## II.B.11  Discovery of New NOx Reduction Catalysts for CIDI Engines Using Combinatorial Techniques

*Richard J. Blint (Primary Contact, General Motors), Gerald Koermer (Engelhard Corporation), George Fitzgerald (Accelrys, Inc.)*
General Motors Corporation (GM)
Research and Development Center
Mail Code 480-106-185
30500 Mound Road
Warren, MI  48090-9055

*DOE Technology Development Manager:  Ken Howden*

*NETL Project Manager:  Mr. Carl Maronde*

*Subcontractors:*
Engelhard Corporation, Iselin, NJ
Accelrys, Inc, San Diego, CA

### Objectives

- Develop new NOx selective catalytic reduction (SCR) catalysts that can operate in the lean exhaust of diesel or lean gasoline engines.  These catalysts will:
  - utilize the onboard fuel as the reductant, i.e., hydrocarbon-SCR (HC-SCR)
  - have NOx conversion efficiencies in excess of 80%
  - span the operating range (e.g., temperature and flow rate) for these lean engines
  - have sufficient durability and resistance to poisoning to meet the 120,000 mile emission standard for light-duty vehicles

### Approach

- Use fast-throughput techniques to synthesize and measure the activities of a large range of materials for NOx reduction properties (Engelhard)
- Use design of experiment and statistical analysis to predict optimum compositions from materials identified in the discovery (fast throughput) phase of materials evaluation using the CombiMat 2.5 database developed for this project (Accelrys and GM)
- Scale up, evaluate and do a feasibility analysis of potential NOx reduction catalysts identified from the discovery phase of the project
- Test the most promising materials on an engine

### Accomplishments

- Tested over 4500 materials for NOx reduction potential since the initiation of the project
- A series of loading studies on monolith cores with the first downselected material determined the composition for scale-up to full-size engine monoliths
- Four 5-liter monolith "bricks" were coated for engine testing using the first downselected catalytic material

- Tests of one of the downselected materials on an engine dyno show NOx reductions greater than 80% under some engine conditions even though the net NOx reductions on the Highway and the US06 Federal driving cycles were relatively low
- The GM reactor results using a hydrocarbon mixture of dodecane and xylene (to simulate diesel fuel) indicate what converter/engine conditions are necessary to increase the net NOx reduction

**Future Directions**

- Modify the discovery system in order to use a simulated diesel fuel as the reductant
- Continue the discovery phase of the project to identify materials which increase the net NOx reduction using simulated diesel fuel
- Refine the engine operating strategy to increase the NOx reduction over a full engine cycle
- Develop cold-start/low-temperature engine strategies to meet emission standards over a light-duty Federal Test Procedure (FTP) cycle

## Introduction

The goal of this project is to develop new NOx reduction catalysts for lean combustion systems such as both light- and heavy-duty diesels and for stratified charge gasoline engines. These new catalysts are needed to enable these engines to meet the light-duty vehicle Tier 2 NOx standards for the North American market and the heavy-duty engine standards that are being phased in over the time period between 2007 and 2010.

## Approach

Selective catalytic reduction (SCR) with reductants from the fuel (HC-SCR) is the technology that is the focus of development of these new catalytic materials. The approach is to use high-throughput technology to develop the new materials (Engelhard), informatics to mine the data arising from the fast-throughput experimentation (Accelrys and GM) and classic reactor evaluation to determine the suitability of the new materials for automotive applications (GM and Engelhard). Figure 1 shows the structure of the responsibilities within the project.

## Results

To date at Engelhard, over 4500 new materials have been evaluated on the discovery system since the initiation of the project. Over 100 of these materials have been downselected for detailed
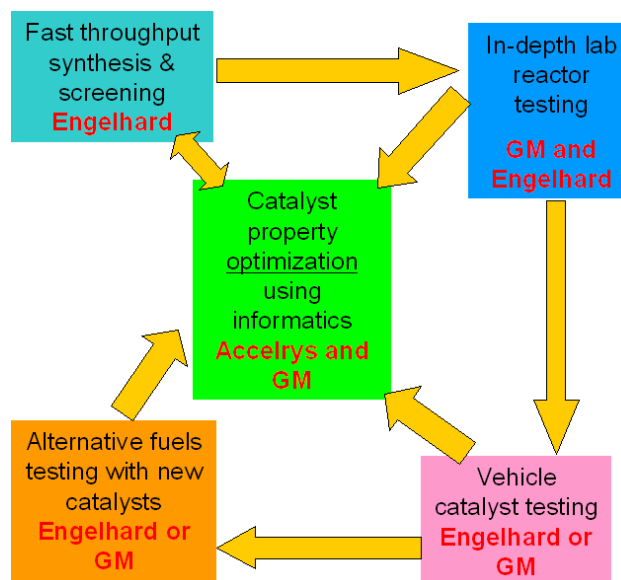


**Figure 1.** Schematic of the NOx Discovery Project and Separation of Tasks

laboratory reactor study. The original selection of a reductant for this study was n-octane, which is representative of the long chain alkanes in typical diesel fuel. Based on those detailed reactor studies, the project has developed materials that give conversions more than twice as efficient as the industry standard for HC-SCR and that compare favorably with urea-SCR for high-temperature applications (see Figure 2). To date, the results from this approach have led to the downselection of at least two materials for intensive feasibility analysis.
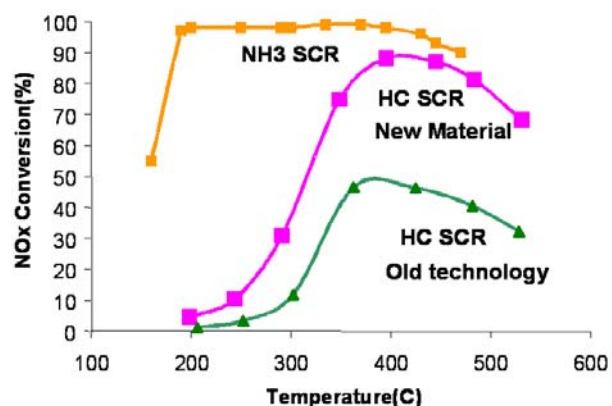
**Figure 2.** Comparison of Urea-SCR, HC-SCR (old technology) and the fast-throughput technology (new material). The HC-SCR materials are coated on monoliths.



**Figure 3.** Schematic shows the test cell design for measurement of emission reduction using the full-size HC-SCR converters. TEX indicates species detectors for the emissions at various points within the aftertreatment system. HC-INJ indicates a system for controlled injection of hydrocarbons into the exhaust stream. TC indicates thermocouples.

These intensive feasibility analysis studies have included reactor studies with a simulated diesel fuel, coating and canning of the materials on full-size monolith bricks and engine testing of these catalysts.

Testing of these materials on GM reactors has evolved from n-octane to using a simulated diesel fuel comprised of 67 vol% n-dodecane and 33 vol% m-xylene. Results on the GM reactor using the simulated diesel fuel are found to be consistent with the engine experiments on the dyno at GM using the canned full-size converters coated with the first downselected material.

The catalyst/dyno setup is shown in Figure 3. The converter can contains two five-liter monoliths for engine testing. This design includes a diesel oxidation catalyst (DOC) to clean up the engine-out hydrocarbons and a dosing system for controlled addition of hydrocarbon to the SCR catalysts. The mixer is added to ensure full vaporization of the fuel before the HC-SCR catalyst. This system is designed for flexibility in modification of the architecture of the experimental aftertreatment system (see Figure 4).

This dyno test system has been used to evaluate the effects of hydrocarbon dosing (carbon to NOx ratios), oxygen concentrations, space velocities and transient effects in the engine environment. Instantaneous NOx conversions measured on the US06 (Figure 5) are consistent with those observed
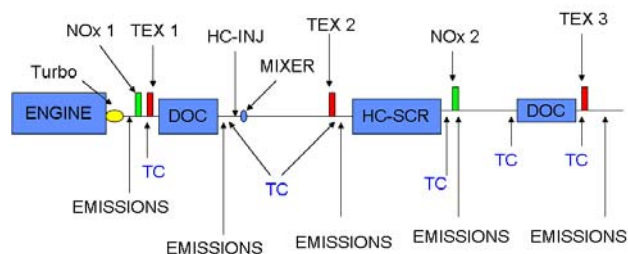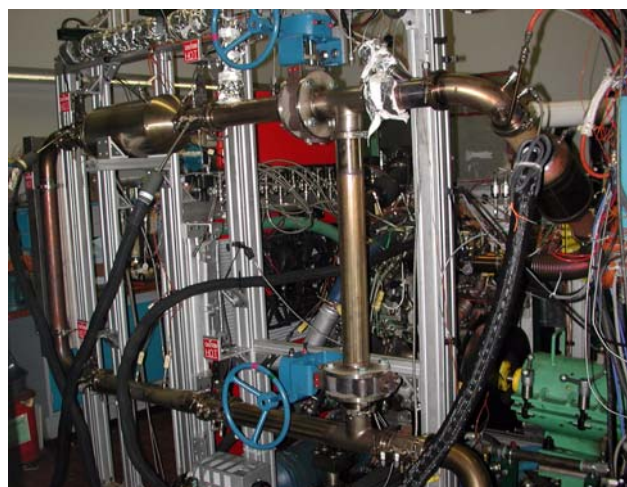


**Figure 4.** Picture of the aftertreatment rack in the test cell designed for the full-size HC-SCR converters and flexibility for the change and modification of the aftertreatment architecture.

from the laboratory reactor experiments (Figure 2). This first set of engine tests has resulted in changes in the conditions that are being used on the discovery system and the conditions that are being used to test scaled-up materials in the GM reactors.

## Conclusions

High-throughput discovery approaches are being applied to finding new NOx reduction catalytic materials that use fuel as the reductant. This
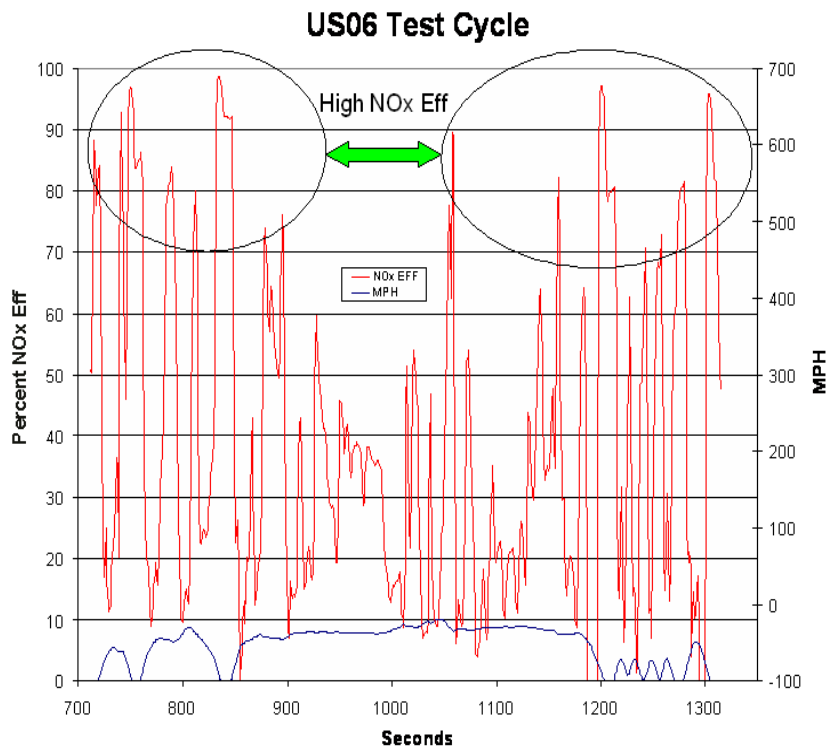
**Figure 5.** Graph of the instantaneous NOx conversion for this HC-SCR dyno measurement over a part of the US06 test cycle. For presentation convenience, the miles per hour in the test cell is added to -100 to move it to the bottom of the graph of the NOx conversion.

approach has been used to test over 4500 materials for NOx reduction potential in approximately 30 months using n-octane as the reductant. Full-size monolith bricks were coated with some of these materials for engine testing. Tests of those bricks on an engine dyno show NOx reductions greater than 80% under some engine conditions, demonstrating a potential for these materials as lean NOx-reducing catalysts. Recent GM reactor testing using a hydrocarbon mixture of dodecane and xylene to simulate diesel fuel shows what engine conditions are needed to develop a viable NOx-reducing system using these catalysts. Further testing is planned to demonstrate the efficacy of these materials as NOx reduction catalysts for lean combustion systems.

**FY 2005 Presentations**

1. "Update on HC-SCR Combinatorial Studies", Eighth CLEERS (Cross-Cut Lean Exhaust Emissions Reduction Simulation) Workshop, University of Michigan-Dearborn, May 17-19, 2005.

2. "Discovery of New NOx Reduction, Hydrocarbon SCR Catalysts Using High Throughput Technologies", the Society of Automotive Engineers (SAE), Government/Industry Meeting, Washington, D.C., May 9-11, 2005.

3. "Discovery of New NOx Reduction, Hydrocarbon SCR Catalysts Using High Throughput Technologies", Gordon Conference on Combinatorial & High Throughput Materials Science, Queens College, Oxford, UK, August 14-19, 2005.

## II.B.12  Efficient Emissions Control for Multi-Mode Lean DI Engines

*Brian H. West (Primary Contact), Shean Huff, John Storey*
*Oak Ridge National Laboratory*
*2360 Cherahala Boulevard*
*Knoxville, TN 37932*

*DOE Technology Development Manager:  Ken Howden*

### Objectives

*   Examine benefits of using hydrocarbon (HC) emissions from low-temperature combustion (LTC) to achieve hydrocarbon selective catalytic reduction (HC-SCR) of NOx.
*   Investigate unusual engine control approaches to enhance catalyst performance.
*   Assess potential for combining HC-SCR with a lean-NOx trap (LNT) to provide an aftertreatment solution for multiple operational modes (e.g., LTC vs. conventional diesel combustion).

### Approach

*   Characterize engine-out emissions in multiple diesel modes (leveraged with other research activities).
*   Evaluate candidate catalysts (leveraged with other research activities).

### Accomplishments

*   Modified LNT regeneration strategies to generate engine-out hydrogen and other reformate products under net-lean conditions.
    *   Individual cylinder control provides up to 0.8% hydrogen with over 1% CO, and 3000 ppm cracked HCs with 9% oxygen in the exhaust.
*   Acquired three commercial HC-SCR catalysts for evaluation.
    *   Leveraged Fuels Technologies Program activity to conduct a preliminary catalyst experiment.
*   Prepared SAE paper for 2006 World Congress meeting.

### Future Directions

*   Evaluate commercial HC-SCR catalysts (Pt, Cu, and Ag) and Pacific Northwest National Laboratory (PNNL) HC-SCR catalyst under variety of engine conditions.
    *   Conventional diesel combustion
    *   LTC
    *   Late-cycle post injection or in-pipe injection of fuel
    *   Individual cylinder control

### Introduction

New combustion regimes are being investigated as a means to improve the efficiency of diesel engines.  Lower engine-out NOx emissions can remove some burden from post-combustion emissions controls and can thereby reduce the fuel penalty associated with NOx reduction.

Additionally, new combustion regimes are sought that will result in improvements in brake-specific fuel consumption (BSFC).  While these regimes will be exploited to the extent possible in future production engines, it is expected that diesels will still run in the more conventional modes at certain operating conditions.  The wide range of operating conditions provides a challenging environment for

the aftertreatment system. Multi-mode operation of the engine will almost certainly require a multi-mode aftertreatment system. This project aims to leverage existing combustion and aftertreatment R&D at Oak Ridge National Laboratory (ORNL), collaborating with industry partners to develop and characterize advanced catalysts to fill this need. While LNT and urea-SCR technology show great promise for reducing NOx under conventional diesel combustion conditions, the lighter-load, low-NOx regimes may require different catalyst technology. Treatment of the HC and CO emissions during low-temperature combustion is of concern. Because of the relatively high HC to NOx ratio in LTC modes, HC-SCR may be an attractive option to augment the LNT or urea-SCR systems.

## Approach

This research has been conducted at ORNL in conjunction with ongoing engine studies. Three related projects at ORNL ("Measurement and Characterization of LNTs" and "Exploring Advanced Combustion Regimes for Efficiency and Emissions" in the Advanced Combustion Engines Program, and "Fuel-Borne and Fuel Derived Reductants" in the Fuels Technologies Program) are being leveraged with this modest activity. Experiments to date have shown that LTC can result in an order of magnitude reduction in NOx, with PM emissions and BSFC comparable to levels at "factory" calibrations. Under these combustion modes, HC emissions have been speciated, and a wide range of reactive compounds have been found, including light alkenes, oxygenates, and other compounds known to be effective HC-SCR reductants. As these HC emissions must be treated, it is logical to consume them as NOx reductant rather than to simply oxidize them. When operating in more traditional combustion regimes, the HC requirements of the aftertreatment system might be fulfilled by injecting additional fuel by a number of means, including in-cylinder injection. The ongoing LNT studies at ORNL have developed strategies for periodic rich operation (necessary for LNT regeneration). Variations of these strategies were developed (under this "Multimode Catalysis" project) to investigate reformate production under net lean conditions. Results of these experiments will be discussed in the Results section. Commercial HC-SCR catalysts have

been obtained from a Manufacturers of Emission Controls Association (MECA) partner and will be evaluated at a variety of conditions in FY 2006. A preliminary catalyst experiment has been conducted (leveraged to and reported by the Fuels Technologies Program activity).

A second approach worthy of study is to examine the potential for a LNT to provide benefit in non-traditional combustion regimes as well as in normal engine operation. Perhaps a HC Lean NOx catalyst upstream of a LNT catalyst would improve HC and NOx treatment for multi-mode engine operation beyond the benefits offered by the LNT. The HC-SCR catalyst would function most or all of the time to remove engine-out HC emissions and treat a portion of the NOx, and the LNT would adsorb the remainder of the NOx, requiring periodic rich operation and regeneration. In addition, some of the in-cylinder fuel reforming approaches used for LNT regeneration may prove useful to HC-SCR, as these strategies can be tuned for high reductant formation while still in an overall lean regime.

## Results

Strategies developed for LNT regeneration have included a late-cycle post injection (80 degrees after top dead center, or Post80), and a delayed extended main (DEM) strategy in which the main injection pulse is extended into the rich regime and retarded to offset any torque increase associated with overfueling. These strategies have been well characterized and results published [1] under the auspices of the related LNT project. An interesting finding in the study of these regeneration strategies was that while the reductant levels from the DEM strategy decreased with increasing air:fuel ratio (AFR), only the HC level changed significantly with leaner AFR for the Post80 strategy (Figure 1). That is, the carbon monoxide (CO) and hydrogen ($H_2$) peaks were relatively constant across the rich AFR sweep for Post80.

Another reported application of reformate is to enhance HC-SCR catalyst function [2-4]. Researchers have shown reformate, or more specifically $H_2$, to significantly improve NO conversion over $Ag/Al_2O_3$ catalysts across a wide temperature range. Additionally, $H_2$ has been shown
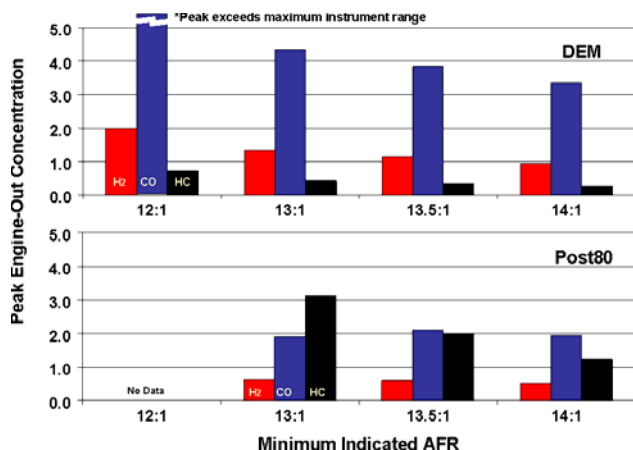
**Figure 1.** Peak Engine-Out Hydrogen, Carbon Monoxide, and Total HC for AFR Sweep, DEM and Post80 Regeneration Strategies
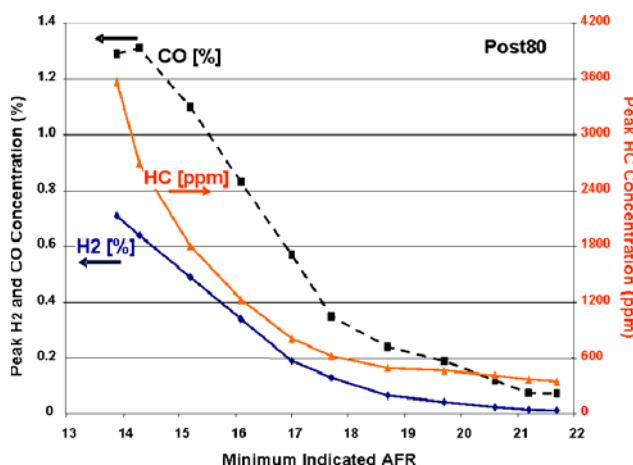


**Figure 2.** Peak Engine-Out Hydrogen, Carbon Monoxide, and Total HC for Post80 AFR Sweep (3 second excursion)

to offset performance losses of HC-SCR catalysts associated with increased space velocity and sulfur presence. The presence of $H_2$ in lean exhaust can also serve to accelerate catalyst light-off [5-7].

The observation with Post80 described above (Figure 1) and in the literature [2-7] led to extending the AFR sweep to leaner conditions, to examine whether the $H_2$ production trend could be extended into the lean regime. Results of this experiment are shown in Figure 2. The data show that for a short (3 second) fueling pulse, appreciable concentrations of hydrogen can be produced even at lean indicated AFR. Peak $H_2$ concentration during these "regenerations" drops from a peak of 0.7% near 14:1

AFR to about 0.1% at 18:1 AFR. The objective of this experiment was to assess the $H_2$ production for an extension of a well-characterized LNT regeneration strategy [1]. A similar experiment was conducted using the DEM strategy, and much lower $H_2$ levels were detected, dropping rapidly above AFR leaner than stoichiometry.

The DEM LNT regeneration strategy produces more $H_2$ and less HC than Post80, but as the strategy is leaned out, $H_2$ production drops quickly to zero. The concept of individual cylinder control to generate reformate in net lean conditions was developed to overcome this limitation. The strategy commands that 1 cylinder be rich while the other 3 cylinders remain lean. To preclude engine imbalance and perhaps premature engine wear, each cylinder is programmed to run rich for only 400 milliseconds (ms), although this parameter is adjustable. For example, cylinder 1 runs rich for 400 ms while cylinders 2-4 run lean. When cylinder 1 transitions back to lean operation, cylinder 3 (the next cylinder in firing order) transitions into the rich regime. For the data shown above in Figure 1, and in typical LNT regenerations, the throttle is ramped down to some minimum, excess fuel is injected, then the throttle is returned to full open during lean operation. For the individual-cylinder DEM experiments described herein, the throttle was fixed at 20% open while individual cylinders were cycled through rich operation for 400 ms at a time. For the engine condition studied (nominally 1500 RPM, 5 bar BMEP), using this throttle strategy, the nominal AFR drops from about 31 to about 26 (for all 4 cylinders). For this condition, the pilot and main pulse widths are 220 and 600 microseconds (µs), respectively. An AFR sweep was conducted in which the selected "rich" cylinder was fueled at 1.0, 1.5, 2.0, 2.5, and 3.0 times the normal main injection (600, 900, 1200, 1500, and 1800 µs, respectively). Figure 3 shows results of the individual-cylinder DEM AFR sweep on reductant formation. Continuous rich operation of one cylinder at a time can produce over 0.7 percent $H_2$ with about 1.3% CO, about 3000 ppm total HC (THC), with over 9% oxygen remaining in the exhaust.

Examining some of the HC species with Fourier Transform Infra-Red (FTIR) reveals copious amounts of methane for the richest case (300%
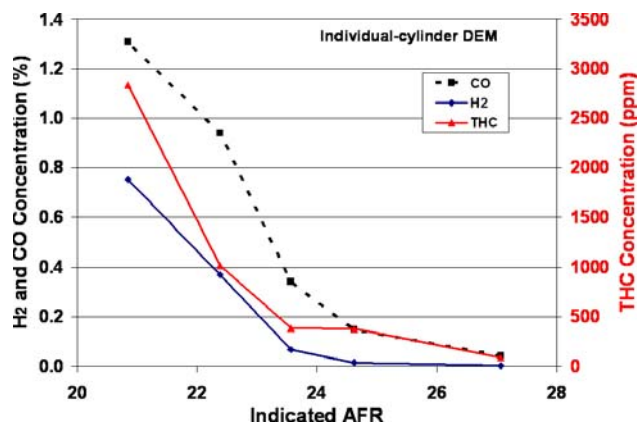
**Figure 3.** Continuous Hydrogen, CO, and Total HC Emissions for Individual-Cylinder DEM Strategy
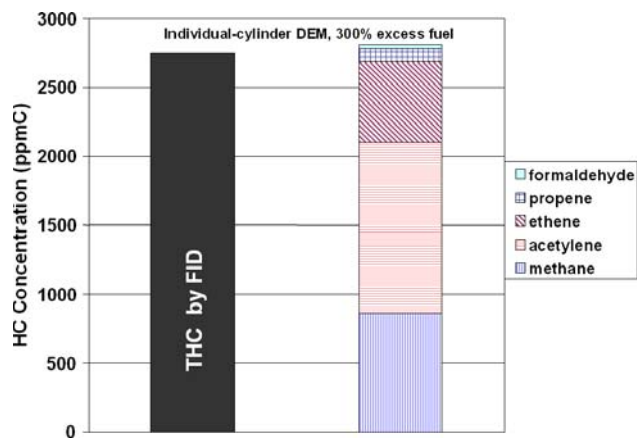


**Figure 4.** Engine-Out HC Species (by FTIR) for Continuous Individual-Cylinder DEM Strategy

excess fuel in main injection for 1 cylinder). Figure 4 shows that a few light HC species readily quantified by FTIR more than account for the total flame ionization detector response. With the exception of methane, these species are known to be effective HC-SCR reductants [8-9].

These results are encouraging for potentially enhancing catalyst performance or for promoting catalyst system warmup. A preliminary HC-SCR catalyst experiment was conducted at the richest individual-cylinder DEM condition, and results are reported in the "Fuel-Borne and Fuel Derived Reductants" submission in the Fuels Technologies Annual Report.

## Conclusions

Strategies previously developed for in-cylinder regeneration of LNTs have been modified to allow production of $H_2$ and other reformate products (e.g., CO, light HCs) under net-lean exhaust conditions. Notable conclusions are the following:

- Reducing the excess fuel for the normally rich Post80 LNT regeneration strategy results in net lean production of $H_2$, CO, and HC. Moderating the DEM in a similar fashion produces very little $H_2$ and CO in the lean regime.

- Running 1 of 4 cylinders with a rich DEM strategy can produce a continuous stream of up to 0.8% $H_2$, over 1% CO, and 3000 ppm HC in net lean exhaust with over 9% $O_2$ remaining.

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2. Shigeo Satokawa, Junji Shibata, Ken-ichi Shimizu, Atsushi Satsuma, Tadashi Hattori, "Promotion Effect of $H_2$ on the Low Temperature Activity of the Selective Reduction of NO by Light Hydrocarbons over $Ag/Al_2O_3$," Applied Catalysis B: Environmental, 2003, 42, 179-186.

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## FY 2005 Publications

1. Brian West, Shean Huff, James Parks, Matt Swartz, Ron Graves, "In-Cylinder Production of Hydrogen During Net-Lean Diesel Operation," SAE World Congress, April 2006 (in press).

## FY 2005 Presentations

1. Brian West, Shean Huff, James Parks, Matt Swartz, Ron Graves, "In-Cylinder Production of Hydrogen During Net-Lean Diesel Operation - Preliminary Results," presented to the Advanced Combustion and Emission Control Technical Team, November 10, 2005.

## II.B.13  Advanced NOx Control for Diesel Engines Based on Hydrocarbon Oxygenates as Active Reductants over Lean-NOx Catalysts

*Darrell R. Herling (Primary Contact), Ken Rappe, Chris Aardahl*
*Pacific Northwest National Laboratory*
*P.O. Box 999, MS: K2-03*
*Richland, WA  99352*

*DOE Technology Development Manager:  Ken Howden*

### Objectives

The goal of this project is to provide fuel-efficient and economical oxides of nitrogen (NOx) emission control options for continued use of lean-burn energy-efficient diesel engines for off-highway industries.  Specific project objectives include:

*   Achieve a minimum of 70% NOx reduction

*   Demonstrate compatibility with fuel-sulfur levels up to 3,000 ppm

*   Treat mass flow rates up to 15 lbs/sec, with NOx concentrations up to 1,500 ppm

*   Obtain <1.5% fuel economy impact

### Approach

*   Develop process for the conversion of fuel to oxygenates
    *   Hydrocarbon reformation of alkanes to syngas via:
        -   Partial oxidation (POx), autothermal, cracking/pyrolysis
        -   Non-thermal plasma and plasma-catalyst combinations
    *   Chemical synthesis of reformate ($H_2$/CO) to produce desired reducing agents, such as alcohols, dimethyl ether (DME), etc.
*   Use oxygenates as the active reductant or intermediate in lean-NOx chemistry, supported by formulation development
*   Use of oxygenates as reductants has been shown to enhance lean-NOx performance

### Accomplishments

*   Demonstrated DME to be an excellent reducing agent for NOx

*   DME shown to exhibit high selectivity of NOx to $N_2$; acceptable NOx reduction can be achieved at $C_1$:NOx = 3 over an alumina catalyst

*   Confirmed that methanol is also a good reductant, but DME/methanol blending has not been performed to date in bench experiments

*   Initiated mechanistic studies to determine why DME is an effective reagent and to determine effects of syngas on lean-NOx performance

*   Reformer-assisted method shows good promise as an effective means of significantly increasing lean-NOx performance, without a significant brake-specific fuel consumption (BSFC) penalty

### Future Directions

*   Continue process development for POx

- – Examine alternate reforming catalysts
- – Use exhaust as oxidant and water source
- Continue evaluation of flash-distillation concept
- Complete mechanistic work to determine why DME is such a good reductant, and elucidate syngas effects
- Examine DME/methanol blends
- Lock in catalyst formulations and scale up for demo
- Assist General Electric (GE) with engine demonstration
  - – Provide catalyst washcoating expertise
  - – Provide reductant synthesis apparatus for engine test
- Consider fuel-borne DME as a path forward for locomotive fuel
  - – Collaboration with Oak Ridge National Laboratory (ORNL)

## Introduction

The diesel engine is the dominant power source for heavy-duty off-road vehicles worldwide due to its relatively high thermal efficiency, reliability, and ability to deliver power under extended high-load conditions. Despite its attractive operating cost and power delivery features, diesel combustion is under challenge due to significant NOx and particulate emissions in the exhaust.

Aftertreatment technology often comes at the price of fuel efficiency. For aftertreatment technology to be successfully introduced, it must be robust, retrofittable to older platforms, tolerant of higher sulfur levels (especially for off-road vehicles), and have a minimal impact on fuel efficiency. Experience with automobile aftertreatment has shown that a successful catalytic system can have a high degree of commercial viability. The case for catalytic aftertreatment in off-road applications is not different except for the additional technical challenges inherent in the diesel fuel source and powertrain system.

Several technologies are being examined for on-road applications, including selective catalytic reduction (SCR) with urea, active lean-NOx catalysis, and regenerative lean-NOx traps (LNT). A survey of the off-road industry shows a strong bias to avoid carrying urea on-board the vehicle. In addition, off-road fuel does not currently allow the use of LNT technology because of the relatively high level of sulfur in the fuel typically used for off-road. The relatively steady-state exhaust temperatures of

most off-road applications ($\sim$ 350-450°C) makes lean-NOx catalysis a judicious choice for developing a durable approach, without the need to carry an additional reagent such as urea. Over the past few years, several -alumina-based catalysts have been discovered that show promise for active lean-$NO_x$ catalysis in temperature ranges applicable to off-road diesel exhaust. Results have also shown that use of hydrocarbon oxygenates as a reducing agent significantly improves the NOx reduction selectivity and decreases the sensitivity to fuel-sulfur.

## Approach

The research focus for this project is to develop a process to transform diesel fuel to active reagents that are highly selectable for lean-$NO_x$ catalysis. An additional focus is on catalyst investigation and discovery of enhanced formulations that work synergistically with specific alcohol, ether, and aldehyde reducing agents to reduce NOx. The scope of work involves building the necessary understanding of hydrocarbon (HC) reforming to execute design and testing of catalytic reactors capable of converting diesel fuel HCs into oxygenated species, such as methanol, dimethyl ether, or acetaldehyde. Such oxygenates are known to be active reagents for lean-NOx catalysis. This process will then be demonstrated on a bench-scale lean-NOx system, followed by slip-stream engine testing.

The technical approach includes a three-step method involving the conversion of diesel fuel (light fraction) to syngas, followed by a synthesis process

to form dimethyl ether (DME) and methanol (MeOH) utilizing the syngas feedstock. Catalytic partial oxidation (cPOx) reforming is the most attractive approach for reforming fuels with high sulfur levels, primarily due to high process temperatures where sulfur compounds are less likely to absorb, and is the one selected for use.

The specific steps utilized for hydrocarbon fuel treatment and conversion to oxygenates are as follows:

- Distillation of diesel fuel to separate light HC fraction ($<C_{12}$) from the heavier HC portion which contains the majority of sulfur components.
- Reforming of light HC fraction by POx to produce syngas
- Synthesis of DME/MeOH mixtures at pressure from syngas feedstock

Oxygenate products are then injected upstream of the lean-NOx catalyst for subsequent deNOx chemistry and enhanced lean-NOx performance. A schematic of the system is shown in Figure 1, and Figure 2 shows a schematic of the bench-scale POx
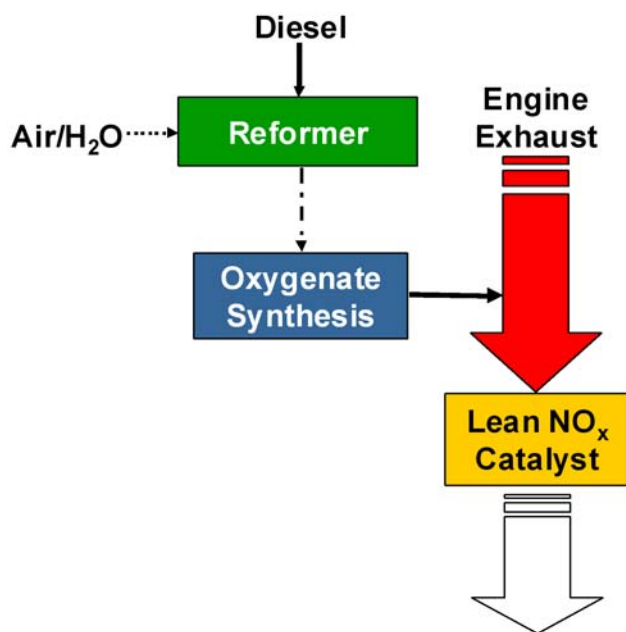
reactor apparatus used for the experimental work, from which the effluent then feeds into the chemical synthesis system. These systems are used for the evaluation of the processes, product speciation, and process parameter development of POx and reductant synthesis methods.

## Results

The effect of aftertreatment on vehicle fuel consumption is a serious issue surrounding new catalysis technologies. All emerging aftertreatment technologies require some degree of reagent be used for reducing NOx in a predominately oxygen-rich exhaust environment. For most technologies, the fuel penalty (or equivalent in the case of urea-SCR) is typically 4-6%. This is a significant amount of fuel utilization for emission reduction, and fuel that could otherwise be used for propelling the vehicle.
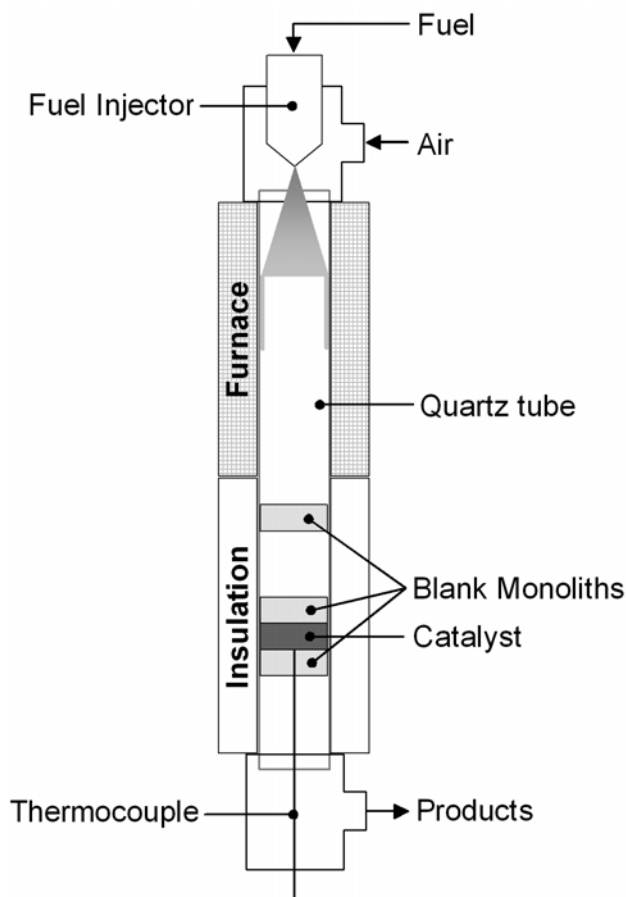


**Figure 1.** Conceptual Schematic of Fuel Processing System and Integration with Lean-NOx Catalyst Aftertreatment



**Figure 2.** Schematic of the Experimental POx Reactor Design

One of the objectives of this project is to improve the conversion efficiency and selectivity of NOx to $N_2$, such that the fuel penalty associated with treating the exhaust pollutants is minimized to a point less than 1.5%. Using DME as the primary reagent has shown that the $C_1$:NOx ratio required for 70% NOx reduction can be as low as 3:1. This is in contrast to typical lean-NOx performance, which requires 6:1 or even 12:1 $C_1$:NOx ratios to achieve only 40% NOx reduction. However, even with this reduction in reagent requirement and fuel penalty, further fuel consumption reduction is being investigated by re-tuning of the engine in conjunction with the aftertreatment. As shown in Figure 3, the concept involves adjusting the engine timing in order to decrease engine fuel requirements. When the engine timing is changed one result is that the combustion temperature increases. An increase in temperature tends to increase the engine NOx concentration output. In such a scenario the efficiency (activity) of the aftertreatment system becomes ever more critical for control of NOx output. If the aftertreatment technology can be designed to successfully treat the higher engine-out NOx concentration, then with the overall BSFC (engine + aftertreatment fuel consumption) can likely be minimized. Modeling results of the BSFC for a diesel engine with the reformer-assisted lean-NOx aftertreatment system suggests the fuel required for adequate NOx aftertreatment reduction can be less than 1.5%.
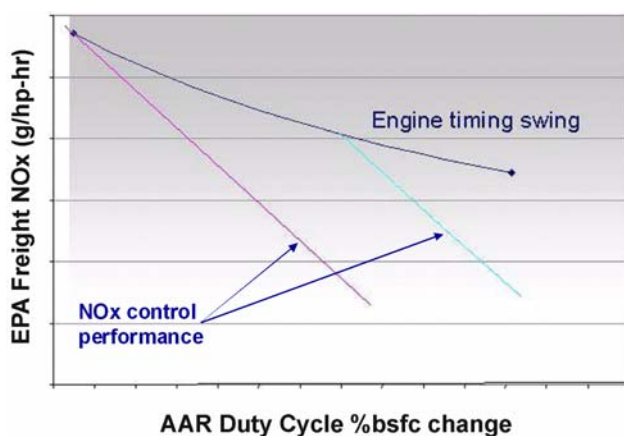
**Fuel-Sulfur Removal via Flash Distillation**

Some lean-NOx catalyst formulations and the synthesis catalysts utilized for DME/MeOH production are susceptible to sulfur poisoning. Therefore, a method to reduce the level of sulfur in the fuel prior to fuel reforming is necessary in order to meet system performance and durability goals. The method employed for this system consists of separating the light hydrocarbon fraction ($<C_{12}$) from a slip-stream of diesel from the fuel tank. The make-up and design of this system were described in previous reports. Figure 4 shows an update on the sulfur removal performance with this system. Modeling results predict that about 60% of the sulfur will be removed from this stream, where experimental validation results show that over 70% of the sulfur is actually removed. This results in a much lower concentration of sulfur prior to the DME synthesis step, further reduction of which is achievable by employing a zinc-based sulfur getter.

**Catalytic Partial Oxidation of Fuel**

The gas-phase HCs from the distillation step are then fed into the POx to convert the fuel to syngas. With the right operating conditions, there is potential for direct partial oxidation from diesel to mixtures of olefins, aldehydes, and organic acids. For the conversion of diesel fuel to syngas, the approach must of course be sulfur-tolerant, resistant to coking,
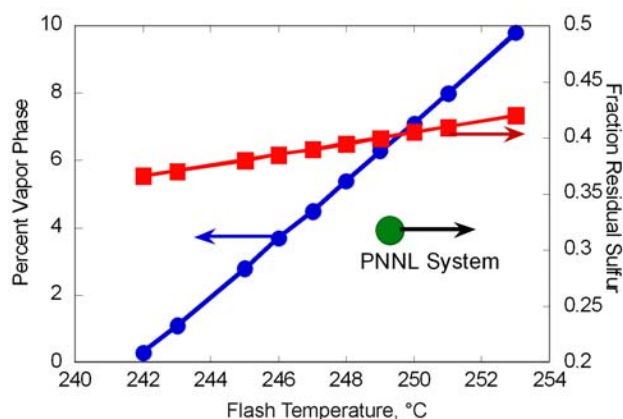


**Figure 3.** Aftertreatment and Engine Tuning Impact on NOx Cycle & BSFC



**Figure 4.** Flash Distillation Modeling and Experimental Results Using 1000 ppm Sulfur (Dibenzothiophene) in Diesel Fuel

and have good selectivity to CO and $H_2$. The ideal ratio of $CO/H_2$ in the products is 2:1 for use as the feedstock into the chemical synthesis process for the production of DME and MeOH. Because POx is an exothermic reaction, and temperatures range from 700°C-900°C, the process is expected to be resistant to sulfur poisoning and coking. However, since it is not necessarily an equilibrium-controlled process, there is a relatively low degree of control over product distribution beyond selecting the proper C/O inlet ratio, reforming catalyst formulation, and catalyst contact time.

Experimental results from cPOx of n-decane (used as a surrogate diesel fuel) are shown in Figures 5 and 6, showing good conversion and fair selectivity to $H_2$ and CO products. The reactor pressure was maintained at 1 atm, at which the combustion ratio (C/O) for n-decane is 0.323, and the C/O ratio was adjusted above this point in order to determine at what ratio the peak $H_2$ and CO yield occurs. Experiments were conducted at a flow rate that achieved a contact time of 6 ms. The reforming catalyst used was comprised of an 80-ppi reticulated -alumina monolith used for the catalyst support, which was washcoated with -alumina and doped with 4-6 wt% Rh metal.

The work focused on chemical characterization of cPOx products and the oxidation catalyst evaluation. This was achieved using a customized sampling/chromatographic assembly on-line, which allows accurate characterization of the unburned fuel; cracking and incomplete oxidation products; C, H, and O balances. This analytical method is essential, as accurate product stream analysis will provide direction on cPOx reactor operation and performance.

**DME/MeOH Synthesis**

The catalytic chemical synthesis of DME/MeOH was chosen for production of reductants due to the decrease in operating pressure required versus MeOH synthesis alone. DME/MeOH synthesis from syngas is an exothermic process that is equilibrium-favored at relatively low temperatures (240-280°C) and relatively high pressures (200-600 psig). Synthesis gas conversion to DME/MeOH is equilibrium-hindered by nitrogen dilution (from the POx reaction) via a decrease in the partial pressure of $H_2$ and CO. The DME selectivity at various temperatures and pressures is shown in Figure 7. The effect of nitrogen dilution on the equilibrium conversion and experimental data is presented in Figure 8.
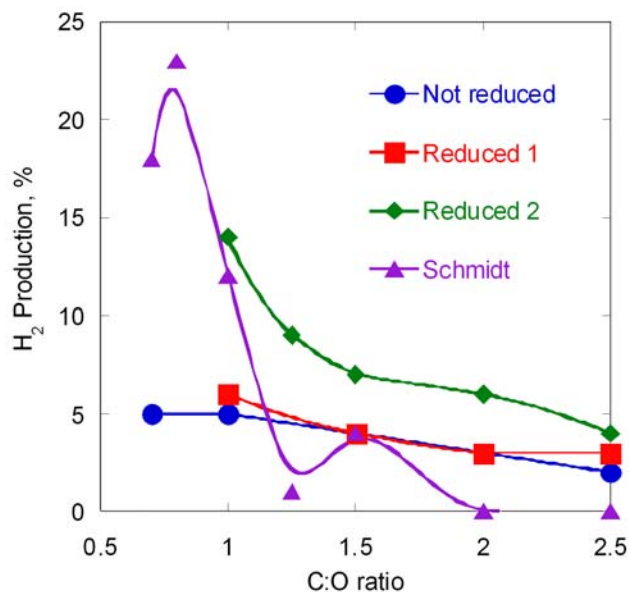


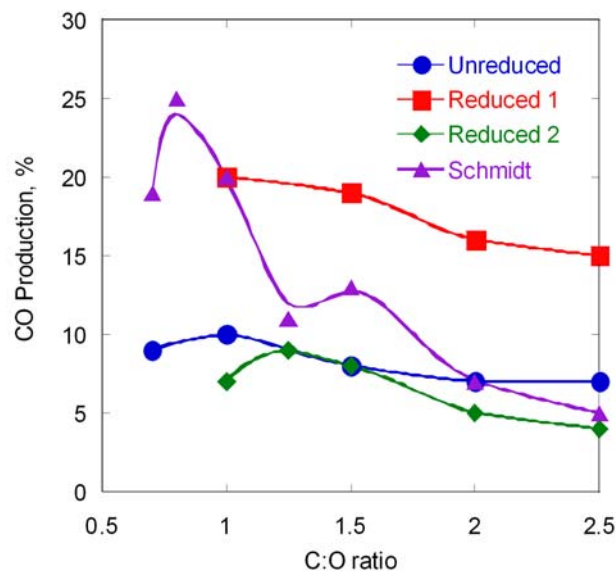**Figure 5.** Hydrogen Production from n-Decane via cPOx (8 SLPM reactor flow)



**Figure 6.** Carbon Monoxide Production from n-Decane via cPOx (8 SLPM reactor flow)

The syngas stream produced from the fuel POx reformer is pressurized to 200-300 psig and passed over a Cu/Zn catalyst which is physically mixed with a 1:1 ratio of an acidic -$Al_2O_3$ at 240-280°C to form a mixture of DME, MeOH, hydrogen, carbon monoxide, carbon dioxide, and nitrogen. The current testing apparatus utilizes simulated syngas which is delivered via Brooks mass flow controllers. The simulated syngas is pre-heated before entering an oil-heated catalytic reactor at the desired reaction pressure (100-300 psig). The product gas mixture from the reactor is then chilled to remove condensable constituents ($H_2O$ and MeOH) prior to analysis via an Agilent four-column micro-GC which utilizes thermal conductivity detectors.

**Lean-NOx Catalyst Formulation**

The benefits of using fuel-based oxygenates for lean-NOx catalysis are better selectivity and higher activity, while reducing the $C_1$:NOx ratio necessary for adequate conversion. The enhanced selectivity means that higher space velocities can be achieved, which results in smaller catalysts and more efficient on-vehicle packaging. In addition, the use of certain oxygenates has been shown to improve the sulfur tolerance of common lean-NOx catalysts.

High-throughput screening techniques are being used to accelerate testing of numerous variables within the catalyst design space, while facilitating the high-risk, innovative experiments that would be too costly and time consuming in a conventional reactor system. To date, screening of over 400 mixed-metal oxide catalyst formulations has been completed using five specific reductants, two of which where DME and MeOH.

In addition to the combinatorial catalyst screening of new formulations, micro-reactor scale testing of -$Al_2O_3$ has been performed. These experiments were designed and conducted to provide insight on the performance and sensitivities of using DME and MeOH as reagents. This study revealed that DME is an excellent reducing agent for NOx, with greater than 70% peak NOx conversion and higher selectivity compared to using alkanes or diesel fuel as the reductant. The highest activities were achieved with no amount of metal promoter mixed into the alumina, which suggests that DME may be a direct reagent for NOx (i.e., no intermediate species formed on the catalyst surface). Another possible pathway is oxydehydrogenation of DME to produce formaldehyde, which is thought to be the actual active reagent for NOx.

Since the reforming method consists of producing syngas feed for on-board DME synthesis, it is likely that a portion of the product stream feeding the lean-NOx catalyst bed will include some amount of $H_2$ and CO. Because of this possibility, experiments were conducted to determine the effect of syngas on the NOx conversion performance in the
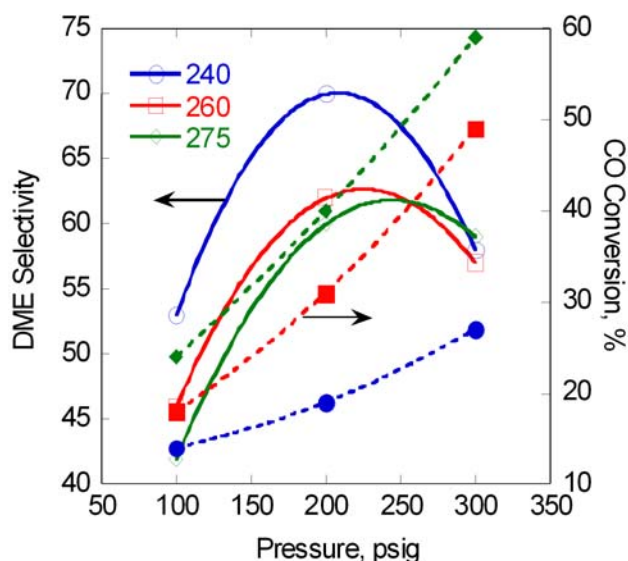


**Figure 7.** Experimental Selectivity Results for DME Production from Syngas
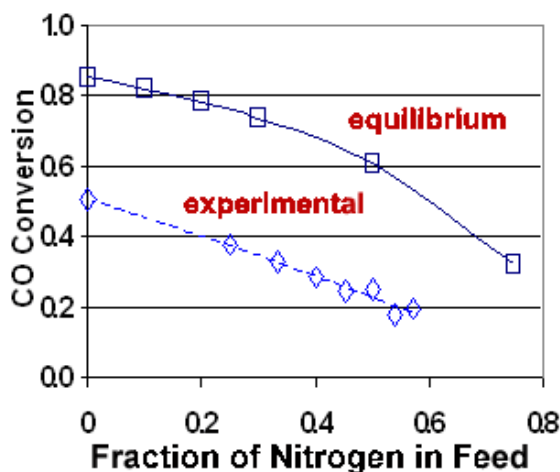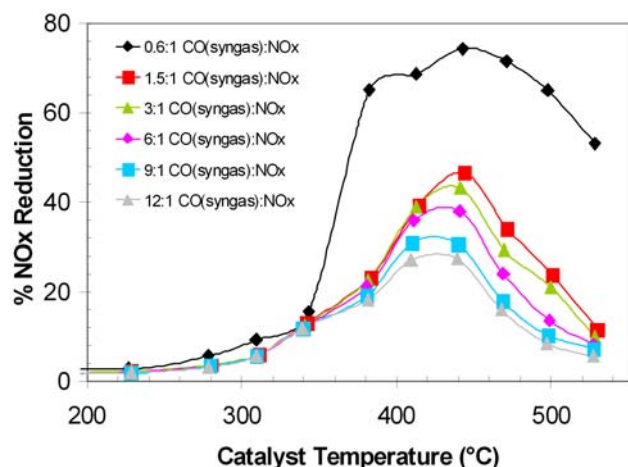


**Figure 8.** Nitrogen Dilution Effect on DME Synthesis

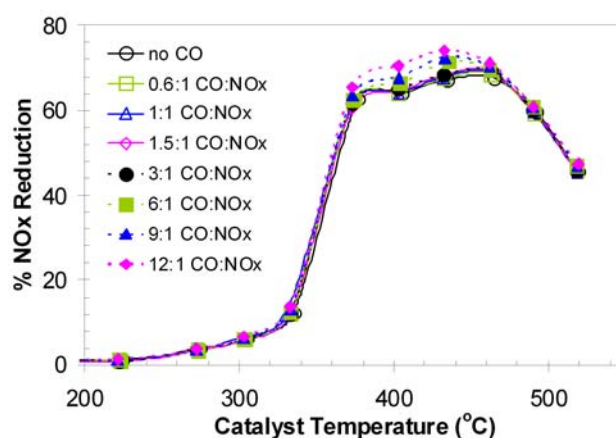**Figure 9.** Effect of Syngas with DME Lean NOx



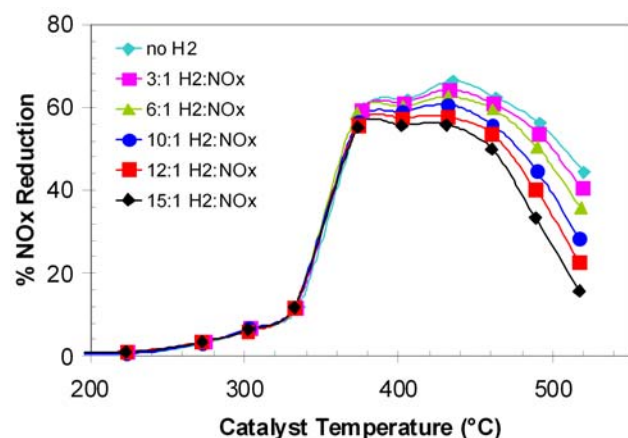**Figure 11.** Effect of Carbon Monoxide on NOx Conversion



**Figure 10.** Effect of Hydrogen on NOx Conversion

presence of DME. Figure 9 shows the experimental results. When syngas is supplied to the catalyst in ratios much above 1:2 compared to the NOx concentration, a significant reduction in NOx conversion occurs. However, as shown in Figures 10 and 11, this reduction in activity is not the case when just $H_2$ or CO is supplied in the stream. There appears to be some sort of synergistic effect when $H_2$, CO, and DME are all applied to the catalyst. A mechanistic study has been initiated to understand the reaction sequence associated with this phenomenon and to determine why DME and formaldehyde are such good reagents.

## Summary

High NOx reduction activity of >70% was demonstrated using lean-NOx catalysis with DME and MeOH as the reagent. These validation experiments were conducted using a micro-reactor synthetic gas bench and undoped –alumina. This reflects a performance increase of over 30% relative to using the same catalyst formulation with diesel or propene as the reagent. Two other specific oxygenates were identified to work well with conventional lean-NOx catalyst and also demonstrated enhanced performance when used in conjunction with specific multi-mixed metal oxide catalyst formulations. Over 400 specific catalyst formulations and variations were screened using combinatorial catalysis methods, the results of which have revealed some strong leads on catalyst-reductant pairs.

A bench-scale cPOx reactor experimental apparatus was designed and constructed for fuel reforming process development. In addition, an alcohol synthesis reactor was updated to process syngas for the production of DME and MeOH. Experimental work was initiated to develop a database on selectivity and activity of products possible using the reductant synthesis process from syngas feedstock. To date, the concept of reforming a diesel fuel surrogate to syngas, followed by DME synthesis, has been demonstrated at the bench scale.

## Special Recognitions & Awards/Patents Issued

1. Method of Generating Hydrocarbon Reagents from Diesel, Natural Gas and other Logistical Fuels, filed May 2005.
2. Catalyst System and Method for the Reduction of NOx, filed December 2004.
3. Catalyst System and Method for the Reduction of NOx with SOx, filed December 2004.

## FY 2005 Publications/Presentations

1. Chris Aardahl, Darrell Herling, Ken Rappe, "Reformer-Assisted Catalysis for NOx Emissions Control," 2nd Annual Advanced Reciprocating Engine RD&D Meeting, Diamond Bar, CA, March 2005.
2. Chris Aardahl, Darrell Herling, Ken Rappe, "Reformer-Assisted Lean NOx Catalysis for Diesel Engine Emissions Control," 229th National Meeting of the American Chemical Society, San Diego, CA, March 2005.
3. Ken Rappe, "Reformer-Assisted Lean-NOx Catalysis for Diesel Emissions Control," Green Car Congress, March 2005.
4. Chris Aardahl, Darrell Herling, Ken Rappe, "Reformer-Assisted Catalysis for NOx Emissions Control," 19th North American Meeting of the North American Catalysis Society, Philadelphia, PA, May 2005.
5. Jonathan Male, "Accelerated Catalyst Discovery," 8th Annual CLEERS Workshop, Dearborn, MI, May 2005.

## References

1. Orehowsky, G., "Emission standards for locomotives and locomotive engines," Locomotive Emissions and System Efficiency Workshop, 2001, January 30–31, Argonne National Lab., Argonne, IL.
2. Hoard, et.al., SAE (2001)
3. Panov, et.al., SAE (2001)
4. Tran, D.N.; Aardahl, C.L.; Rappe, K.G.; Park, P.W.; Boyer, C.L.; "Reduction of NOx by plasma-facilitated catalysis over In-doped -alumina," Applied Catalysis B: Environmental, Vol: 48, Issue: 2, March 18, 2004, pp. 155-164.
5. Rappé, K.G.; Hoard, J.W.; Aardahl, C.L.; Park, P.W.; Peden, C.H.F.; Tran, D.N.; "Combination of low and high temperature catalytic materials to obtain broad temperature coverage for plasma-facilitated NOx reduction," Catalysis Today, Vol: 89, Issue: 1-2, February 29, 2004, pp. 143-150.

## Acknowledgments

# II.B.14 NOx Control for High Power Density Hydrogen Engine

*Todd J. Toops (Primary Contact) and Jim E. Parks*
*Oak Ridge National Laboratory*
*2360 Cherahala Blvd.*
*Knoxville, TN 37932*

*DOE Technology Development Manager: Ken Howden*

## Objectives

- Develop testing matrix for the appropriate evaluation of NOx control systems
- Evaluate NOx abatement catalyst systems under typical $H_2$ internal combustion engine (ICE) exhaust conditions
  - Lean NOx traps (LNTs)
  - $H_2$ selective catalytic reduction (SCR)
  - Urea SCR

## Approach

- Conduct literature search to determine appropriate catalysts to use for each area of interest
- Work with industry to establish a meaningful testing protocol for each system and to establish typical $H_2$ ICE exhaust conditions
- Evaluate powder catalysts on a bench-scale reactor
- Analyze the effect of precious metal loading on LNT catalysts when only $H_2$ is used in the rich cycle

## Accomplishments

- Demonstrated greater than 90% NOx conversion for the LNT system between 300 and 400°C, with an approximate fuel penalty less than 5%
  - Greater than 60% NOx conversion at 500°C
- Achieved greater than 95% NOx reduction from 300 to 600°C using $NH_3$ concentrations between 200 and 1600 ppm

## Future Directions

- Evaluate LNT catalysts with core reactor to more accurately assess fuel penalty constraints
  - Better approximation of onboard system
  - More detailed analysis of cycling effects
  - Fully-formulated catalyst for high-temperature applications
- Evaluate urea SCR catalysts with core reactor study
  - Incorporate urea solution rather than $NH_3$ gas
  - Core reactor analytical tools allow verification of reductant slip
- No current plans to continue $H_2$ SCR study with core reactor

## Introduction

An increasing national focus on moving towards a hydrogen economy calls for hydrogen-enabled internal combustion engines as a near-term transition technology. While there is potential for these engines to reduce carbon emissions from vehicles, NOx emissions are still problematic (Ford Motor Company in SAE#2002-01-0242), and control of NOx emissions with aftertreatment will most likely be required. Delegates at the DOE Advanced Combustion and Fuels Workshop (held June 16 and 17 of 2003) also noted the need for emission controls on hydrogen-fueled engines. Oak Ridge National Laboratory's (ORNL's) support to the Systems Analysis Program has for several years focused on providing data for important engine and emissions control related systems for use in larger systems-analysis models that estimate the fuel economy and emissions potential of multiple vehicle configurations. This area is a unique strength of ORNL and is the area in which ORNL can contribute the most to the FreedomCar Vehicle Systems Program. ORNL's involvement with the fuels, engines, and emissions control research areas puts ORNL in a unique position to bring input from these areas to the Systems Analysis Program.

## Approach

Since little work has been performed in the area of lean NOx reduction for hydrogen ICEs, it is not clear which NOx reduction strategy is best suited to meet the emissions requirements. It is expected that one of the systems being studied for compression ignition direct injection (CIDI) engines – i.e. lean NOx, urea SCR, or NOx adsorber catalysts – will be required in a hydrogen ICE. The ORNL team will investigate these strategies on a bench flow reactor under typical operating conditions to determine which is best suited to hydrogen-fueled vehicles. The catalyst or trap materials and cores for the experimental work will be sought from major suppliers through informal collaborations. Additionally, ORNL can formulate catalyst samples (model catalysts) for bench-scale work as needed.

Urea SCR uses ammonia (from the urea source) to reduce NOx in oxidative conditions. Current models of SCR catalysts in CIDI exhaust conditions

will need to be evaluated and modified for lean-burn hydrogen engines.

Lean NOx and NOx adsorber catalysts can make use of on-board fuel (hydrogen) to reduce NOx. Successful expansion of current CIDI models of these catalysts for hydrogen applications will require in-depth investigation of the interaction of hydrogen with the catalysts under lean-burn hydrogen engine exhaust conditions. Lean NOx catalyst performance will depend on the selectivity of new catalyst materials that must preferentially react hydrogen with NOx instead of oxygen. NOx adsorber catalysts are expected to adsorb NOx in a similar fashion to CIDI applications, but NOx reduction ("regeneration") with pure hydrogen fuel will be a dynamic chemical and thermal process that will require thorough evaluation and study for efficient and safe catalyst operation.

## Results

Discussions with Bob Natkins at Ford have resulted in a research plan for the three catalyst systems of interest: LNTs, urea SCR, and $H_2$ SCR. The temperature range will cover 300 to 600°C, with a space velocity of 30,000 h$^{-1}$ and a lean exhaust concentration based on =0.55 (400 ppm NO, 8.4% $O_2$, 10% $H_2O$, balance Ar). For LNT studies that require a brief rich excursion, the concentrations will be based upon a 5% fuel penalty with 43 s lean and 3.4 s rich. The powder reactor and chemisorption system is equipped with a four-way fast-switching valve and a quadrupole mass spectrometer for lean/rich cycling and monitoring of the effluent, respectively.

LNT powder experimentation is complete. Initially, experimentation compared barium-based (1% Pt/20% BaO/Al$_2$O$_3$) and potassium-based (1% Pt/8% K$_2$CO$_3$/Al$_2$O$_3$) LNT catalysts, and no significant difference was observed, as shown in Figure 1. It was decided to focus the remainder of the LNT effort on the most widely studied LNT, Pt/Ba/Al$_2$O$_3$. Figure 1 also shows that the LNT approach to NOx reduction is effective between 300 and 400°C, but activity begins to drop off at 500°C, and virtually no activity is observed at 600°C. The amount of Pt was varied from 1.0% to 0.5% in this study, and the individual isotherms were measured
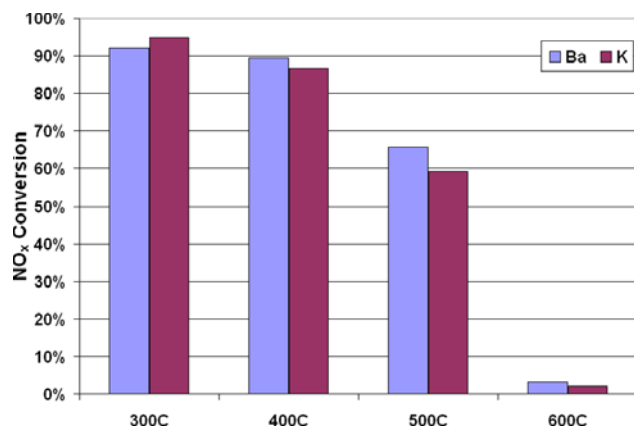
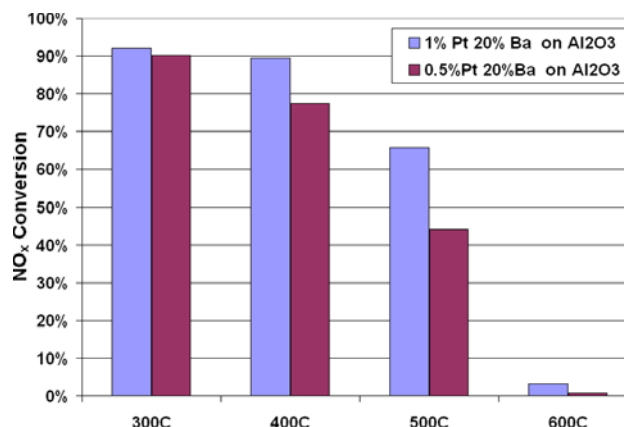**Figure 1.** K- and Ba-based Model LNTs Evaluated from 300-600°C Show Nearly Identical NOx Conversion.
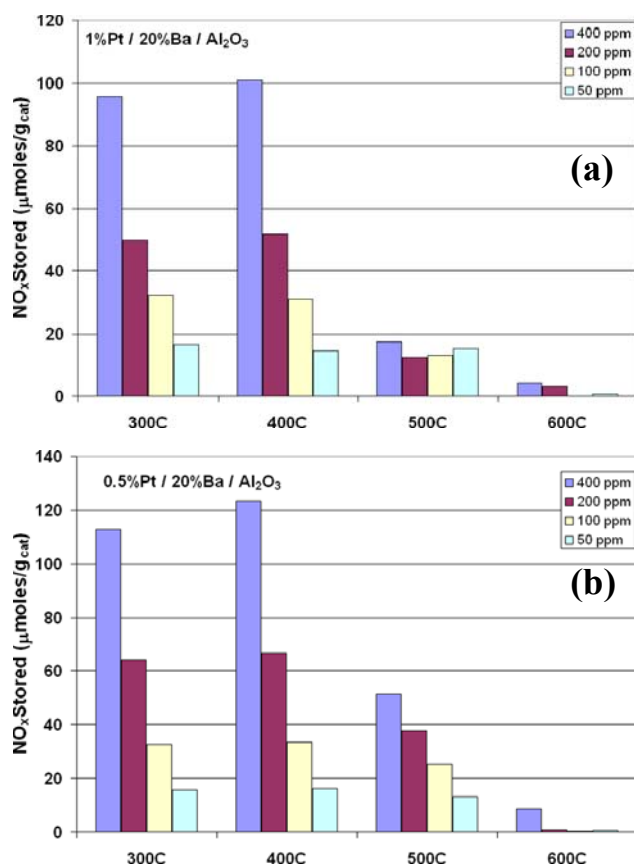


**(a)**

**(b)**

**Figure 2.** NOx Isotherms for (a) 1.0% Pt/20% BaO/ Al$_2$O$_3$ and (b) 0.5% Pt/20% BaO/Al$_2$O$_3$ Measured Between 300 and 600°C with Feed Concentrations Varying from 50 to 400 ppm NO.

for these two catalysts to gauge the effect of Pt loading on storage and rate of uptake. Figure 2 shows the NOx storage results of a typical long



**Figure 3.** NOx Conversions for (a) 1.0% Pt/20% BaO/ Al$_2$O$_3$ and (b) 0.5% Pt/20% BaO/Al$_2$O$_3$ Measured Between 300 and 600°C.

cycle, 15 minutes lean and 10 minutes rich, which is commonly used in modeling to illustrate the isotherm behavior. Figure 3 suggests that if the exhaust temperature is kept below 400°C, it may be possible to use less precious metal. Even though the Pt content decreased by a factor of 2, the net NOx conversion was unaffected at 300°C and only decreased from 86% to 73% at 400°C. The effect is more severe above 400°C, where LNTs are less active. These results are comparable to diesel results, which illustrates the minimal impact of CO$_2$ in the exhaust. Future experiments will incorporate a fully formulated form of this catalyst into a core-bench reactor to further evaluate its potential.

For the urea SCR analysis, a zeolite-based catalyst was obtained from Ford that has been the focus of the Cross-Cut Lean Exhaust Emissions Reduction Simulation (CLEERS) urea SCR efforts. The initial experimentation was carried out in a powder reactor and used a mass spectrometer to analyze the effluent. Due to difficulties interpreting the results, isotopically-labeled $^{15}$N$^{18}$O was implemented for these studies. This allowed direct observation of nitrogen formation from the reduction of $^{15}$N$^{18}$O with NH$_3$. Figure 4 shows that the total NO conversion over the entire temperature range, 300-600°C, is greater than 95% regardless of NH$_3$ concentration (200-1600 ppm). While nearly all of the NO was converted in these experiments, it is important to understand what products were formed during the reaction. The most desirable product for NO reduction by NH$_3$ is N$_2$, but it is also possible for
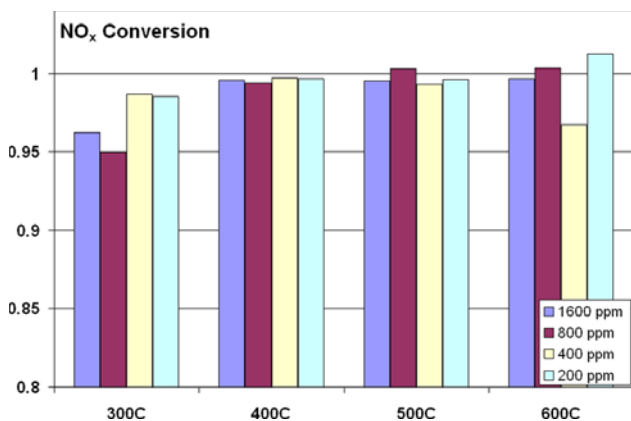
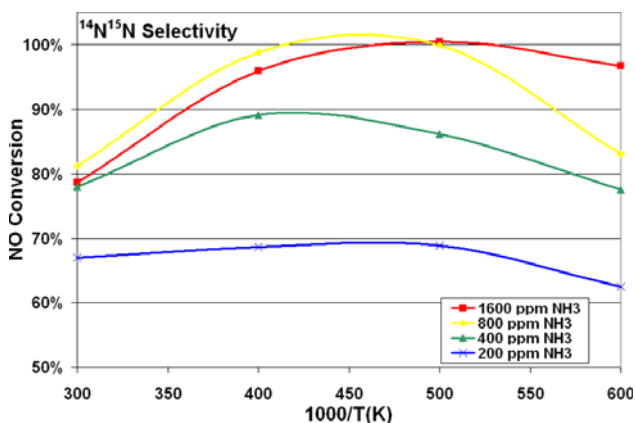**Figure 4.** NOx Conversion for Zeolite-based Urea-SCR Catalyst Using 200-1600 ppm $NH_3$ as the Reductant.



**Figure 5.** Zeolite-based Urea SCR Catalyst $^{14}N^{15}N$ Selectivity as a Function of Temperature and $NH_3$ in the Feed.

other side reactions to occur that would result in the formation of byproducts, such as $N_2O$. This measurement is referred to as selectivity and is often dependent on catalyst, temperature, and $NO/NH_3$ ratio. Selectivity to $N_2$ is defined as the percentage of NO (N isotopically labeled; m=15) that was reduced by $NH_3$ (naturally occurring N; m=14) to form di-nitrogen, $^{14}N^{15}N$, or:

$$^{14}N^{15}N \text{ Selectivity} = \frac{^{14}N^{15}N \text{ formed}}{^{15}N^{18}O \text{ reacted}} \cdot 100\%$$

Figure 5 shows how this selectivity is affected by temperature and $NH_3$ concentration. The most likely side product is $N_2O$, but the current mass spectrometer is unable to detect this particular species. Future experiments will incorporate this catalyst into a core-bench reactor to further evaluate its potential using aqueous urea.

$H_2$ SCR is not as favorable as the LNT results. $Pt/K/Al_2O_3$ was investigated, and there was very little selectivity for NOx reduction compared to the 8.4% $O_2$ in the feed. Conversion was never greater than 20%. $Ag/Al_2O_3$ was also investigated, but little improvement was observed, so experimentation was abandoned.

## Conclusions

- $NH_3$ and LNT systems are the most promising candidates for $H_2$ ICE NOx abatement
  – Will proceed with core reactor experimentation
- $H_2$ SCR will likely require extensive catalyst research
  – Catalyst must selectively reduce NOx vs. $O_2$
  – $H_2$ is not selective
- Experimentation remains to determine limits of reduction conditions
  – Lean rich cycle for LNT
  – Concentration for urea/$NH_3$

## FY 2005 Publications/Presentations

1. T.J. Toops, J.E. Parks, "$H_2$ ICE $NO_x$ Aftertreatment", Advanced Combustion and Emissions Control Meeting, September 8, 2005, Southfield, MI.

# II.B.15  Cross-Cut Lean Exhaust Emission Reduction Simulation (CLEERS)

*Stuart Daw*
*Oak Ridge National Laboratory (ORNL)*
*National Transportation Research Center*
*2360 Cherahala Boulevard*
*Knoxville, TN  37932-6472*

*DOE Technology Development Manager:  Ken Howden*

The following report is for three separate activities that are included under CLEERS:

• Administrative support (Stuart Daw and Sreekanth Pannala);

• Joint development of benchmark kinetics (Stuart Daw, Kalyana Chakravarthy, Todd Toops, Jae-Soon Choi, Jim Parks, and Josh Pihl);

• Micro-scale catalyst modeling for performance and durability (Bill Shelton and Sreekanth Pannala).

## Objectives

Administrative Support

Provide coordination of the CLEERS activity for the Diesel Cross-Cut Team in accomplishing the following:

• Promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.

• Promote development of performance models for emissions control components such as exhaust manifolds, catalytic reactors, and sensors.

• Provide a consistent framework for sharing information about emissions control technologies.

• Help identify R&D needs and priorities.

Joint Development of Benchmark Kinetics

• Coordinate ORNL's collaboration with Pacific Northwest National Laboratory (PNNL) and Sandia National Laboratories (SNL) in the development of kinetics information needed for aftertreatment component simulation.

• Provide benchmark laboratory measurements of NOx reduction chemistry and reaction rates.

• Coordinate laboratory measurements of lean NOx trap (LNT) materials with ongoing test-stand/vehicle studies in the National Transportation Research Center (NTRC) facility.

• Develop and validate global chemistry and (low-order) models for LNT kinetics.

Micro-Scale Catalyst Modeling

• Develop a simplified computational model that relates the effects of catalyst surface morphology on the chemistry and performance of critical aftertreatment components.

• Utilize this model in combination with experimental performance data and microscopic surface characterizations to correlate and predict trends in aging, sulfur poisoning, and component regeneration.

## Approach

Administrative Support

• Set up and coordinate meetings of the CLEERS Planning Subcommittee.

• Co-lead the LNT Focus Group.

- Provide overall coordination and secretarial assistance in planning and carrying out the CLEERS public workshops.
- Maintain the CLEERS website on an ORNL server accessible via the internet.
- Provide periodic status updates and summary reports to the Cross-Cut Team.
- Respond to general requests and inquiries about CLEERS from the public and technical community.

Joint Development of Benchmark Kinetics
- Maintain regular interactions with PNNL and SNL through the Focus Groups and direct meetings.
- Conduct experimental measurements of LNT chemistry and reaction rates using the pre-competitive adsorber materials in the ORNL bench-flow and diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) reactors.
- Analyze test-stand/vehicle LNT data collected at the NTRC facility, and compare this data with the laboratory bench-flow and DRIFTS measurements.
- Write and validate simplified computer LNT codes that can be used to evaluate the laboratory and test-stand rate measurements.
- Publish and post experimental/modeling results from ORNL in journals and on the website.

Micro-Scale Catalyst Modeling
- Develop a computer code that uses a simplified rule-based Monte-Carlo process to simulate surface morphology changes in supported catalysts as they age and the impact of those changes on reaction conversion efficiency.
- Initially apply the code to simulating LNT aging and sulfur poisoning.
- Validate the code predictions with experimental data.
- Apply the results of the Monte-Carlo simulations to global LNT performance models.

**Accomplishments**

Administrative Support
- Continued co-leading the CLEERS Planning Committee.
- Assisted in facilitating the Selective Catalytic Reduction (SCR) Focus Group teleconferences and protocol planning.
- Continued co-leading LNT Focus Group; organized monthly teleconferences.
- Provided assistance as needed for Diesel Particulate Filter (DPF) Group planning.
- Provided regular update reports to DOE Diesel Cross-Cut Team.
- Held 8th CLEERS workshop at University of Michigan, Dearborn on May 17-19.
- Maintained website functionalities, security, and data to facilitate web meetings and serve Focus Group interactions.

Joint Development of Benchmark Kinetics
- Continued testing and validation of the LNT material characterization protocol in conjunction with the LNT Focus Group, SNL, and PNNL and collaborating suppliers.
- Continued benchmarking of Umicore commercial reference LNT material in LNT standard protocol.
- Continued micro-characterization of the Toyota diesel particulate and NOx reduction (DPNR) device and LNT samples from Ford.
- Began in-depth study of the global kinetics of LNT regeneration, with specific emphasis on formation of byproduct $N_2O$ and $NH_3$ and effective fuel penalty.

- Continued upgrading the ORNL bench-flow reactor to insure compliance with key requirements of the draft characterization protocol.

Micro-Scale Catalyst Modeling

- Terminated in-house modeling activity as result of funding cuts.
- Established collaboration with University of Tennessee to continue model development and validation in conjunction with LNT rapid aging activity.

## Future Directions

Administrative Support

- Continue co-leading CLEERS Planning Committee.
- Continue co-leading the LNT Focus Group and supporting the DPF and SCR Focus Groups as needed.
- Continue providing standard reference LNT materials and data for Focus Group evaluation.
- Organize 9th CLEERS workshop sometime after March 2006.
- Continue maintenance and expansion of CLEERS website.
- Continue providing regular update reports to the DOE Diesel Cross-Cut team.

Joint Development of Benchmark Kinetics

- Complete full automation of the ORNL bench-flow reactor.
- Continue development and demonstration of methods for utilizing LNT protocol data to generate global reaction kinetics and simulate device-scale performance.
- Continue characterization of Umicore LNT reference material at multiple scales and transmit results to the LNT Focus Group as they become available.
- Update global LNT models with input from SNL, literature, and ORNL experimental data as these become available, and post revised models.
- Continue chemical analysis, powder and bench-flow reactor measurements, and microscopic characterization of the Toyota DPNR and LNT samples as resources permit.
- Coordinate kinetic and microscopic characterization measurements with LNT durability tests developed under the rapid aging protocol.

Micro-Scale Catalyst Modeling

- Provide consulting assistance to the University of Tennessee in applying the micro-scale particle coarsening and sulfur poisoning models to experimental LNT aging studies.

## **Introduction**

Improved catalytic emissions controls will be essential for utilizing high-efficiency lean-burn engines without jeopardizing the attainment of the U.S. Environmental Protection Agency emission standards scheduled to take effect in 2007 and 2010. Simulation and modeling are recognized by the DOE Diesel Cross-Cut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity was initiated to promote development of improved computational tools and data for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. While CLEERS does not directly support the development of extensive full-emissions-system performance simulation codes, it does provide explicit support for the following activities:

- Public workshops on key emissions control topics.
- Collaborative interactions among Cross-Cut Team members, emissions control suppliers, universities, and national laboratories under specially organized topical focus groups.

- Development of experimental data, analytical procedures, and computational tools that are directly useful for understanding component performance and the behavior and durability of catalytic materials.

- Development of consistent frameworks for sharing information about emissions control technologies.

- Development of explicit recommendations to DOE and the DOE Cross-Cut Team regarding the most critical emissions control R&D needs and priorities.

ORNL is currently involved in two separate DOE-funded tasks that support CLEERS:

- Overall administrative support.
- Joint development of benchmark LNT kinetics with SNL and PNNL.

Previous work on micro-scale catalyst modeling for performance and durability has been terminated due to funding reductions.

In the administrative task, ORNL staff members coordinate the CLEERS Planning Committee, the CLEERS focus groups, the public workshops, and the CLEERS website (www.cleers.org). The joint kinetics development task involves collaboration among ORNL, SNL, and PNNL to produce key kinetics information needed for predicting the performance of lean-NOx adsorbers and catalyzed particulate filters. The results of this work are discussed with the LNT and DPF Focus Groups prior to publication to provide technical review and guidance to the labs. The collaboration is structured to build on the strengths of each lab and leverages against other DOE-funded activities to maximize benefits. The micro-scale modeling task is intended to help improve understanding of catalyst morphology, how changes in that morphology relate to aging, and how those changes affect practical component performance.

## Approach

### Administrative Support

In FY 2005, ORNL continued acting as the lead coordinator of the overall functions of the CLEERS Planning Committee and Focus Groups. Stuart Daw

of ORNL is responsible for providing general assistance to each of the Focus Groups and is a co-leader (with Dick Blint of GM) of the LNT Focus Group. George Muntean and Darrell Herling from PNNL are co-leaders of the DPF and SCR Focus Groups, respectively, and report on their activities elsewhere. ORNL organizes and implements the public workshops under guidance from the Focus Groups and Planning Committee, providing both technical and secretarial support. The CLEERS website is maintained (under direction of Sreekanth Pannala) on an ORNL server accessible via the internet. Both public and restricted areas have been set up on this website to facilitate distribution of technical information, workshop information and presentations, and interactive web meetings. Stuart Daw provides assistance to Dick Blint (GM) in presenting periodic status updates and summary reports to the Cross-Cut Team. Both Stuart and Sreekanth Pannala at ORNL respond to general requests and inquiries about CLEERS from the public and technical community.

### Joint Development of Benchmark Kinetics

ORNL's responsibility in this activity is to set up and conduct experimental measurements of LNT chemistry and reaction rates that will help to define the critical physical characteristics of LNT materials responsible for determining practical performance (i.e., NOx emissions reduction and energy efficiency). In this function, ORNL utilizes reference non-competitive adsorber materials in the ORNL bench-flow and DRIFTS reactors. Where possible, these bench measurements are also supplemented with other specialized measurement capabilities such as high-resolution microscopy at the ORNL High Temperature Materials Laboratory (HTML). ORNL maintains regular interactions with PNNL and SNL and the industry collaborators through the LNT Focus Group in order to maximize the value of the data generated and provide feedback that can be considered in planning future experiments. Where possible, laboratory results are compared with and analyzed in the context of test-stand/vehicle LNT measurements generated in parallel projects at ORNL's NTRC facility. For assistance in interpreting trends, ORNL utilizes simplified computer LNT codes that can be used to evaluate the laboratory and test-stand data. Results

are published in peer-reviewed journals, presented in public meetings, and/or posted on the CLEERS website.

**Micro-Scale Catalyst Modeling**

In prior years, we applied previously developed methods for rule-based Monte Carlo simulations to construct a computer code that captures the key physics of surface morphology changes in aging LNT catalysts. In addition to reflecting the changes in morphology, the code is designed to help guide the modeling of how NOx conversion efficiency and fuel consumption should relate to aging. The initial target phenomena were Pt particle sintering (coalescence) and sulfur poisoning. Due to funding reductions, in-house activities at ORNL on this modeling have been terminated. The code is being made available to the University of Tennessee, where experimental studies associated with the LNT rapid aging protocol are underway.

## Results

**Administrative Support**

The eighth CLEERS workshop was held May 17-19 at the Dearborn campus of the University of Michigan. This was the largest workshop to date, with a total of 120 registrants, including many participants from emissions controls suppliers. All three emissions control technology areas (LNTs, DPFs, and SCR) were covered. The complete technical program, meeting summary, and most of the presentations are available on the website (www.cleers.org). More detailed summaries were also provided to the Diesel Cross-Cut Team. One overriding conclusion repeatedly voiced by the participants was that emissions control technology in all three areas is still far from mature. There are a number of issues for each technology area where simulation capabilities are critical and where CLEERS can make meaningful contributions.

The LNT, SCR, and DPF Focus Groups have continued regular phone/web meetings throughout the year, and summary reports of the meetings have been provided to group members and the Diesel Cross-Cut Team. The meeting topics have included reviews of experimental data donated by members, technical presentations by outside invited experts

(e.g., from non-member universities), and discussions of technical needs and priorities among the Cross-Cut member companies. Regarding the latter, there has been an increased sense of urgency from the Cross-Cut member companies for implementing a standard protocol for urea-SCR materials analogous to the LNT protocol. The SCR Group members from Ford have proposed a basic outline for the protocol that has been adopted by the rest of the group with slight modifications. Ford has also provided samples of two candidate zeolite-based urea-SCR catalysts. Limited testing of the protocol using these catalysts has been done by PNNL, but the national labs are currently unable to continue this work due to insufficient funding for SCR under CLEERS. Efforts continue to identify options for continuing this work.

One of the main activities of the LNT Group in FY 2005 has been the continued evaluation of the standard LNT protocol for generating characteristic measurements of candidate LNT materials. The resulting data are intended to be used for reconstructing global kinetics rate expressions for simulations and also as a template for transferring information between suppliers and users. Field protocol evaluations by LNT Group members have continued and have been discussed at length in the Focus Group meetings. This was also a major topic of discussion at the May workshop. Most of the LNT protocol work has focused on a commercial reference material marketed for gasoline direct injection (GDI) applications and supplied by Umicore. Because these samples are commercial, complete physical and chemical characterizations can be made for correlating with the bench measurements.

**Joint Development of Benchmark Kinetics**

Work has continued to more fully automate the ORNL bench-flow reactor. This includes installation of a new data acquisition and control computer as well as updated LabView software. Almost all of the valve and flow operations are fully programmable. The high-speed lean/rich cycling capability is fully functional, and the gas analysis instrumentation includes a standard automotive oxygen sensor that allows correlation of the actual gas species concentrations with the oxygen readings that would typically be available on vehicles. The time response
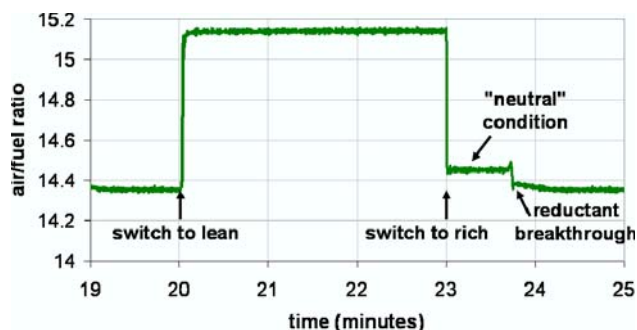
**Figure 1.** The oxygen sensor has turned out to be useful for observing the details of the rich-lean transition in the bench reactor. With the metal protective cover removed, the response time appears to be <0.1 s. In this figure, NOx has been eliminated from the exhaust to observe the effects of oxygen storage alone.

of the oxygen sensor (with the protective shield removed) appears to be less than 0.1 s, and we now appear to be able to complete the lean-rich transition in less than 0.2 s, as shown in Figure 1. Such rapid rates are typical of the times involved for lean/rich transitions on engines.

Bench reactor studies using SpaciMS for tracking $H_2$, CO, and total NOx have provided new insights into the LNT regeneration efficiencies of these two reductant species ($H_2$ and CO). Such insights are important in determining the required CO/$H_2$ ratio needed for in-pipe or engine-based LNT regeneration. To date, ORNL engine testing has indicated that $H_2$ and CO are the two most important reductant constituents in rich exhaust. At 300°C, both $H_2$ and CO appear to have similar regeneration efficiencies. At lower temperatures (e.g., 200°C), however, $H_2$ appears to be significantly superior to CO, as shown in Figure 2. We speculate that this efficiency degradation for CO may be related to CO poisoning of the Pt. This result suggests that $H_2$ should be maximized for low-temperature regeneration.

Another major finding related to LNT regeneration efficiency has been the observation of relatively large amounts of $N_2O$ and $NH_3$ byproducts under certain regeneration conditions. As shown in Figure 3, the concentrations of these species can be similar to the original level of NOx in the exhaust. The formation of these byproducts is undesirable
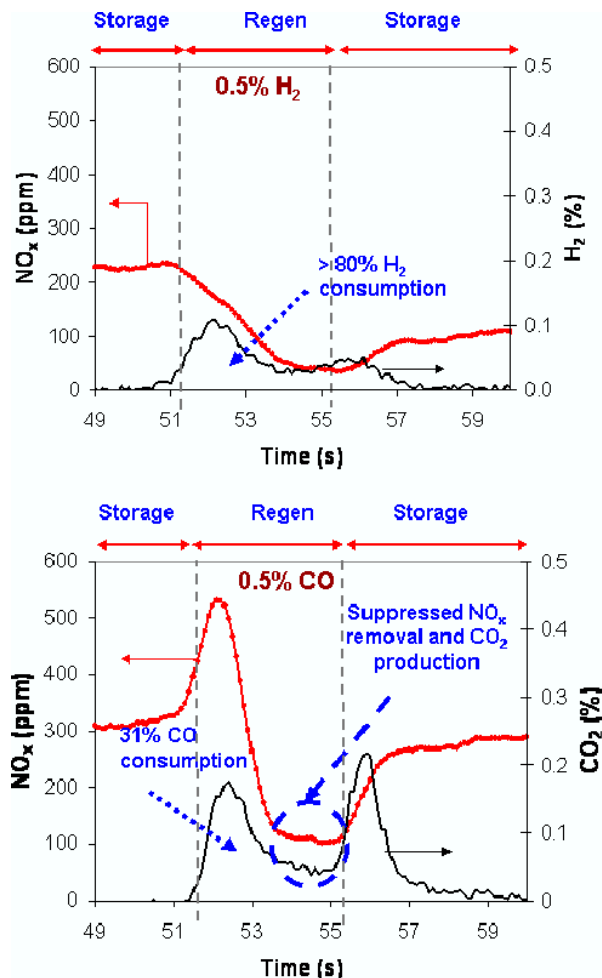


**Figure 2.** Bench SpaciMS studies reveal that $H_2$ is a more effective reductant than CO at low temperature. The illustrated NOx, $CO_2$, and $H_2$ breakthrough profiles were measured at the midpoint of a 3-inch long Pt/K/Al$_2$O$_3$ monolith for a 200°C exhaust temperature.

because their generation consumes significantly more reductant than does $N_2$ formation, thus increasing the regeneration fuel penalty as well as creating an additional pollutant. Typically, the highest byproduct levels are observed at low temperatures (e.g., 200°C) and high reductant concentrations (>0.5%). It also appears that these species are mostly observed during conditions of over-regeneration (i.e., after all the stored NOx is reduced but reductant continues to be added), and typically $NH_3$ is observed after $N_2O$. As discussed below, other studies of the kinetics of regeneration have led to a conceptual model for byproduct formation that can be used to guide LNT simulation.
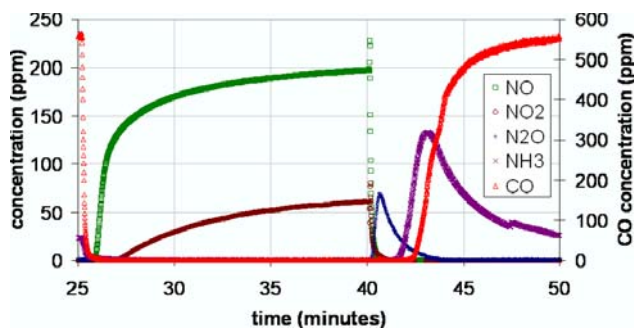
**Figure 3.** At some conditions, significant $NH_3/N_2O$ is observed in the LNT protocol measurements. The example shown is for a long cycle condition from the protocol at 200°C and mixed $CO/H_2$ reductant. The sorbent is the Umicore reference material. Note that $N_2O$ emerges before $NH_3$.

The relative error introduced by not properly accounting for the $N_2O$ and $NH_3$ byproducts is illustrated in Figure 4. Here we observe the results for two different simulations of LNT performance under fast cycling conditions using the ORNL simplified model. There is an over-prediction of NOx reduction to $N_2$ that increases with increased reductant level, suggesting that it is related to inadequate accounting of byproduct formation. Further changes are being made to the simplified LNT model to account for the fuel penalty and performance effects of $NH_3$ and $N_2O$.

Another set of bench reactor experiments has been conducted by Josh Pihl, a University of Wisconsin graduate student, to develop the information needed to reconstruct the global kinetic rate expressions for $NH_3$ and $N_2O$ formation during regeneration. In these experiments, the ORNL bench reactor has been operated under steady-state reducing conditions in order to measure the relative reaction rates of NO with $H_2$ and CO to form $N_2$, $N_2O$, and $NH_3$ in the absence of $O_2$ and NOx storage reactions. Figure 5 illustrates the general type of trends Josh has observed for NO reaction with $H_2$ over the Umicore catalyst as a function of temperature. One clear trend so far is that $NH_3$ and $N_2O$ formation are much higher at relatively low temperatures (e.g., < 250°C). Further experiments and data analysis in collaboration with PNNL and SNL are underway.
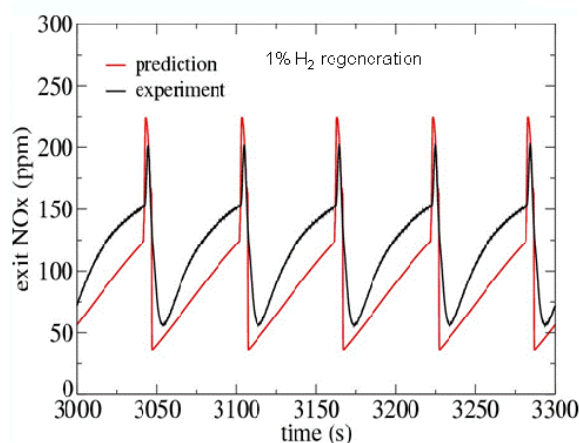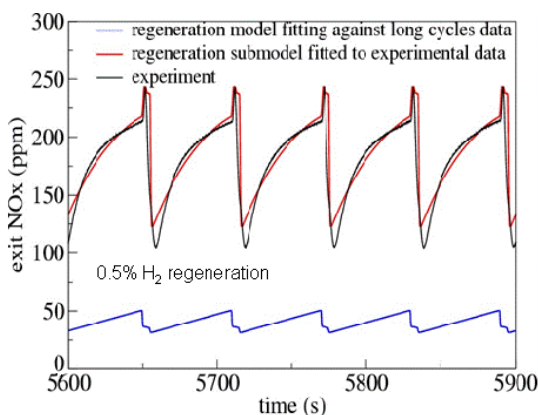


**Figure 4.** Comparison of observed and predicted NOx breakthrough for fast cycling of a Manufacturers of Emission Control Association sorbent sample at 300°C. Lack of accounting for $N_2O$ and $NH_3$ in the simple ORNL model results in an under-prediction of NOx breakthrough as the reductant concentration increases.

**Micro-Scale Catalyst Modeling**

The development of a continuously distributed NOx storage site model that includes the effects of precious metal coarsening is necessary to understand the aging process and interpret microscopy experiments. As described in prior reports, we developed a rule-based Monte Carlo simulation code that captures the key physics of surface morphology changes in aging LNT catalysts. In addition, post-processing tools were created to visualize the coarsening effects and also to track the particle size distribution with time. This code and associated tools have now been made available to the University
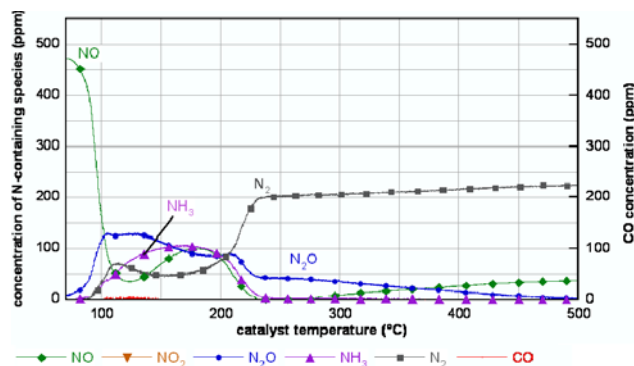
**Figure 5.** Example near steady-state conversions for a mixture of 500 ppm NO, 500 ppm $H_2$, 5% $H_2O$, 5% $CO_2$, balance $N_2$ fed to a Umicore sample in the ORNL bench reactor. The space velocity is 100,000 $hr^{-1}$ and the temperature ramp is 5°C/min.

of Tennessee, where LNT rapid aging experiments can be used to provide data for model improvement and validation. Due to funding reductions, in-house activities at ORNL on this modeling have been terminated.

## Conclusions

### Administrative Support

The eighth CLEERS workshop was held May 17-19 and was the largest workshop to date, with a total of 120 registrants. The complete technical program, meeting summary, and most of the presentations are available on the website (www.cleers.org). One overriding conclusion was that emissions control technology in all three technology areas (LNT, DPF, and SCR) is still far from mature.

The LNT, SCR, and DPF Focus Groups have continued regular phone/web meetings throughout the year. The meeting topics have included reviews of experimental data donated by members, technical presentations by outside invited experts (e.g., from non-member universities), and discussions of technical needs and priorities among the Cross-Cut member companies. There is an increased sense of urgency for implementing a standard protocol for urea-SCR materials analogous to the LNT protocol. The LNT Group has continued evaluation of the standard LNT protocol for generating characteristic measurements of candidate LNT materials.

### Joint Development of Benchmark Kinetics

Bench reactor studies using the upgraded ORNL bench reactor and SpaciMS have provided new insights into the LNT regeneration efficiency for $H_2$ and CO reductants. At 300°C, both $H_2$ and CO appear to have similar regeneration efficiencies, but $H_2$ appears to be superior to CO at lower temperatures. We speculate that CO poisoning of Pt may occur at low temperatures.

Relatively large amounts of $N_2O$ and $NH_3$ byproducts are formed during LNT regeneration at low temperature and over-dosed conditions. The formation of these byproducts is undesirable because their generation consumes more reductant than does $N_2$ formation. Steady-state experiments under reducing conditions are underway to evaluate the kinetics for these byproduct reactions relative to $N_2$ formation. Further changes are being made to the simplified LNT model to account for the fuel penalty and performance effects of the byproduct reactions.

### Micro-Scale Catalyst Modeling

The rules-based Monte Carlo code and associated computational tools for studying Pt sintering and S poisoning have been made available to the University of Tennessee. Due to funding reductions, in-house activities at ORNL have been terminated.

## FY 2005 Publications/Presentations

1. J.-S. Choi, W. P. Partridge, C. S. Daw, "Spatially-resolved *in situ* measurements of transient species breakthrough during cyclic, low-temperature regeneration of a monolithic Pt/K/$Al_2O_3$ NOx storage-reduction catalyst", *Applied Catalysis A: General*, 293, pp 24-40, 2005.

2. K. Chakravarthy, C. S. Daw, "Simple global model for lean NOx adsorbers", CLEERS website, http://www.cleers.org/databases

3. Multiple presentations by J. Parks, J.-S. Choi, T. Toops, S. Daw, K. Chakravarthy, J. Pihl, 8th CLEERS Workshop, http://www.cleers.org , 2005.

4. Presentations on LNT by J. Parks, J.-S. Choi, T. Toops, 19th North American Catalysis Meeting, May 2005.

5.  J. Pihl, "Byproduct formation in lean NOx traps for diesel exhaust aftertreatment", 2004 EPA STAR Graduate Fellowship Conference, October 2004

6.  T. Toops, D. B. Smith, W. P. Partridge, "Quantification of the in-situ DRIFT spectra of Pt/K/gamma-Al$_2$O$_3$ NOx adsorber catalysts", *Applied Catalysis B: Environmental*, 58(3-4), pp 245-254, 2005.

7.  T. Toops, D. B. Smith, W. S. Epling, J. E. Parks, W. P. Partridge, "Quantified NOx adsorption on Pt/K/gamma-Al$_2$O$_3$ and the effects of CO$_2$ and H$_2$O", *Applied Catalysis B: Environmental*, 58(3-4), pp 255-264, 2005.

8.  T. Toops, D. B. Smith, W. P. Partridge, "NOx adsorption routes on Pt/K/Al$_2$O$_3$", *Catalysis Today*, in press.

9.  B. West, S. Huff, J. Parks, S. Lewis, J.-S. Choi, W. P. Partridge, and J. Storey, "Assessing reductant chemistry during in-cylinder regeneration of diesel lean NOx traps", SAE Technical Paper Series 2004-01-3023.

# II.B.16  CLEERS DPF Modeling

*Mark Stewart, George Muntean (Primary Contact), Tom Gallant, Gary Maupin*
*Pacific Northwest National Laboratory*
*P.O. Box 999, MSIN: K5-22*
*Richland, WA  99352*

*DOE Technology Development Manager:  Ken Howden*

## Objectives

- Develop improved modeling capabilities for diesel particulate filtration
  - Create improved models of the local properties of the soot filter, e.g., cake permeability, density, morphology, etc.
  - Develop improved sub-grid representations of the local soot oxidation reactions in diesel soot filters, e.g., oxidation mechanisms, detailed kinetics, global rates, etc.
- Coordinate and lead the Cross-Cut Lean Exhaust Emission Reduction Simulation Diesel Particulate Filter (CLEERS DPF) sub-team activities
  - Provide project updates to the industry sub-team, solicit feedback, and adjust work scope accordingly
  - Lead technical discussions, invite distinguished speakers, and maintain an open dialogue on DPF modeling issues

## Approach

- Map the substrate microstructure to create a computational "physical" domain
- Apply a lattice-Boltzmann flow field solution
- Incorporate soot particle motion and deposition
- Incorporate soot oxidation mechanism(s)
- Validate models with experimental results
- Perform parametric analysis with the detailed model
- Develop low-dimensional sub-models from the parametric data

## Accomplishments

- Digital pore geometry maps have been created for the Corning EX-80 cordierite substrate
- A micro-scale discrete particle deposition model has been developed using the lattice-Boltzmann method
  - Simulations of initial filter loading were performed
  - Parametric studies have been performed using idealized, single-pore geometries
  - Simplified filter regeneration studies were carried out using micro-scale models
  - A study was made of the potential for defects in the soot layer to be caused by features of the underlying substrate microstructure via fluid dynamic effects
- A single channel filter loading technique has been developed
  - Individual filter channels have been loaded under a variety of conditions
  - Pressure drop data was collected for comparison to micro-scale models
  - Loaded channels were examined using advanced analytical techniques such as ultra small angle x-ray scattering (USAXS)
  - Apparatus can be configured to observe active regeneration events on the loaded channel surfaces

- Coordinated and led monthly teleconferences for DPF sub-team

**Future Directions**

- Improve characterization of substrate microstructures
- Incorporate more sophisticated soot oxidation mechanisms into pore-scale models, including:
  - heat transfer
  - surface catalytic reactions
  - transport of active gaseous species
- Perform further parametric studies to characterize the effects of microstructural substrate features
- Perform further loading and regeneration experiments using single channel methodology
  - Study new substrate materials such as Corning Duratrap RC
  - Perform multiple experiments with a variety of catalyst coatings
- Develop simple device-scale models and establish relationships between model parameters and observed pore-scale mechanisms

## Introduction

High fuel efficiency, and corresponding low emissions of greenhouse gasses per power generated, make diesel engines an environmentally attractive technology for meeting the short- to medium-term transportation needs of the ever growing global economy [1]. There is little doubt that DPFs will play a key role in providing environmentally responsible diesel transportation over the coming decades. While significant progress has been made in the application of DPFs, several challenges remain unresolved. Of particular concern is the potential for a significant degradation in fuel efficiency of diesel-powered vehicles employing DPFs. This degradation is due to two inherent features of DPFs:

- Increased engine backpressure and
- Energy input for active regeneration.

Minimization of both of these items is linked to the fundamental properties of soot capture and oxidation on the nano/micron length scales, where direct experimental observation is difficult or impossible. It is becoming increasingly apparent that modeling and simulation are essential aspects of the needed R&D [2] because exhaustive experimental evaluation of each possible system configuration is simply too costly and too time-consuming to be practical. In particular, both industry and DOE need the ability to accurately simulate trends and make objective comparisons of the various options for

system materials and designs so that empirical experimentation can be minimized.

Through several technical workshops sponsored by the DOE Diesel Cross-Cut Team under CLEERS, the diesel emissions control stakeholder community (including automotive and engine companies, national labs, and universities) has identified the most pressing un-addressed needs for modeling and simulation. For DPFs, the modeling parameters of greatest concern are those associated with:

- Local properties - cake permeability, density, morphology
- Kinetics - oxidation mechanisms, detailed kinetics, global rates
- Simple 1-D models (using the information from the first two bullets) for systems modeling
- Detailed 3-D models for understanding capture and oxidation phenomenon (for design and optimization of the device)
- Flow distribution - packing, anisotropic regenerations (for practical engineering considerations)

Of the above, the current project focuses on the first two bullets – local properties and kinetics – and how these interact with the physical distribution of particles to determine peak regeneration temperature, backpressure and capture efficiency.

## Approach

A computer program has been developed to predict the nature and location of soot deposits within porous filter substrates by simulating the flight and deposition of individual soot particles. Detailed digital maps of the microscopic pores in various substrate materials are created from resin-impregnated sections. The lattice-Boltzmann method is used to solve for the flow field of exhaust through the substrate microstructure as soot deposits form. The motion of simulated soot particles is derived from the exhaust flow field and includes random Brownian motion. The lattice-Boltzmann model can also include reactions at catalyst-coated surfaces, transport of active gaseous species, and oxidation of accumulated soot. Experimental methods have been developed to observe the loading and regeneration of external surfaces of individual channels, allowing meaningful comparisons to model predictions.

## Results

The pore-scale discrete particle deposition model uses the lattice-Boltzmann method to solve for the three-dimensional flow field through the tortuous, microscopic pores of DPF substrates. The lattice-Boltzmann method allows efficient calculation of complex fluid dynamics problems using multiple processors on large parallel computers. The model introduces soot particles and tracks their individual flight paths as they enter the porous substrate microstructure. Particle motion is derived from the local exhaust velocity vector, using an appropriate relationship for fluid dynamic drag, and from a Brownian motion term which depends upon the particle size and the exhaust temperature.

Filtration is modeled via the capture of soot particles by collision of the particles with pore walls or with previously deposited particles. As soot deposits form, they exert a local resistance to flow, and the flow field is continuously updated as it shifts to the paths of least resistance. This is a unique feature in pore-scale studies of DPF filtration carried out to date. The feedback between soot deposit formation and the flow patterns of the particulate-bearing exhaust is crucial for accurate representation of pore-scale filtration processes.
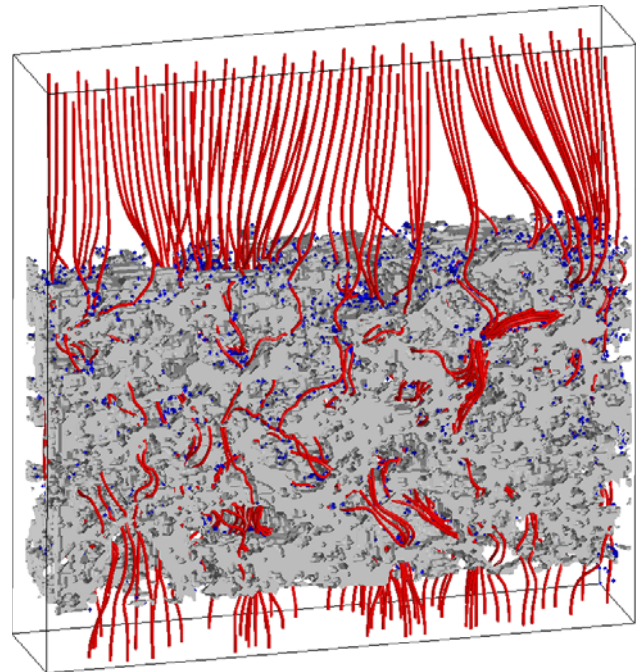


**Figure 1.** Exhaust Streamlines through Cordierite DPF Substrate during Initial Stages of Loading
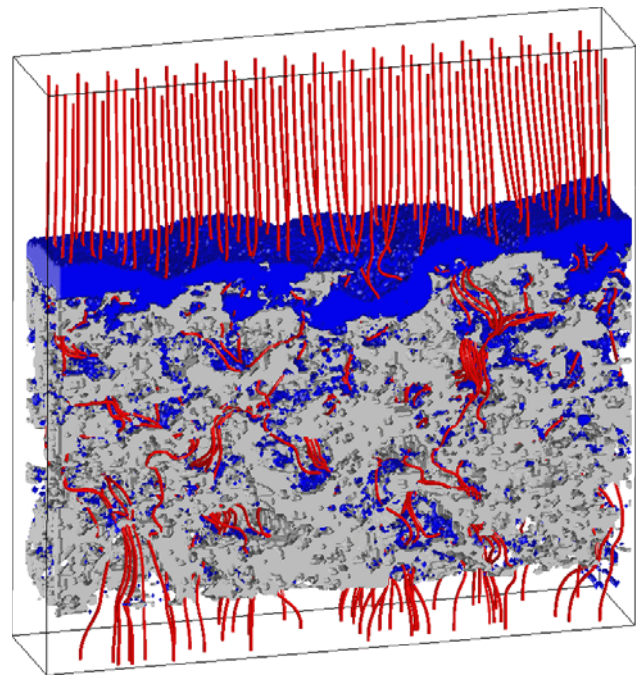


**Figure 2.** Soot Deposits and Streamlines at Intermediate Loading

Figure 1 and Figure 2 show streamlines through a cordierite substrate microstructure at initial and intermediate stages of loading. Flow is not well distributed through the clean substrate, with
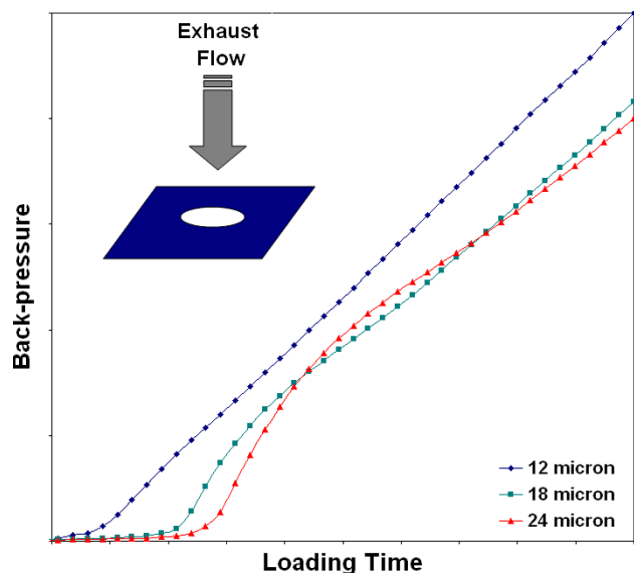
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**Figure 3.** Pore-Scale Loading Study with Square-Edged
Orifices Having Various Diameters

relatively few large flow paths carrying the bulk of the exhaust. This allows initial penetration of soot mass into and through the substrate. As key bottlenecks in the flow pathways are bridged over by soot, the flow becomes more evenly distributed. Significant deposits form within the substrate wall early in the filtration process, but eventually pore mouths near the surface become blocked, and a transition is made to cake filtration. Figure 2 indicates that the flow becomes well distributed over the filter surface as the cake thickens, but beneath the wall surface, much of the exhaust flow is still born by relatively few important pathways. Figure 2 also suggests that the thickness of the soot cake can remain relatively irregular, even at later stages of loading.

Parametric studies have been carried out, beginning with simple individual pore geometries, in order to better understand pore-scale filtration and regeneration mechanisms. Figure 3 shows the results of a study in which individual pores were represented as square-edged orifices in flat plates. These orifices could be thought of as representing the key bottlenecks in the flow paths through a porous DPF substrate. For the smallest pore mouth examined, the transition to cake filtration was rather abrupt. Larger pores took longer to become blocked with soot and exhibited a more dramatic increase in pressure drop while the transition was taking place. Other

parametric studies examined the effect of three-dimensional pore shape on loading behavior.

Initial pore-scale regeneration studies using constant soot oxidation rates have also been carried out in idealized pore geometries. Qualitative features of experimental data have been reproduced and can be explained in terms of pore-scale phenomenon. One puzzling experimental observation involved a dramatic decrease in backpressure after initial loading of a catalyzed filter. Pore-scale modeling suggests that this behavior may occur as soot penetrating into pores during the initial depth filtration mode is oxidized quickly due to close proximity to catalysts within the substrate, clearing key constrictions in major flow paths and lowering the overall pressure drop. Previous modeling work had examined the recycle of active gaseous species from catalytic sites on the substrate surfaces through a uniform layer of soot on the filter wall surface [3]. Future studies will extend this approach to the complex, irregular structure of soot deposits which penetrate into the substrate microstructure.

Another modeling study examined the possibility that defects within the fully developed soot layer on the filter wall may play an important role in both active and passive filter regeneration. It is thought that a few areas of unusually high permeability through the DPF substrate walls may lead to persistent defects in the soot layer as soot deposition is prevented by high local shear rates. This could allow continued penetration of particulate mass into the substrate wall where higher oxidation rates may exist during passive regeneration. During active regeneration, these defects in the soot layer may serve as local "hot spots" from which a flame front moves outward through the soot layer [4]. By setting a threshold velocity for soot deposition, pore-scale lattice-Boltzmann models have been created in which the postulated soot layer defects can be sustained by local fluid dynamics. Future studies will focus on how these defects might alter the local transport phenomena involved with DPF regeneration.

A primary goal of pore-scale modeling efforts is to study the effect of substrate microstructural features on DPF performance. Single channel loading experiments and micrographs of filter wall cross-sections suggest that a relatively impermeable "skin" of ceramic material near the wall surfaces may
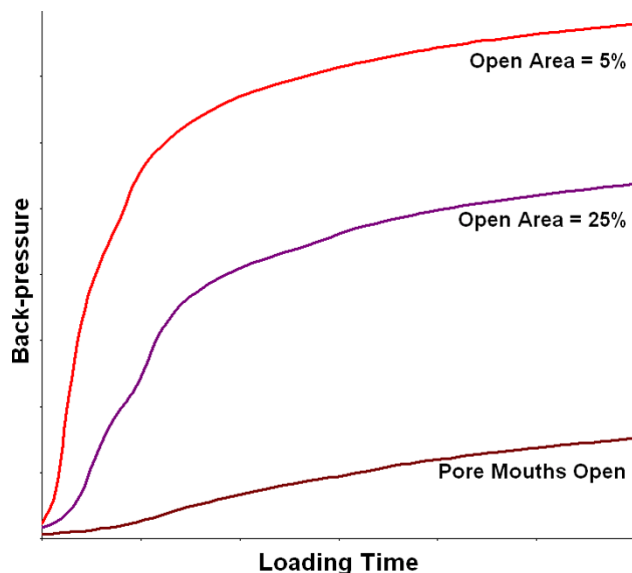
**Figure 4.** Effect of Thin, Low-Permeability Structures at Cordierite Wall Surfaces



**Figure 5.** Schematic of Single Channel Experimental Apparatus

be a common microscopic feature in cordierite substrates. It is known that cordierite crystallites can be preferentially aligned in extruded parts, resulting in anisotropy of physical and thermal properties [5]. It is possible that alignment of these platy structures is greatest at the wall surface, where shear rates are the highest during extrusion. A pore-scale modeling study was carried out to examine the possible effects of this type of structure on filter performance. Three duplicate digital maps were created for a small segment of cordierite filter wall. Thin structures covering different proportions of the wall surfaces were added to two of the geometries. The pressure drop response for the three geometries was dramatically different, as show in Figure 4. Clearly, structural features comprising a relatively small fraction of a substrate's solid volume can have a significant impact on device behavior. An understanding of the nature and size scales of microscopic substrate features impacting macroscopic performance could be an important contribution in the future study and optimization of these devices.

The many layers of complexity involved in the loading and regeneration of an entire DPF device have often proven an obstacle to meaningful interpretation of experimental data. Experimental techniques involving single channels have been developed at PNNL in order to remove some of this complexity while facilitating more direct study of
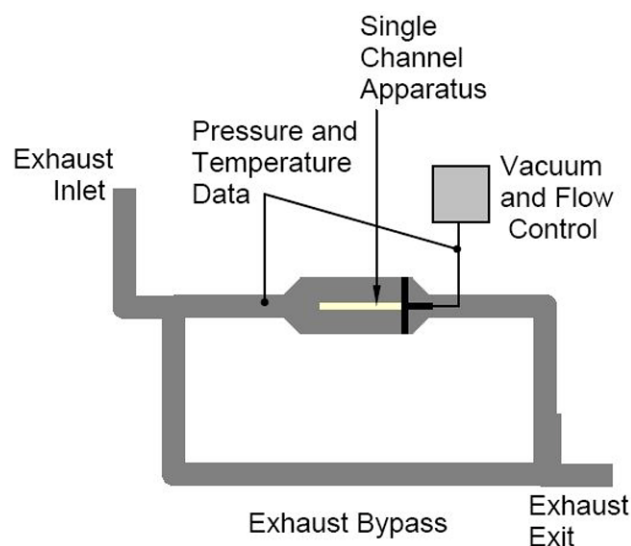
filtration and regeneration mechanisms. A schematic of the experimental apparatus is shown in Figure 5. Individual channels are cut from DPF filters and mounted on a specially designed fitting for insertion into the exhaust stream. The external surfaces of the channel are loaded by drawing exhaust through at a controlled flow rate using a vacuum pump. This allows the filter wall-flow velocity to be set independently from the engine operating conditions.

The single channel configuration eliminates the possibility of radial variation observed in the loading and regeneration of an entire DPF brick, and the use of relatively short channel segments minimizes the effects of axial variation. Removing these uncertainties allows more confidence in the study of fundamental processes. The loading of exterior rather than interior filter surfaces allows observations and measurements with minimal disturbance of the fragile soot deposits. A number of single channel runs have been performed to date, providing pressure drop versus loading behavior for comparison to pore-scale models. Figure 6 shows data gathered during a typical run.

The single channel apparatus may also be configured to allow the direct observation (thermal and visual) of filter regeneration on the loaded external surfaces. This technique will be used to study the initiation of regeneration events, possibly shedding light on the role of defects in the soot layer caused by underlying features of the substrate
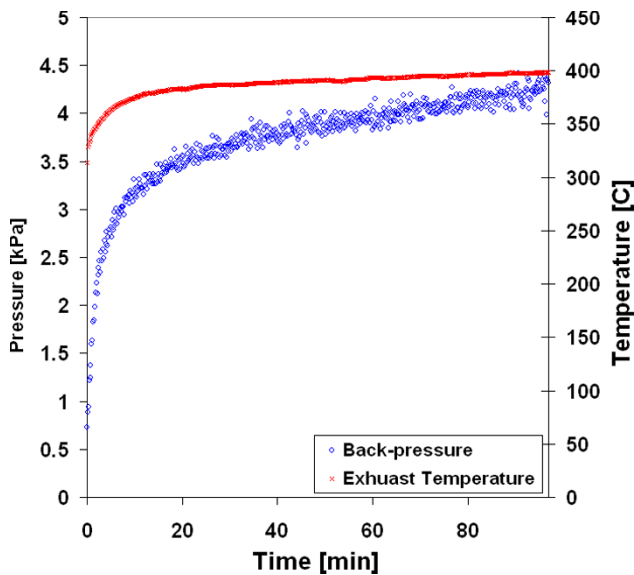
**Figure 6.** Example of Data Gathered During Single Channel Loading Experiments

microstructure. Multiple runs will be performed with various catalyst coatings to study their effects on regeneration events.

## Conclusions

- Discrete particle deposition models using the lattice-Boltzmann method have produced soot deposits which share many qualitative features with those observed in real filter substrates.

- The interplay of the evolving exhaust flow field and the formation of soot deposits is critical in the accurate representation of pore-scale filtration and regeneration mechanisms.

- Pore-scale loading studies underscore the importance of microstructural substrate features in determining macroscopic performance.

- Initial regeneration studies have reproduced trends in experimental data, including a dramatic drop in backpressure under certain conditions after initial loading of a catalyzed filter.

- Single channel loading and regeneration experiments provide an effective means of observing fundamental aspects of DPF operation while removing much of the complexity associated with an entire honeycomb filter.

## Special Recognitions & Awards/Patents Issued

1. The presentation "A Mechanistic Model for Particle Deposition in Diesel Particulate Filters Using the Lattice-Boltzmann Technique" by M. Stewart, D. Rector, G. Muntean, and G. Maupin, received the Best Presentation award from the 2004 American Ceramic Society Cocoa Beach Meeting.

## FY 2005 Publications/Presentations

1. M. Stewart, G. Maupin, T. Gallant, and G. Muntean, "Diesel Soot Filter Characterization and Modeling", presentation at the DOE Advanced Combustion Engine Review, April 2005.

2. M. Stewart, G. Maupin, T. Gallant, and G. Muntean, "Micro-scale Modeling of Diesel Particulate Filters", presentation at the 8th CLEERS workshop, May 2005.

3. M. Stewart, G. Maupin, D. Rector, and G. Muntean, "Micro-Scale Study of Ceramic Diesel Particulate Filter Performance", presentation at the American Ceramic Society Pacific Rim Conference on Ceramic and Glass Technology, September 2005.

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## II.B.17 Development of Metal Substrate for DeNOx Catalysts and Particulate Traps

*Michael Pollard (Primary Contact), Craig Habeger, Paul Park, Herbert DaCosta, Matthew Stefanick*
Caterpillar Inc. Technical Center
Advanced Materials Technology Department
P.O. Box 1875
Peoria, IL 61656-1875

DOE Technology Development Manager: John Fairbanks

### Objectives

- Evaluate materials that would suffice as metallic substrates for catalytic converters. Materials must have a lower cost than the current material used with properties sufficient for off-highway diesel applications.
- Evaluate alternate substrate designs that increase catalyst performance to allow smaller designs with less substrate weight and precious metal content.
- Successfully implement these material and design changes into off-highway production units.

### Approach

- Material Identification and Testing: New and existing materials will be identified which meet the current requirements of coating adhesion, strength, and oxidation resistance at the lower temperatures experienced in diesel engines. Material testing will compare these to the current material.
- Alternate Design Testing: Alternate designs will be evaluated that increase catalyst performance with minimal change in backpressure.
- Implementation: Durability testing will be performed to ensure that design and material changes do not lower the useful life of the converter.

### Accomplishments

- Hot shake testing of straight-channel prototypes with low-cost material showed little difference in performance compared to current material.
- Small prototypes of the new design substrate were bench tested and found to have better performance than equivalent straight-channel designs.
- Full-scale prototypes were successfully produced with the new design substrate.
- Relative performance of the new design with different geometry parameters was modeled.

### Future Directions

- Complete engine testing of full-scale prototypes with the new design to verify improved emissions performance.
- Complete modeling of the new design to determine the optimum geometry to maximize activity while minimizing backpressure.

### Introduction

To meet estimated Tier 2 and Tier 3 Environmental Protection Agency emission limits for off-highway vehicles, it may be necessary to add exhaust aftertreatment devices. Two technologies under consideration are DeNOx catalysts and particulate traps that utilize a packaged cordierite honeycomb catalyst support. This package performs well in on-highway applications; however,

off-highway applications are much harsher. Ceramic material properties are not expected to be adequate for the severe conditions found in off-highway applications, such as high-vibration loads (>10 x gravity). Additionally, the ceramic matrix requires relatively thick walls between cells, causing high flow resistance, which translates to increased engine exhaust backpressure and a corresponding approximate 2-3% fuel consumption increase. Because metallic substrates have superior mechanical properties over ceramics in this application, they are a possible solution to both durability and flow resistance issues. Metallic substrates are expected to be a key enabler for durable, commercially viable off-highway exhaust aftertreatment devices.

## Approach

The development of the metal catalyst substrate is focused in two areas: materials and design. The materials focus includes investigating metals that are more applicable to the diesel exhaust environment. Current metallic catalyst substrates are made from higher-cost alloys that have properties that are necessary for the automotive market. Since diesel engine applications are less demanding in terms of maximum temperature than the automotive market, the search for a less costly material was a major driver. The material selected must have a few key qualities: good oxidation resistance at diesel exhaust gas temperatures, catalyst coatability and adhesion, and good formability.

On the design side, the investigation is moving to alternative design shapes and packages. Current commercially available catalyst supports have straight channel passages. The current work looks to optimize the flow path, thereby increasing catalyst efficiency and potentially reducing necessary catalyst volume. The approach relies on computation methods to give design direction. The package shape is also critical since off-highway vehicles have severe space limitations on additional equipment.

## Results

Preliminary modeling of new designs with non-linear channels was performed. The analysis was done by predicting heat transfer coefficient and

friction factor as relative approximations for converter efficiency and backpressure, respectively. The modeling showed increasing heat transfer for non-linear geometries compared to straight channels. However, any increase in heat transfer coefficient was accompanied by an increase in friction factor, which correlates to an increase in backpressure. It should be noted that all modeling was done based on the non-linear design with a flat layer between each corrugated layer. It is possible to produce a substrate with no flat layers between the folded layers when non-linear channels are used. However, due to the complexity of the air flow through such a converter, this was not modeled.

Small samples of the non-linear channel substrates were produced in the previous year. One substrate was produced with flat plates between corrugated layers. The other was produced with each folded layer shifted by ½ period so that the layers contacted at high points rather than nesting. This method allowed the removal of flat foil layers which would potentially create even more mixing with a lighter design. Bench tests were done to compare the relative catalytic activity of these two non-linear designs with a straight-channel design. The results showed that both of the non-linear channel substrates had lower light-off temperatures than the straight-channel samples (see Figure 1). The non-linear channel sample without any flats consistently had the lowest light-off temperature, while the non-linear channel with flats also performed well. The increase
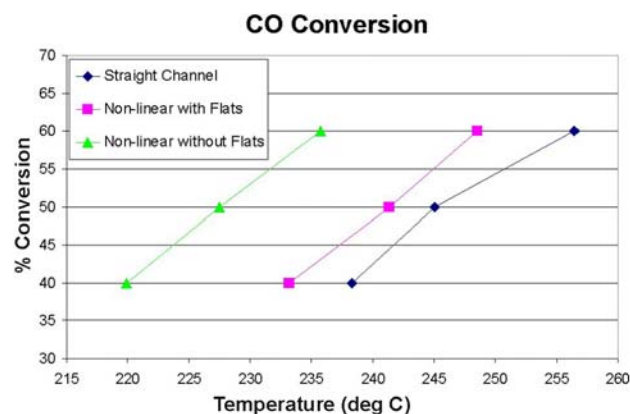


**Figure 1.** Carbon Monoxide Oxidation Light-Off for Non-Linear Channel Designs Compared to Straight Channel (Average of three trials)
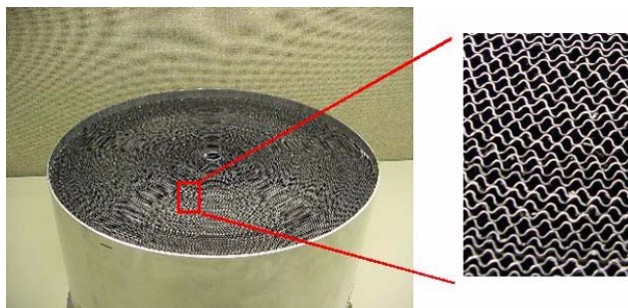
**Figure 2.** Full-Size Prototype with Non-Linear Channels and No Flat Layers



**Figure 3.** Hot Shake Test Fixture with 45° Mounting to Create Two-Dimensional Vibration, Which Is More Representative of Vehicle Vibration

in backpressure in both cases was modest. Modeling was done to optimize the non-linear geometry for the design with flat layers. As expected, the heat transfer (which was used as an approximation for catalytic activity) increases as the wavelength is decreased and the amplitude is increased. Further modeling will be completed to optimize the geometry for a full-scale converter with many channels. Also, the catalytic activity will be modeled rather than using heat transfer as an approximation.

Since the non-linear channel sample without flats performed so well during bench testing but is not easily modeled, full-scale prototypes were produced with this configuration (see Figure 2). The foil was folded and wound with two separate layers of foil so that the layers would not nest into each other. The substrate was then washcoated. These samples are now awaiting engine testing for full-scale emissions measurement.

Hot shake testing of full-size straight-channel samples with lower-cost materials was completed. Previous hot shake testing had only used vibration at a steady-state temperature with no thermal cycling. For this testing, the vibration profile was increased to

create an accelerated, yet realistic test. In addition, the substrate was tilted to 45° to give the sample side-to-side loading as well as the up-down vibration (see Figure 3). Finally, a severe thermal cycle was created instead of testing isothermally. This caused all of the samples tested to fail before the 100 hr. limit. There is no significant difference in durability between the foil materials tested. Therefore, both new, lower-cost materials were deemed to be sufficient for service in diesel engines at much lower cost than standard FeCr alloy metals.

## Conclusions

The two candidate alloys have passed all durability requirements and are capable of meeting all requirements for use in diesel engines. Also, the new non-linear design substrate has shown promise for improved catalyst efficiency in a smaller package size.

# II.B.18 NOx Reduction in Diesel Exhaust Using Ceramic Catalysts

*Ralph Slone*
Noxtech, Inc.
1939 Deere Ave.
Irvine, CA 92606

*DOE Technology Development Manager: John Fairbanks*

*NETL Project Engineer: Carl Maronde*

## Objectives

- Demonstrate the Noxtech PAC (plasma-assisted catalyst) system on a 60 kW diesel generator under the subsequent performance criteria:
  - 90% NOx reduction
  - 30,000 $hr^{-1}$ space velocity and 200-500 deg C
  - Generate data for scale-up to a 250-280 horsepower (hp) system
- Continue to improve the performance, costs, ease of fabrication, operating range and efficiency of the PAC system components and integrated system:
  - Improve NOx catalyst: increase space velocity, make more selective, improve low-temperature activity and enhance durability
  - Reductant generation: refine reductant formation/composition and optimize for NOx catalyst performance
  - Plasma: Move into the exhaust system and inject active species into exhaust, reduce power requirements and size
- Use the data generated from designing and testing the 60 kW integrated PAC unit and its components to design, build and evaluate a PAC unit capable of reducing over 90% of the NOx from a 250-280 hp high speed diesel engine.

## Approach

- <u>Basic Approach</u>: Use modified cracking/reforming catalysts and ceramic materials, containing no precious metals, to crack/reform diesel fuel to act as a reductant over a very thermally and chemically stable NOx catalysts to reduce NOx to very low levels. This approach leads to a simple, low cost NOx reduction system for diesel exhaust that uses on board fuel and is resistant to thermal and chemical poisoning.
- <u>Personnel and Facilities</u>: Team with Analytical Engineering, Inc. (AEI) to provide the test capabilities and talent needed to expedite the project.
- <u>System Improvement</u>: Improve and optimize the performance, costs, ease of fabrication, operating range, efficiency and understanding of the controlling mechanisms for the PAC components and integrated system.
- <u>Design and Demonstrate</u>: Design and conduct a Ceramic Catalyst System (CSS) aftertreatment demonstration test on the exhaust of a 60 kW high speed diesel engine using data from the component improvement work.
- <u>Design</u>: Use the data and component enhancements/improvements from the previous tasks to design and build a CSS for a 300 hp diesel engine.

## Accomplishments

- Eliminated the plasma generator as an active component of the Noxtech PAC system, thereby producing a catalytic NOx reduction system with very attractive features:
  - Simplified low-cost system that does not use precious metals
  - Sulfur-tolerant, thermally stable
  - Low parasitic requirements (2-3%) and uses on-board diesel fuel for reductant
- Demonstrated 92% NOx reduction on diesel exhaust slip stream at 200,000 hr$^{-1}$ space velocity and 2% parasitic loss, even with 500 ppm SOx (commercial diesel fuel) in the exhaust stream.
- Demonstrated 65% NOx reduction over the Federal Test Procedure (FTP) transient cycle on the full exhaust flow from a 165 hp diesel engine with 500 ppm SOx.
- Formulated over 40 unique cracking/reforming and NOx reduction catalysts.
- Designed and acquired components for a Noxtech CCS to perform a NOx reduction demonstration on a 300 hp diesel engine.

## Future Directions

- Use slip-stream and high-throughput microscreening, to optimize the system cracking/reforming and NOx reduction catalysts to realize these objectives:
  - Extend operating temperature range to achieve over 90% NOx reduction from 600 deg C to 150 deg C
  - Reduce system size by extending space velocity from 30,000 to 50,000 hr$^{-1}$
  - Demonstrate good durability
- Design, build and demonstrate a Noxtech CCS, with the performance characteristics listed in item 1, on a 300 hp diesel engine for both steady-state and transient test conditions:
  - Optimize size and geometry
  - Integrate controls with engine CPU
  - Conduct durability/performance tests

## Introduction

Emission standards in the U.S. will require reduction of diesel emissions for transportation vehicles (light- and heavy-duty diesel-powered trucks and buses) by as much as 90% from the current level in the 2005-2010 timeframe. In addition, boilers-electric generators (especially coal-fired boilers) and internal combustion engine (gas and diesel) powered electric generators are required to meet even more stringent NOx emissions levels. Achieving these levels with acceptable costs and durability will be very difficult for these industries.

NOx reduction approaches presently being developed present many problems and challenges. Catalyst poisoning, high costs, thermal cycling, parasitic losses and difficulty with supplying a practical reductant make the performance and life of NOx adsorbers and lean NOx catalysts problematic.

Urea selective catalytic reduction requires an external fluid to be commercially distributed and carried on commercial vehicles, which has significant enforcement issues. Combustion control technologies such as exhaust gas recirculation (EGR), high injection pressures, variable geometry turbine for air handling and other similar mechanisms used to control NOx emissions from diesel engines add complexity and cost as well as reduce reliability and efficiency.

Analytical Engineering, Inc. (AEI) and Noxtech, Inc. are jointly developing and demonstrating a tailored reductant and ceramic NOx catalyst (TRCNC) system as a promising alternative for exhaust aftertreatment of NOx from diesel exhaust. This system does not have the sensitivity to fuel sulfur levels and operating temperature excursions exhibited by traditional catalyst-based systems. This system significantly reduces parasitic losses

(improves fuel efficiency) and reduces emission control system complexity at much lower costs than other systems being investigated.

## Approach

It was determined early in this project from laboratory/pilot studies that a plasma reactor was not needed to achieve the project's NOx reduction goals. Based on these pilot/laboratory studies, a Ceramic Catalyst System (CCS) was designed that demonstrated over 90% NOx reduction in diesel exhaust. It consists of a small cracking/reforming catalyst reactor (Figure 1), external from the exhaust stream, that will crack and reform a hydrocarbon (preferably diesel fuel or gasoline) to form a very active reductant with a composition of partially oxidized hydrocarbon species and hydrogen. These reductants were optimized for NOx reduction over a ceramic NOx reduction catalyst by controlling the cracking/reforming catalyst composition and operating conditions: temperature, space velocity, and oxygen concentration. The reductants formed in the cracking/reforming reactor were injected into the exhaust upstream of the ceramic NOx reduction catalyst to produce over 90% NOx reduction in diesel exhaust. There are no precious metals used in the cracking/reforming catalyst. A doped ceramic NOx reduction catalyst was placed in-line with the exhaust flow and downstream from the injection of reductants formed by the cracking/reforming catalyst. NOx in the exhaust combines with the active reductants on the surface of the ceramic NOx reduction catalysts to form $CO_2$, $H_2O$ and $N_2$. The ceramic NOx reduction catalyst contains no precious metals and is not susceptible to sulfur poisoning or deactivation.
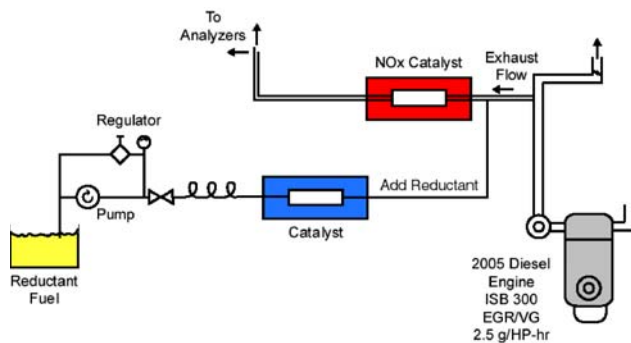


**Figure 1.** Slip-Stream NOx Reduction Schematic

Significant laboratory studies were conducted using synthetic gases and an exhaust slip-stream from a diesel engine to develop an understanding of and to improve the CCS components and process mechanisms. This data was used to design and demonstrate a CCS to remove the NOx from a 165 hp diesel engine. The information developed from the 165 hp test was used to design a CCS for a 300 hp high speed diesel engine.

## Results

Originally it was thought that a plasma reactor was needed to convert NO to $NO_2$ and to crack diesel fuel to produce a reductant before flowing this mixture over a NOx reduction catalyst. The work in this project found that both NO and $NO_2$ could be reacted simultaneously with a reductant formed from a cracking/reforming catalyst and a compatible ceramic NOx reduction catalyst. This eliminated the need for a plasma reactor in the NOx reduction system and greatly simplified and reduced the cost of this system.

Viable generation of a reactive reductant from diesel fuel is a critical requirement for this project. The development work conducted during this project in conjunction with several major commercial catalyst companies demonstrated that tailored reductants could be generated by uniquely formulated cracking/reforming catalysts. Functional reductants were generated from non-precious metal catalysts that are sulfur-tolerant and thermally stable. It was demonstrated that these reductants reacted efficiently and effectively on the surface of a ceramic NOx catalyst without producing undesirable by-products (solid or gaseous). The reductant formation process was refined and controlled to produce the optimum species for reaction with NOx on the NOx catalysts surface but also to prevent the formation of solids and/or noxious gaseous species on the catalyst surface. The reductants generated from these cracking/reforming catalysts were used to demonstrate 92% reduction of NOx in a diesel exhaust slip stream (Figures 2 and 3) and 65% reduction of NOx from the exhaust from a 165 hp diesel engine (Figures 4 and 5).

Component improvement work conducted during this project has yielded excellent results:
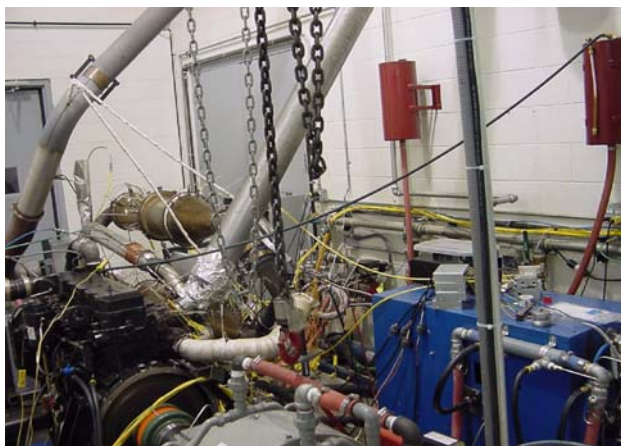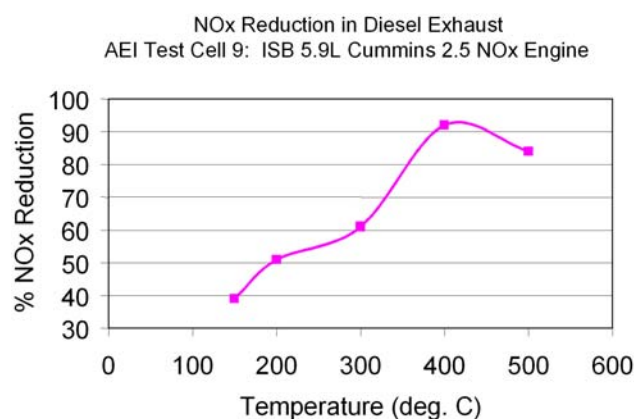
**Figure 2.** Test Cell Slip-Stream Demonstration



**Figure 4.** Test Cell Full-Flow Demonstration



**Figure 3.** NOx Reduction in Exhaust Slip-Stream
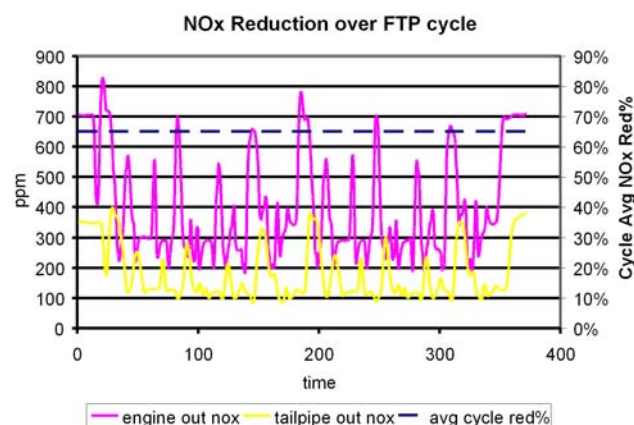


**Figure 5.** NOx Reduction over the FTP Cycle

- Over 90% NOx reduction has been demonstrated at over 100,000 hr$^{-1}$ space velocity.
- All catalysts used have proven to be sulfur-tolerant and thermally stable.
- Precious metals are not required to achieve good NOx reduction and durability.
- The system has proven to be simple to build and scale.
- The system achieved low parasitic loses of 2.5-3.0%.

## Conclusions

- Over 90% NOx reduction can be achieved in diesel exhaust using low-cost non-precious metal catalysts.
- Low-sulfur fuels are not required to achieve high levels of NOx reduction by using sulfur-tolerant catalysts.

- Over 90% NOx reduction can be achieved using a very practical size catalyst, i.e., 50,000 hr$^{-1}$ space velocity.
- Diesel fuel can be catalytically converted to an effective reductant, allowing the use of a single fluid to control NOx on diesel-powered transportation vehicles.
- Over 90% NOx reduction can be achieved in diesel exhaust at very acceptable 2-3% parasitic losses.

## FY 2005 Publications/Presentations

1. May, David; Slone, Ralph; "NOx Reduction in Diesel Exhaust Using Ceramic Catalysts", DOE Diesel Engine Emissions Reduction Conference (2005).

## II.B.19  Innovative Emission Control Device Renewal

*Eugene V. Gonze*
General Motors Corporation – Powertrain Division
Mail Code 483-710-111
895 Joslyn Avenue
Pontiac, MI  48340

*DOE Technology Development Manager:  Ken Howden*

*NETL Project Manager:  Aaron Yochum*

*Subcontractors:*
HRL Laboratories LLC
Michigan Technological University

## Objectives

The objective of this project is the development of a microwave particulate filter regeneration technique that minimizes:

- impact on engine operation
- power consumption
- cost

## Approach

This project aims to develop a new approach to regenerate particulate filters in compression-ignition, direct injection (CIDI) diesel engines.  The technology of spot heating within a diesel particulate filter (DPF) using microwave techniques in order to ignite the soot and allow the heat from the soot oxidation to raise the temperature of the DPF to a temperature sufficient to sustain the oxidation of the soot for complete regeneration has been investigated.  This project has also investigated:

- A range of microwave active materials for both activity and stability in the DPF environment
- A series of spots within the DPF to identify those with the highest soot ignition efficiency
- Modeling to predict the efficiency of spots to absorb energy
- Modeling to predict the optimum spot positioning to ignite and propagate soot oxidation with the minimum energy input
- Alternative approaches to this microwave heating system

## Accomplishments

- Developed a microwave heating technique that uniformly heats the DPF and eliminates parasitic soot absorption
- A number of materials have been evaluated as possible microwave absorbing candidates
- A range of different spots have been modeled for their effectiveness in initiating and propagating soot oxidation
- A proprietary microwave absorbing configuration has been designed and patent applications have been filed
- Engine control strategies for microwave assisted regeneration have been identified

**Future Directions**

This project will examine an alternative regeneration technique which builds off the knowledge gained from the microwave regeneration work and may reduce the fuel penalty of the current approach.

## Introduction and Approach

The goal of this project is to leverage the exotherm of soot oxidation during a DPF regeneration in order to minimize the amount of added energy.  Instead of heating the entire DPF to the soot oxidation temperature, only selected spots are heated to the oxidation temperature of the soot, and the oxidation wave within the soot is allowed to propagate.  To accomplish this, effective stable microwave absorbing materials need to be identified, the optimum positioning of the heat absorbing spots for soot oxidation and propagation need to be determined, an optimally designed microwave cavity within the DPF must be designed and an engine control strategy must be developed that leverages this microwave technology.  This project has addressed each of these needs.

## Results

HRL Laboratories has evaluated a wide range of microwave active materials.  The materials include silicone carbide, indium tin oxide, nickel oxide, iron ferrites, lithium ferrite, cobalt and combinations of aforementioned materials.  The material selected for use in this project has met the following criteria:

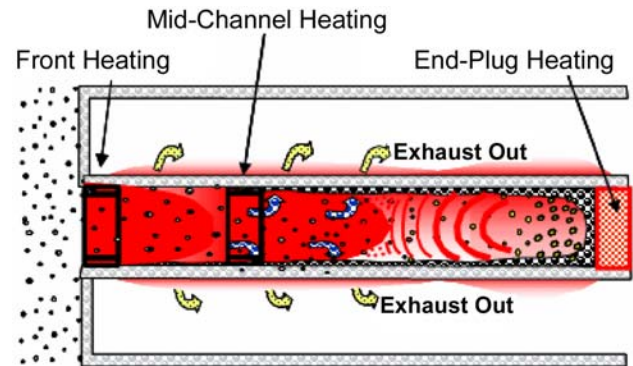- Effectively absorbs microwave energy



**Figure 1.** Schematic of Some Possible Spot Configurations

- Magnetic absorption meets the desired Currie cut-off temperatures

To determine the most effective manner in which to position the microwave absorbing spots (see Figure 1) within the DPF to generate light-off with the highest probability that soot oxidation would create a propagating wave, a series of spot configurations were modeled using the DPF regeneration model developed by Michigan Technological Institute (MTU).  An example of one of these simulations (see Figure 2) shows the evolution of the temperature in a DPF from the addition of heat at three separate locations in the
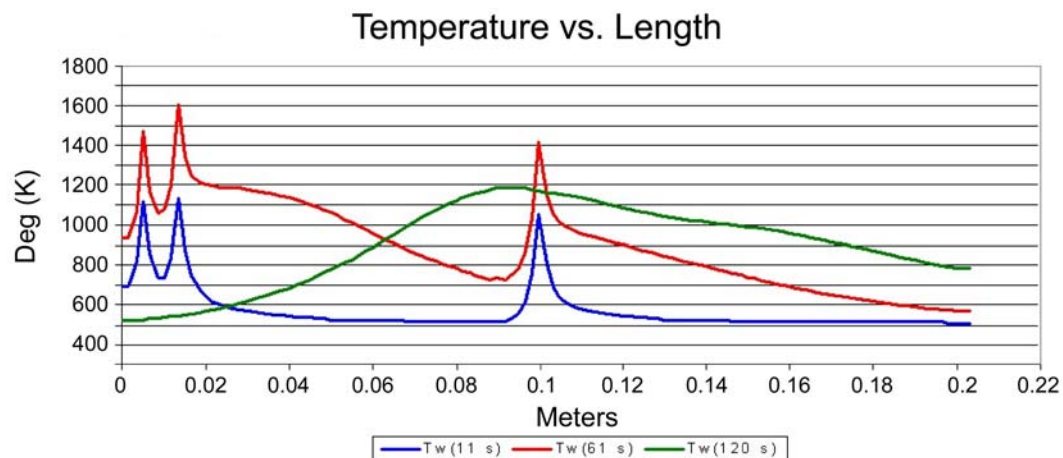


**Figure 2.** Temperature Along the Length of a DPF Where the Soot Has Been Ignited by Three Separate Points
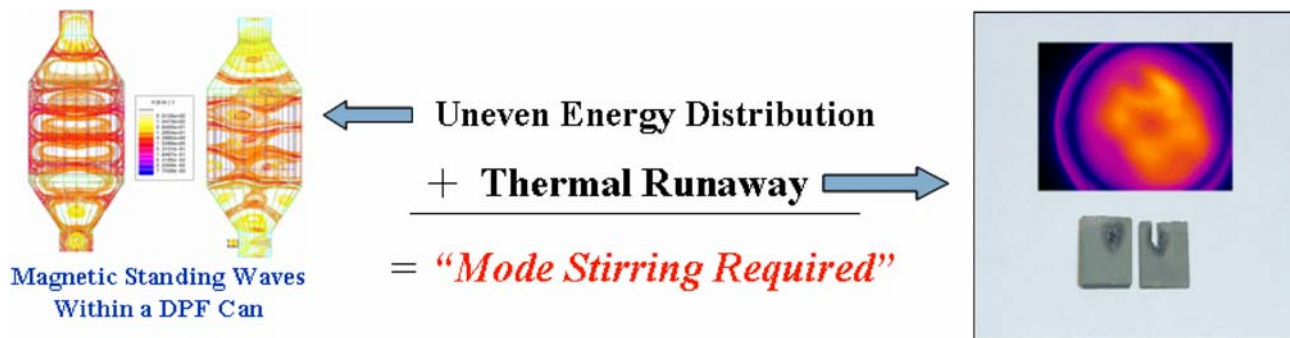
**Figure 3.** Schematic Illustrating the Value of Mode Stirring to Reduce the Possibility of Thermal Runaway

DPF. The blue line shows the temperature just shortly after the addition of the heat, at which point there has been little propagation of a soot oxidation wave. The red line shows the temperature of the DPF after 8 seconds. Clearly, oxidation has begun between the spots. However, the temperature from the spots is still very distinctive. After 20 seconds (the green line), the temperature spikes from the transient heating have largely dissipated, and a soot oxidation wave has begun to propagate down the DPF. Simulations such as these helped to define the optimal spot configuration for the device.

A number of factors were necessary for the optimal microwave energy addition. Among those was the application of mode stirring in order to uniformly distribute the energy deposition (see the graphic in Figure 3). A number of other technologies were developed to efficiently distribute the energy to the selected spot geometry in the doped DPF.

These studies resulted in a high-efficiency microwave heater design that optimizes the deposition of energy from the microwave transmitter.

Once an optimum spot configuration was identified, the MTU DPF regeneration code was used to vary the inlet conditions to the DPF in order to identify the engine conditions that would most enhance the soot oxidation. Those conditions have been included in the general DPF regeneration strategy.

## Summary

This project has developed a highly efficient microwave heater that uses material properties of the microwave absorbers to uniformly heat the DPF. The microwave heater uses magnetic absorption to mode stir a microwave standing wave such that the DPF is uniformly heated. Uniform heating allows the entire DPF to be regenerated. Since our heater is structured to use magnetic energy, only the targeted area is heated. This selected heating reduces the amount of energy required to regenerate the DPF. Further efficiency improvements are obtained by eliminating energy loss through the particulate matter. Overall, this technique is inherently one of the most efficient methods to heat a DPF using microwaves.

## Conclusions

This project has defined an energy-efficient approach to microwave assisted DPF regeneration. The fuel economy penalty for the use of this technology has been quantified and is substantially less than that for the more traditional approaches to microwave initiated DPF regeneration. Based on the discoveries produced by this project, work is under way to evaluate some competitive approaches that can use some or all the technologies from this project.