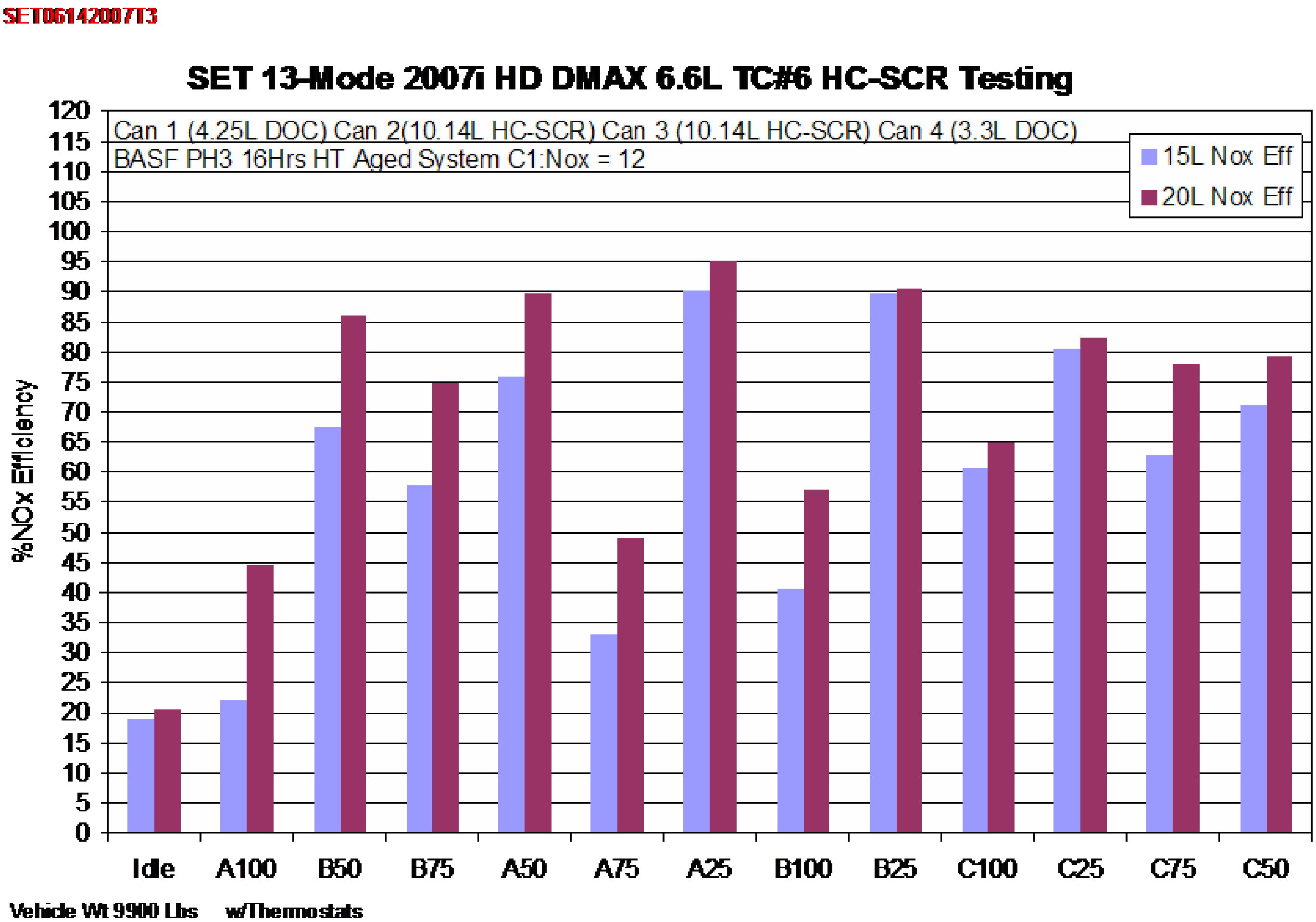


Figure A4. Same data as shown in figure A3; however, data from a similar engine employing a aqueous urea dosing and catalytic are compared with the program catalyst results.

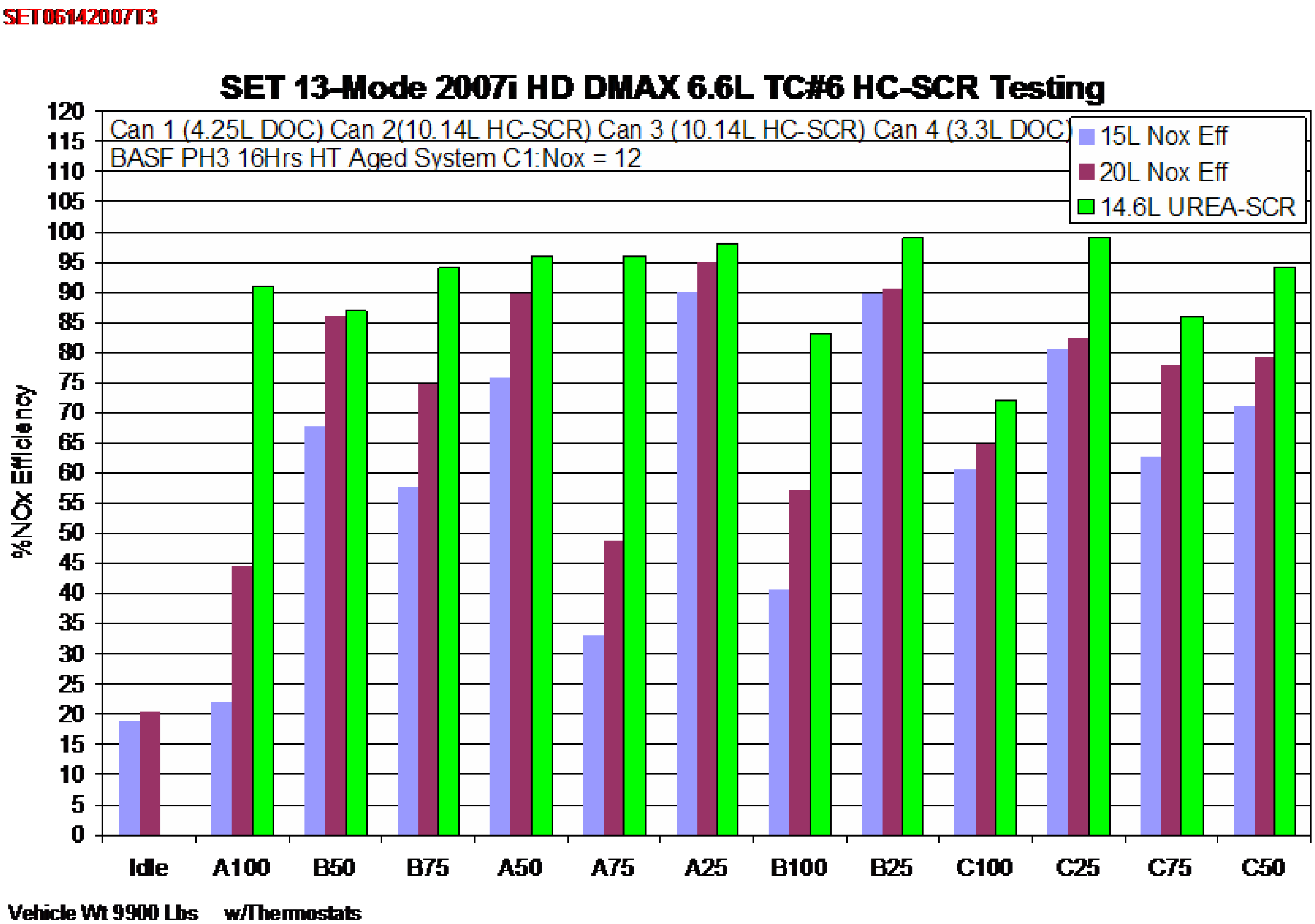


Figure A5. Heavy duty FTP (HDFTP) cycle as defined for chassis certification shows the performance of the aftertreatment architecture as described in figure 10. Ethanol was selected as the reductant and injection was started when the exhaust temperature before the catalyst reached 200 °C which was shortly after engine start.

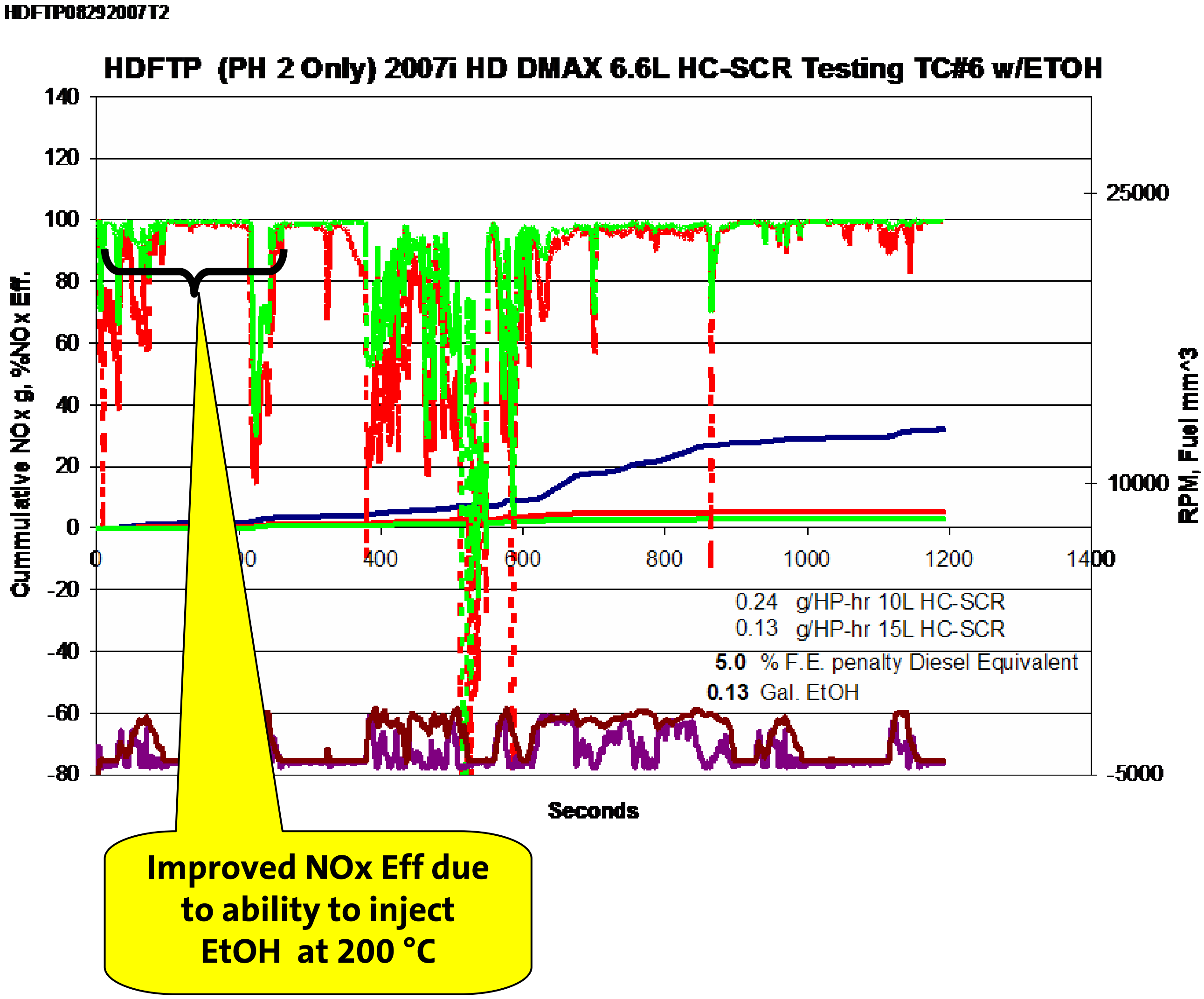


Figure A6. Set 13 points evaluated using ethanol as a reductant. Engine conditions and architecture are the same as those in figure A5. The NOx conversion at the set points are compared to the equivalent urea injection system.

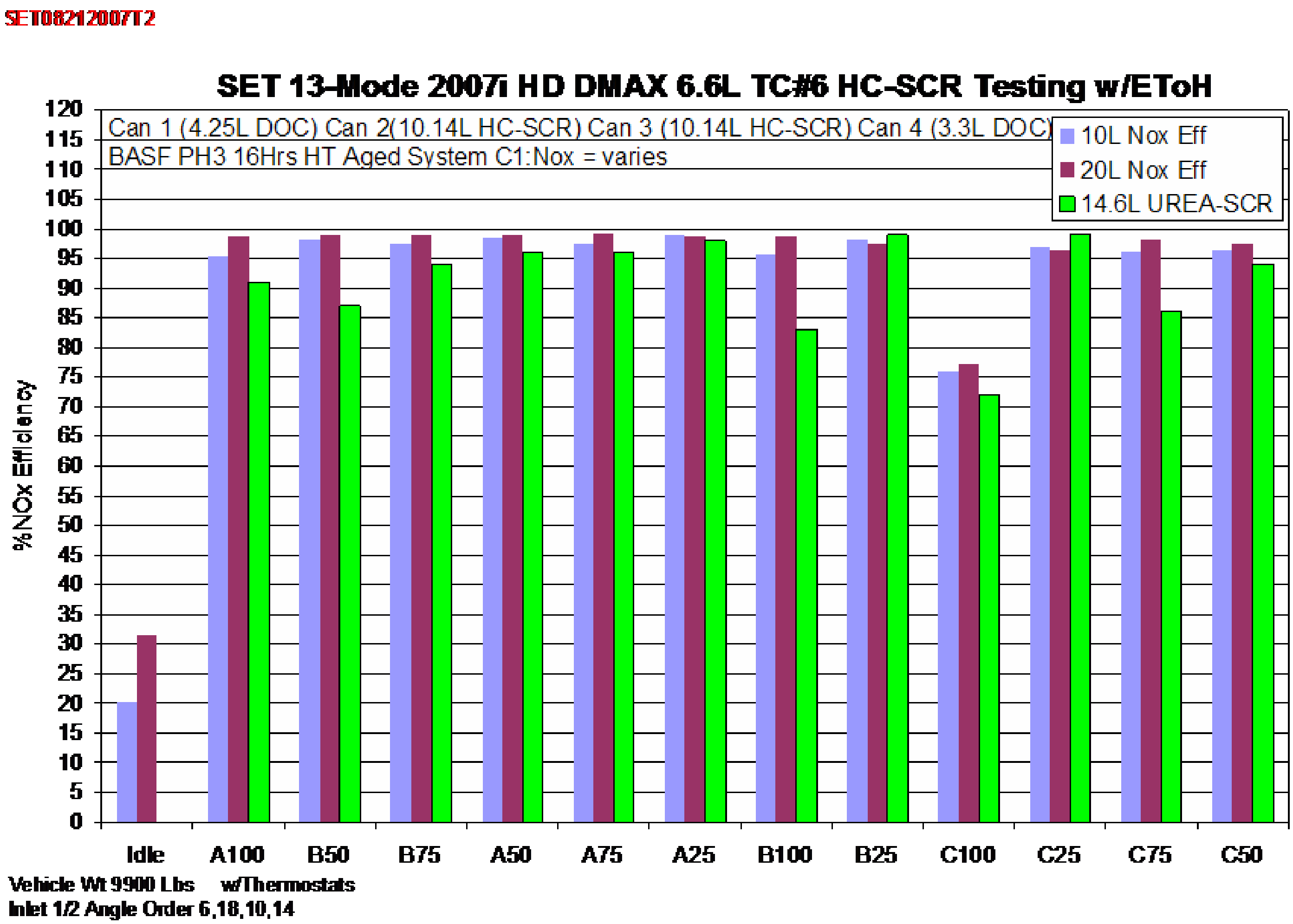


Figure A7. Lean gasoline engine evaluation of the first of the gasoline fuel optimized washcoats over the EUDC drive cycle. This uses the same aftertreatment architecture as the results in figure 13, that is, active dosing is not in use and the program catalysts are the first aftertreatment device coupled to the exhaust manifold.

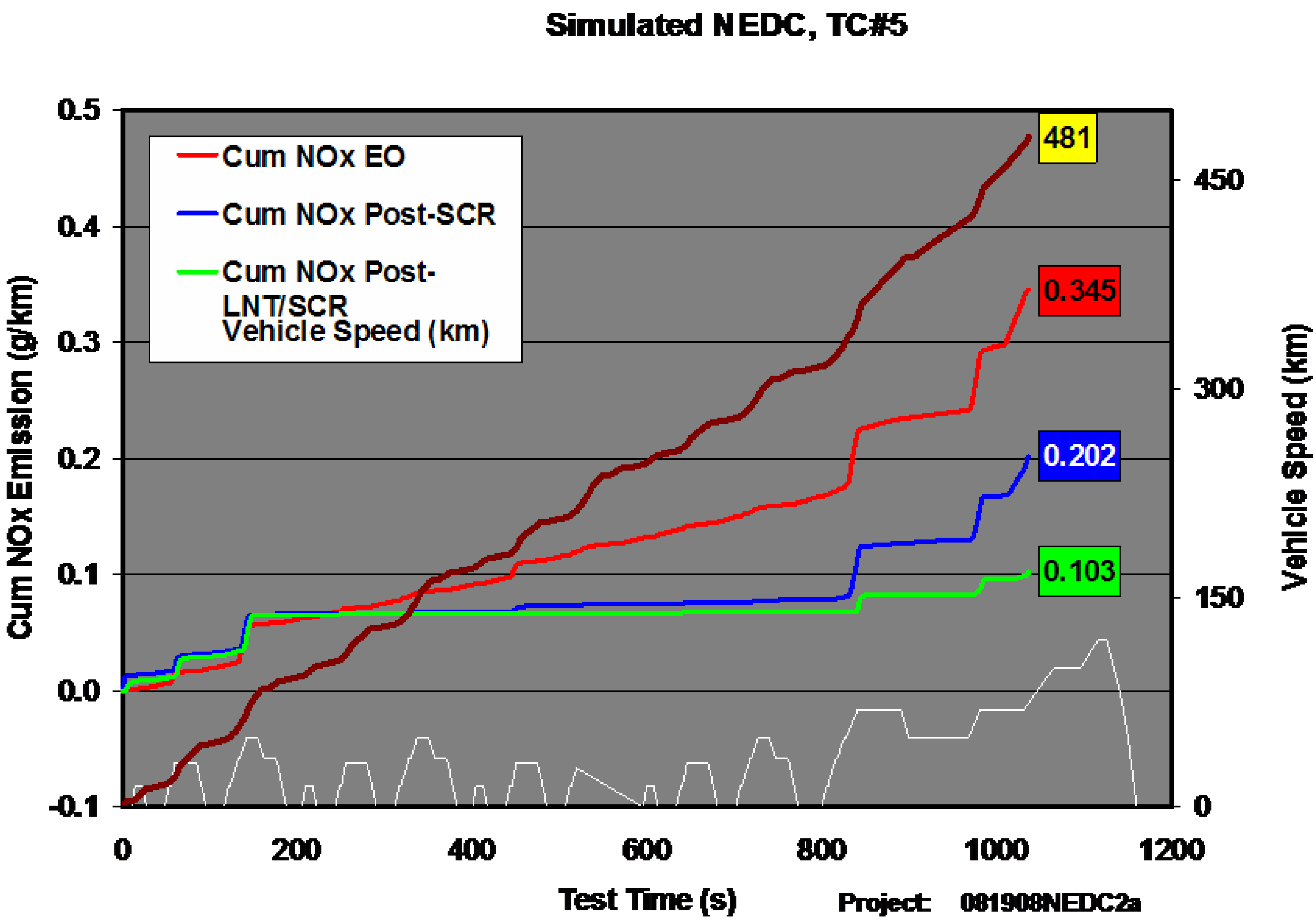


Figure A8. Lean gasoline engine evaluation of the second gasoline fuel optimized washcoat over the EUDC drive cycle. This uses the same aftertreatment architecture as the results in figure 13, that is, active dosing is not in use and the program catalysts are the first aftertreatment device coupled to the exhaust manifold.

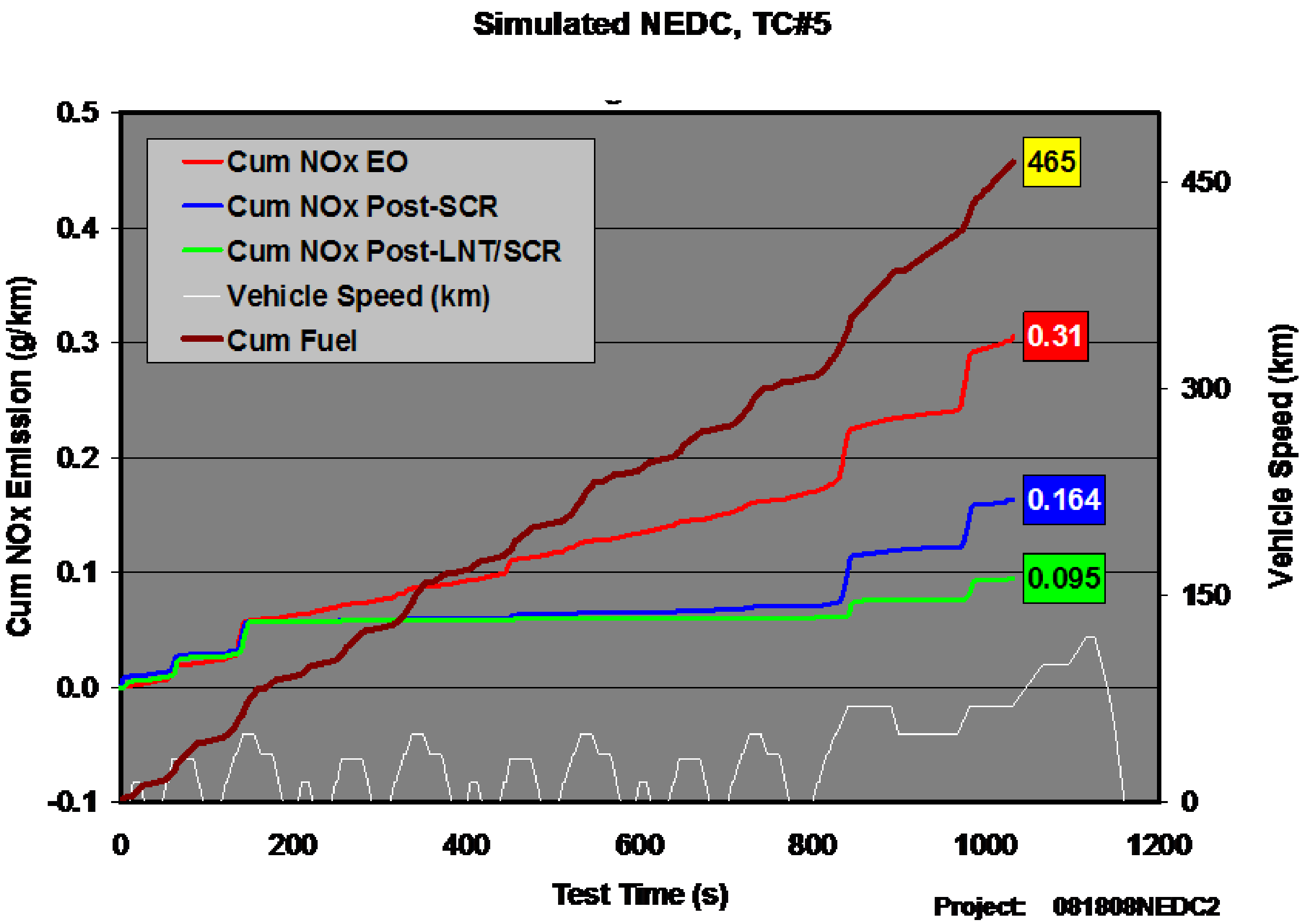


Table A1. Description of catalyst performance needed to design an automotive control strategies. Here temperature is categorized as HIGH > 350°C or LOW < 350°C, space velocity is categorized as HIGH ≥ 50,000 h^{-1} or LOW ≤ 12,500 h^{-1} and exhaust NOx concentration is categorized as HIGH ≥ 250 ppm or LOW ≤ 100 ppm.

Exhaust Condition	#1	#2	#3	#4
Catalyst Temperature	HIGH	HIGH	LOW	HIGH
Space Velocity (Exhaust Flow Rate)	HIGH	HIGH	HIGH	LOW
Exhaust NO_x Concentration	HIGH	LOW	HIGH	HIGH
Control Strategy O_2 concentration: HC_1:NO_x ratio: H_2 concentration:	> 10% ~ 10 - 15 ~ 2000 ppm	> 10% ~ 15 - 20 ~ 1000 ppm	> 10% ~ 4 - 8 ~ 4000 ppm	< 10% ~ 10 - 15 ~ 250 ppm
Exhaust Condition	**#5**	**#6**	**#7**	**#8**
Catalyst Temperature	LOW	LOW	LOW	HIGH
Space Velocity (Exhaust Flow Rate)	LOW	LOW	HIGH	LOW
Exhaust NO_x Concentration	HIGH	LOW	LOW	LOW
Control Strategy O_2 concentration: HC_1:NO_x ratio: H_2 concentration:	~ 10% ~ 10 - 15 ~ 1000 ppm	~ 10% ~ 15 - 20 ~ 1000 ppm	> 10% ~ 10 - 15 ~ 4000 ppm	< 10% ~ 15 - 20 ~ 250 ppm

Table A2. This is a qualitative comparison of the advantages of the second fluid ethanol system with the program diesel catalyst and a urea-SCR aftertreatment system.

	HC-SCR (EtOH)	UREA-SCR
Cost	+ Fuel Inj.	
System Volume	+	
Freezing Issue	++	-
Temperature Window	-	+
DOC PGM Use (less NO2)	+	
Fluid Consumption		+
Additional Fluid Uses	+	-
DPF Regeneration FE Penalty	+	-
DOC Face Plugging	+	-
Infrastructure (E85)	++	-