
Emission Control Research to Enable Fuel Efficiency: Department of Energy Heavy Vehicle Technologies

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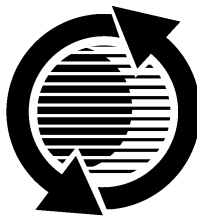
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ABSTRACT

The Office of Heavy Vehicle Technologies supports research to enable high-efficiency diesel engines to meet future emissions regulations, thus clearing the way for their use in light trucks as well as continuing as the most efficient powerplant for freight-haulers. Compliance with Tier 2 rules and expected heavy duty engine standards will require effective exhaust emission controls (after-treatment) for diesels in these applications. DOE laboratories are working with industry to improve emission control technologies in projects ranging from application of new diagnostics for elucidating key mechanisms, to development and tests of prototype devices. This paper provides an overview of these R&D efforts, with examples of key findings and developments.

EMISSION REQUIREMENTS

The emission control requirements are evolving to be considerably more challenging than in 1995 when the DOE accelerated efforts in diesel emission control. Heavy-duty diesels have a target of 2.5 g/hp-h NO_x+HC for 2002, with PM at 0.10 g/hp-h (0.05 g/hp-h for urban bus). At this time, the heavy-duty diesel can likely meet this mark without exhaust emission control devices ("aftertreatment") by implementing cooled EGR and retarding fuel injection. A notable penalty in fuel economy and some degree of concern on durability come with these measures. New proposed rules for heavy-duty die-

sel are forthcoming, expected to require even further reductions of NO_x and PM. NO_x levels may have to be reduced below 0.5 g/hp-h and PM as low as 0.01 g/hp-h over the next 6-8 years. These anticipated rules would most certainly require the application of exhaust emission control devices to heavy trucks and busses.

Application of clean diesels in the light truck, sport utility, and passenger car market is perhaps the most significant petroleum conservation opportunity available in the next two decades. Ironically, the greatest challenge for diesel emissions compliance is in light duty vehicles, especially light trucks, due to requirements set forth in the EPA Tier 2 rules finalized in December 1999. The challenge for the engine + aftertreatment system is depicted in Figures 1 and 2. Even at a relatively "clean" engine-out emissions level, 1.0 % NO_x index, the aftertreatment device may still have to be over 95% effective in a sport utility vehicle for the final phase-in of Tier 2. DOE has accepted a research target of 0.05 g/mi NO_x and 0.01 g/mi PM for vehicles under 8500 lbs GVWR.

EMISSION REDUCTION PATHWAY

Reaching the emissions targets requires a three-pronged integrated approach of engine technology, emission controls components/systems, and fuel formulation. An approximate quantitative pathway is depicted in Figure 3. Most apparent is that PM and NO_x emission controls devices will be required to be 90% or more effective, and this effectiveness must be maintained for 120,000 miles.

Meeting this challenge is the underlying justification for the emission control efforts in OHVT. The efforts include research on mechanisms of NO_x reduction, catalyst performance and degradation, development and evaluation of prototype devices, and finally integration and engineering of multicomponent emission control systems.

NO_x AND PM REDUCTION VIA PLASMA-ASSISTED CATALYSIS – LAWRENCE LIVERMORE NATIONAL LABORATORY

Lawrence Livermore National Laboratory (LLNL) is investigating the use of a plasma for the simultaneous control of NO_x and particulates in diesel engine exhaust.

Diesel particulates are composed primarily of dry carbon (commonly known as soot) and liquid-phase hydrocarbons (known as the volatile organic fraction, VOF). The liquid hydrocarbons in the particulates are a combination of unburned diesel fuel and lubricating oil. Novel catalysts containing high surface area CeO₂ as the active catalytic component have been developed to oxidize the volatile organic fraction to CO₂ and H₂O. On the other hand, novel particulate traps using specially fabricated ceramic fiber structures have been developed and shown to significantly reduce the carbon fraction. Particulate trap efficiency is regenerated by heating the filter to carbon ignition temperatures in order to oxidize the carbon to CO₂. Another method for regenerating particulate traps utilizes the NO_x in the exhaust. In continuously regenerated particulate traps (CRT), a precious metal catalyst is used to oxidize NO to NO₂ upstream of a particulate filter; the NO₂ is then used to oxidize the carbon fraction of the trapped particulates [1]. The CRT method requires low sulfur fuel because the catalyst component that is active in converting NO to NO₂ is also active in converting SO₂ to SO₃. SO₃ leads to the formation of sulfates and ultrafine particulates.

The LLNL project has been investigating various schemes in which a plasma is used for the simultaneous conversion of the particulate VOF, the particulate carbon and/or the NO_x. Both non-thermal and thermal plasma modes are considered. In the non-thermal schemes, the plasma is used mainly as a source of oxidizing radicals. In the thermal schemes, the plasma is used also as a localized heat source.

The first scheme involved using a non-thermal plasma to oxidize the particulate VOF while simultaneously oxidizing NO to NO₂. The NO₂ is then used to oxidize the carbon fraction of the particulates.

An injector for introducing surrogates of the volatile organic fraction (VOF) was constructed and installed. There was previously no data on the plasma conversion chemistry of the VOF. This injector system enabled a study of the chemistry in a controlled manner. The VOF conversion was measured as a function of temperature and plasma power. The desired outcome is the complete oxidation of the VOF to CO₂ and H₂O. When the plasma was operated using five percent or less of the engine power output, only the partial oxidation of the VOF was observed. The study showed that complete non-thermal

NO_x Aftertreatment/Control and Base Engine/Fuel Requirements:
50 mg/mile Tailpipe Standard

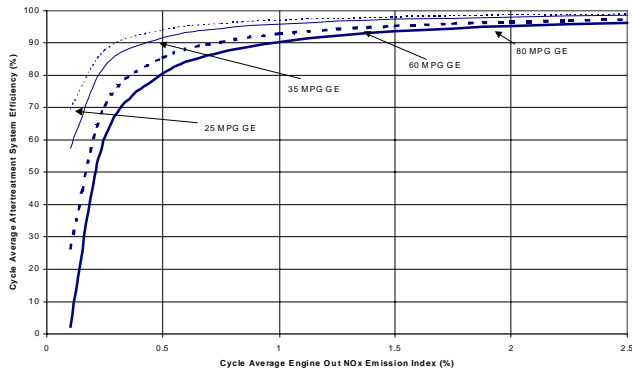


Figure 1.

PM Aftertreatment/Control and Base Engine/Fuel Requirements:
10 mg/mile Tailpipe Standard

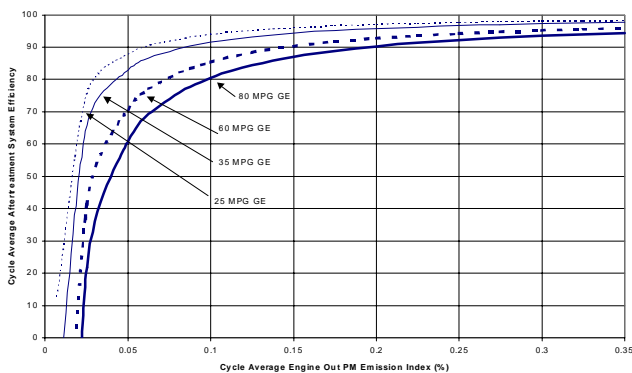


Figure 2.

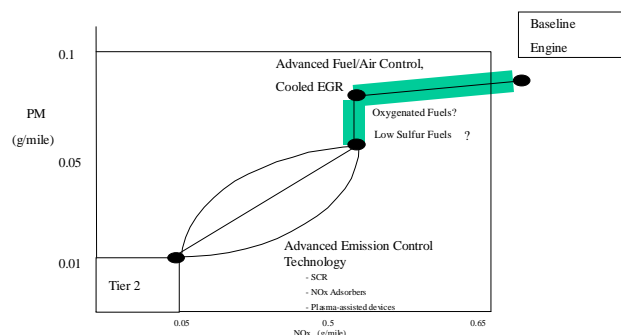


Figure 3. Approximate Emissions Reduction Pathway for a Light Truck with Clean Diesel Engine.

oxidation of the VOF requires excessive electrical power input to the plasma. Therefore, an oxidation catalyst will be required to take care of the remaining hydrocarbons.

Next, the NO conversion was measured as a function of plasma power and VOF concentration. To achieve maximum oxidation of NO to NO₂, there was a trade-off between the plasma power and the VOF concentration. The study showed that the conversion of NO to NO₂ with a modest amount of plasma power requires an unusually high VOF concentration.

Finally, the reaction of NO₂ with the carbon fraction of the particulates was investigated. The desired outcome is the reduction of NO₂ to N₂, and the complete oxidation of the carbon to CO₂. A competing pathway is the backconversion of NO₂ to NO, while the carbon is oxidized only to CO. It was found that the NO₂-plus-carbon system alone, although capable of oxidizing the carbon to CO, is not efficient in removing NO_x. Therefore, a catalyst will be required to take care of the remaining NO_x and CO.

The study mentioned above showed that a non-thermal plasma alone cannot effectively and simultaneously remove NO_x and particulates. The next phase of the project then is to determine if the combination of the plasma with a catalyst is more effective for simultaneous removal of NO_x and particulates. Simultaneous removal may be possible if the following scenario can be accomplished: First, a non-thermal plasma is used to electrostatically trap the particulates and to convert the NO to NO₂. Second, the plasma is operated occasionally in the arc thermal mode to convert the VOF to gaseous hydrocarbons and to thermally oxidize the trapped carbon, thereby regenerating the particulate trap. Third, a catalyst is used to reduce the NO₂ to N₂, using the VOF-derived or additive hydrocarbons as the reductant [2]. The scheme is being studied to determine the optimum mix of NO_x and particulates (and perhaps additive hydrocarbons) that is necessary for the most efficient simultaneous removal of both NO_x and particulates.

Figure 4 shows particulate carbon precipitated on an electrode surface. The bottom photo shows the surface regenerated by thermal plasma oxidation of the carbon.

The LLNL group has been working with Cummins Engine Company to study the scale up of the plasma-assisted catalytic reduction (PACR) process for NO_x to a Cummins B engine. They have also been collaborating with Engelhard Corporation on the development of catalysts that are optimum for combination with a plasma [2].

The LLNL plasma processor has been successfully scaled up to handle the full exhaust flow from a Cummins B5.9 engine. At 100 kW load, the exhaust flow from this engine corresponds to about 9000 standard liters per minute (SLM) and contains around 500 ppm of NO_x. The PACR system consisted of a plasma processor for oxidizing NO to NO₂, followed by a catalyst for reducing NO₂ to N₂ in the presence of a hydrocarbon[2]. The PACR process is described in detail in Reference 2. It is estimated that a plasma energy density of 20 Joules per standard

liter (J/L) of exhaust will be necessary to significantly enhance the reduction of NO_x under the full engine load. A plasma energy density of 20 J/L requires that a power of 3 kW be delivered to the plasma processor. This was accomplished successfully using a plasma reactor volume of only 1.5 L. The plasma reactor had a simple wire-in-cylinder configuration.

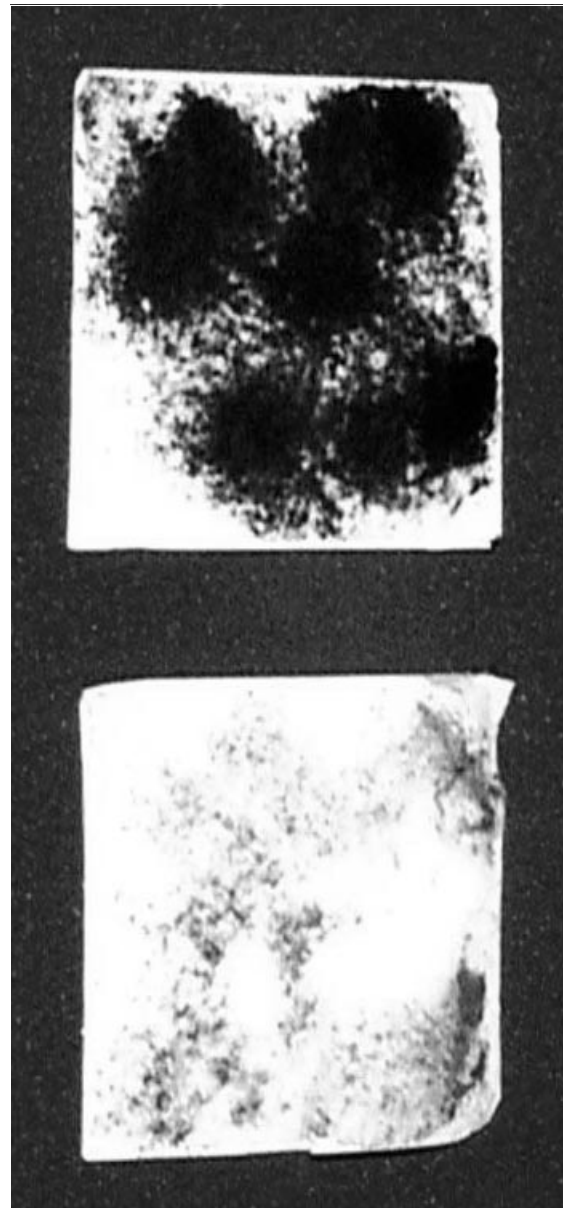


Figure 4. Plasma oxidation of particulate carbon that was precipitated on an electrode surface. The top figure shows the carbon collected on the electrode surface. The bottom figure shows the electrode surface after the carbon was oxidized by the plasma.

Figure 5 shows the NO_x oxidation and reduction efficiencies in the LLNL PACR reactor treating the full exhaust flow from a 100 kW Cummins B5.9 diesel engine. The data on the left shows the effect of the catalyst on the NO_x, without the plasma and without any hydrocarbon. The data shown in the middle shows the effect of the catalyst on the NO_x, also without a plasma but with

kerosene added in the amount of $C1/NO_x = 4$. The data on the right shows the effect of the plasma, with the same amount of kerosene additive. The power input to the plasma was 3 kW. The plasma enhanced the oxidation of NO to NO_2 . The plasma also significantly enhanced the reduction of NO_x to N_2 . The catalyst temperature in all the cases shown in Figure 5 was 260C.

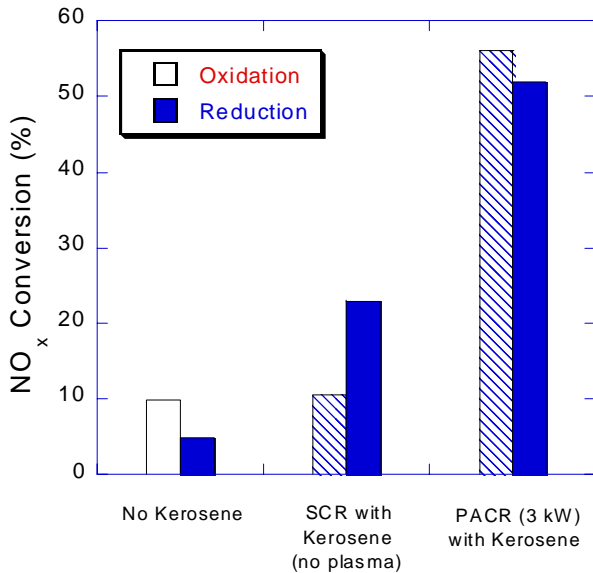


Figure 5. NO_x oxidation and reduction efficiencies in the LLNL PACR reactor treating the full exhaust flow from a 100 kW Cummins B5.9 diesel engine. Hydrocarbon reductant was kerosene, with $C1/NO_x = 4$. The catalyst temperature was 260C. A power of 3 kW was delivered into a plasma reactor volume of 1.5 L.

NO_x REDUCTION VIA PLASMA-ENHANCED CATALYSIS – PACIFIC NORTHWEST NATIONAL LABORATORY, CATERPILLAR INC. CRADA

This ongoing program focuses on plasma-enhanced catalytic abatement of NO_x from heavy-duty diesel exhaust. Major goals of the program include development of a plasma reactor platform capable of handling exhaust streams in excess of 773K and formulation of high surface area catalysts for conversion of NO_x to N_2 . Topics of interest include materials issues for high-temperature plasma reactors, electrical performance at high temperature, and the effect of catalyst physical properties on conversion.

HIGH-TEMPERATURE PLASMA STAND – A number of non-thermal plasma (NTP) reactors have been used in prior work. [3, 4] These include pulsed corona, concentric cylinder and planar dielectric barrier, and packed bed NTP reactors. We have determined that stable operation at a temperature of 773K cannot be obtained with a

packed bed or single dielectric barrier design. At temperatures above 573K many packing materials become conductive, which leads to arcing across the bed, and failure of single barrier–open gap designs has been observed at temperatures above ~623K.

A working prototype for the temperatures of interest was constructed using a dual-dielectric barrier design. This reactor was used for numerous tests over fairly long time periods with no degradation in performance. Power is supplied to the reactor using a typical high-voltage circuit consisting of a waveform generator input to an audio amplifier that drives a high-voltage transformer. Power deposition is monitored by integrating the area of a voltage-versus-current curve (Lissajous figure). Figure 6 shows typical power deposition data for the dual-barrier reactor at three temperatures. Corona onset and power deposition can be achieved at lower voltages as the temperature increases because the mean free path in the gas is considerably larger at high temperature.

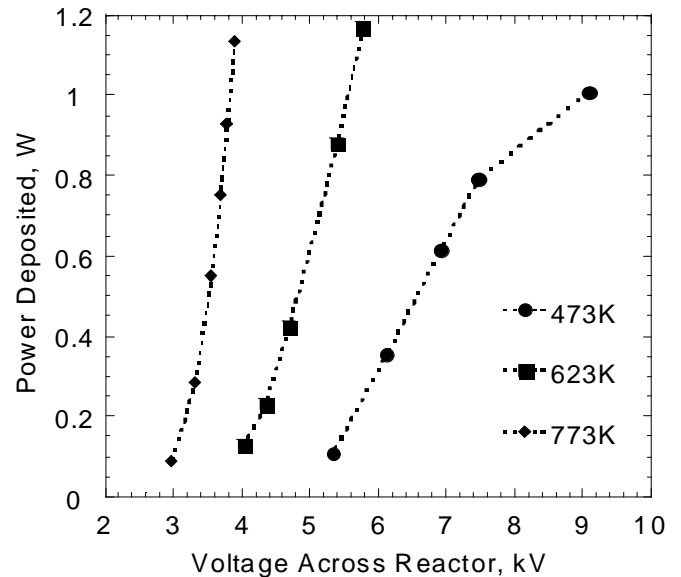


Figure 6. Power deposition characteristics for the dual barrier reactor. Gas flow rate of 1 SLM.

The dual-dielectric barrier reactor has been incorporated into a high-temperature test stand used for plasma catalysis measurements that is shown in Figure 7. Simulated lean exhaust comprising 500 ppm NO, 300 ppm CO, 8% CO_2 , 9% O_2 , 1.5% H_2O , and 20 ppm SO_2 is generated using a gas makeup manifold. Propene is added to this mix at various levels depending on the experiment of interest. Generally, the propene concentration is at least 500 ppm. The balance of nitrogen is passed through a humidification column before addition to the dilute species. A two-stage system is used to reduce NO_x, where the plasma reactor converts NO to NO_2 prior to selective catalytic reduction. The plasma and catalyst reactors are housed in furnaces to enable high-temperature experiments. Gas from the inlet, post-plasma, or post-catalyst is passed through a diffusion dryer and to analytical instrumentation to determine where conversion of NO_x

occurs. Analytical techniques used on this program include chemiluminescent NO_x analysis, FTIR, real-time RGA, and GC-MS.

CATALYST PERFORMANCE – Numerous catalysts have been synthesized and probed for lean-NO_x catalysis and plasma catalysis of NO_x. This program has screened a variety of commercially available and laboratory-synthesized metal oxide-based catalysts. Although commercial catalysts have shown reasonable activity, laboratory-synthesized catalysts have proven more effective for reducing NO_x by plasma-enhanced catalysis. Catalysts are tested by loading 1 g of powder into a quartz flow cell and measuring the conversion of NO_x as a function of plasma power. All catalysts are screened with a simulated exhaust flow of 1 SLM.

Figure 8 shows NO_x reduction data in the absence of sulfur for a proprietary catalyst formulation (Catalyst A) in simulated lean exhaust. The data show that the thermal component of catalytic conversion increases with temperature to a value of 60% at 773K. At 473 and 623K, substantial activation of the catalyst is achieved by the plasma discharge. Figure 9 shows data obtained from the same catalyst with the addition of 20 ppm SO₂ to the lean exhaust mix. Here, there is virtually no effect on conversion at 473 and 773K, but there is a noticeable decrease—about 12%—in activity at 623K. Many of the catalysts that have been screened exhibit degradation in activity with SO₂ present in the simulated exhaust. Catalyst A is one of the least sensitive to sulfur.

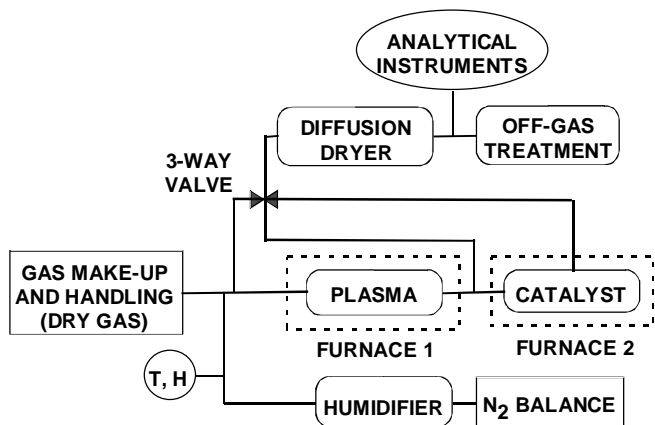


Figure 7. Flow chart for the high-temperature test stand used for plasma-catalysis measurements.

FUTURE DIRECTIONS – The program is in its second year of three. Efforts will continue to be focused on developing more efficient catalysts, but there are other areas where we intend to contribute. The first will be to examine the performance of a bench-scale plasma-catalysis system on a slipstream of a diesel engine at the Caterpillar Technical Center. Other areas of interest include the effects of hydrocarbon speciation on activity and continuing efforts to build prototype reactors for use on vehicles.

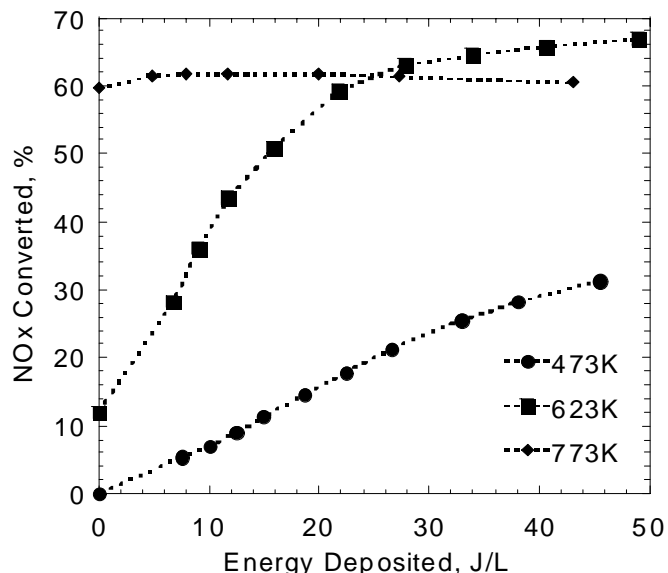


Figure 8. NO_x reduction as a function of energy density for Catalyst A. Gas composition: 500 ppm NO, 300 ppm CO, 8% CO₂, 9% O₂, 1.5% H₂O, 1000 ppm C₃H₆.

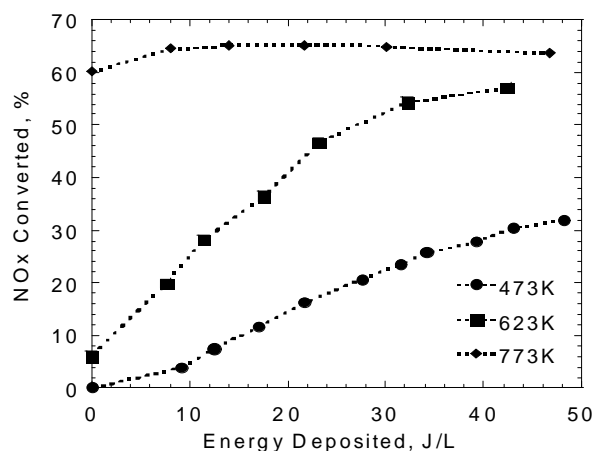


Figure 9. NO_x reduction as a function of energy density for Catalyst A. Gas composition: 500 ppm NO, 300 ppm CO, 8% CO₂, 9% O₂, 1.5% H₂O, 1000 ppm C₃H₆, and 20 ppm SO₂.

IMPROVED DIAGNOSTICS AND EMISSIONS MEASUREMENT – OAK RIDGE NATIONAL LABORATORY

MOBILE MASS SPECTROMETER – Advanced exhaust aftertreatment strategies, which incorporate operation transients, can provide superior performance. For instance, loading and regeneration of NO_x adsorber catalysts are transient processes. Even at a steady engine-operation condition, the exhaust-emissions-control system may be in a dynamic operation mode, and hence be continually cycling through transient states. As a consequence, its performance and emissions characteristics are temporally varying. High-speed measurements, capable of temporally resolving these dynamics, are

required to optimize the aftertreatment strategy. Standard laboratory instrumentation such as chemiluminescence and non-dispersive infrared analyzers do not provide the required speed. Mass spectroscopy (MS) can provide the requisite temporal resolution for detailed evaluation of high-frequency NO_x-adsorber dynamics. We have developed a Mobile MS that provides fast response, species selectivity and is readily transportable. The response of the Mobile MS and a chemiluminescence analyzer to a 400-ms pulse of NO are compared in Fig. 10; the curves in this figure have been shifted to temporally align the two peaks. The peak and full-width-at-half-maximum values are 2204 ppm vs. 804 ppm and 400 ms vs. 1.3 s, respectively for the MS versus the chemiluminescence measurements. This data indicates the superior performance of the Mobile MS for accurately resolving both the species dynamics and instantaneous concentration. The reliability of this comparison is supported by the agreement of the integrated signals from the two measurements to within their uncertainties.

The Mobile MS has been applied to research the dynamics of emissions-control systems of operating heavy-duty engines.

In this harsh environment, the Mobile MS provided superior performance, similar to Fig. 10, for resolving high-frequency NO_x, O₂ and CO₂ dynamics. In fact, the MS has been demonstrated capable of resolving the ultra-high frequency NO_x burst between adsorber regeneration and desorbed NO reduction. This advanced capability for temporally resolving emissions dynamics will be useful in research for developing enabling technologies, including optimizing and assessing regeneration strategies, candidate reductants and reductant combustion.

DRIFT AND RAMAN SPECTROSCOPY ON CATALYSTS – Diffuse Reflectance mid-Infrared Fourier Transform (DRIFT) and Raman spectroscopy are being used for *in-situ* monitoring of catalyst dynamics in bench-scale reactors. These tools are being used to research the details of advanced catalysis strategies. For instance, NO_x is efficiently stored on an adsorber catalyst as a nitrate species. Raman has been used to monitor adsorptive loading of a ca. 14-wt. % barium oxide catalyst supported on magnesium oxide. Dynamic NO_x trapping is evident from corresponding fluctuations in the barium-nitrate signal at 1047 cm⁻¹ (wavenumbers). Similarly, the dynamics of sulfur poisoning are evident from the Raman spectra of Fig 10. Prior to SO₂ exposure, adsorbed oxides of nitrogen are readily apparent by the nitrate features at 1047 and 732 wavenumbers. As sulfur poisoning progresses, available adsorption sites become occupied by trapped SO₂ (in the form of barium sulfate), and adsorbed NO_x is displaced in favor of this more stable sulfate. This is evident in Fig. 11 by the monotonically decreasing nitrate signals, with increasing SO₂ exposure and a corresponding increase in the sulfate Raman signal at 982 cm⁻¹. The broadband signal which increases with SO₂ expo-

sure, is also indicative of increasing sulfate formation. These spectroscopic tools are proving valuable for understanding adsorbed species dynamics in catalyst systems.

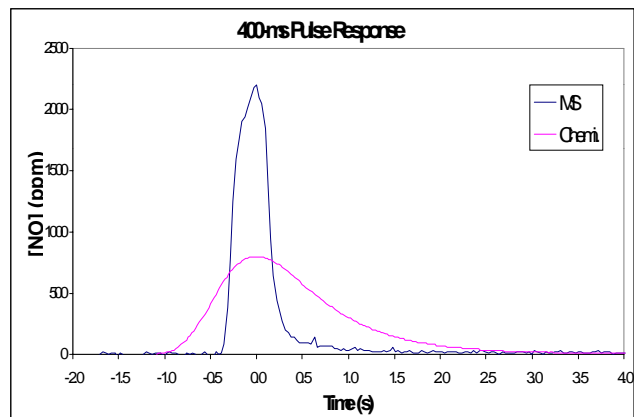


Figure 10. Response of the Mobile MS and Chemiluminescence analyzers to a 400-ms pulse of nitric oxide. The Mobile MS provides a more accurate measurement of the concentration dynamics in terms of both instantaneous magnitude and temporal variations.

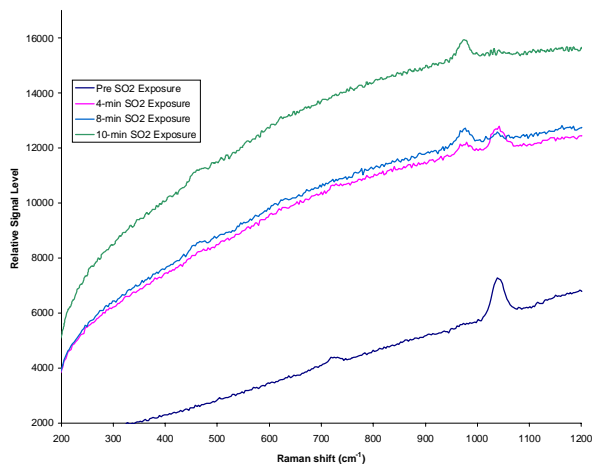


Figure 11. Raman resolved sulfur poisoning of a NO_x storage catalyst. Prior to the sulfur exposure, stored NO is evident from the nitrate features at 732 and 1047 cm⁻¹ (wavenumbers). The progression of sulfur poisoning is characterized by growth of the sulfate feature at 982 cm⁻¹. Additionally, sulfur poisoning displaces adsorbed NO as evident from the decreasing magnitude of the nitrate features with increasing sulfur exposure.

ULTRAFINE PARTICULATE MEASUREMENT – The accurate measurement of ultrafine particles has been the subject of much research and interest. Kittelson and others

[8, 9] showed that dilution conditions strongly affect the number concentrations one obtains. Maricq et al. showed that exhaust transfer line artifacts have a huge effect on what size distribution is measured. A consensus has emerged that normal dilution tunnel conditions make it extremely hard to avoid artifacts either from adsorbed HCs or reactions occurring under the specific tunnel conditions. To avoid some of these problems when measuring ultrafines, many groups are adopting the micro-dilution approach of Kittelson et al. This small dilutor, based on an ejector pump, provides on with a system that is easy to clean and can be used to provide very high dilution.

ORNL evaluated the device with model aerosols, as such data had not been presented in the literature. Because the sample PM goes through a sonic expansion, it was feared that the dilution process might perturb the particles. For instance, the high degree of turbulence might cause agglomeration that might not of occurred otherwise. The microdiluter was built and evaluated with two model aerosols with a mean diameter of 67 nm. The first were NaCl particles that are solid, and the second were dioctyl pthalate (DOP) aerosols that are liquid droplets. The DOP was chosen to represent a “fragile” diesel particle. The assumption was made that if these particles survived the micro-dilution process, a diesel particle would. Figure 12 shows a normalized size distribution for DOP particles before and after the dilution device. The extra scatter in the post-dilution data is easily accounted for by the extra error associated with measuring the fewer number of particles after dilution. It is clear that this device has little or no effect on the size distribution.

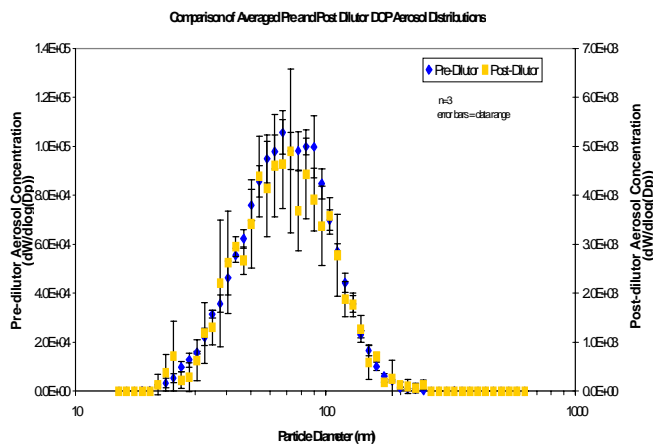


Figure 12. Comparison of size distribution for a model aerosol before and after a micro-dilution device.

NEW METHOD FOR SEMI-VOLATILE ORGANICS – Because diesel fuel is heavier than gasoline, semi-volatile organic compounds (SOCs) are a major component of diesel exhaust emissions. Many of the PAHs as well as unburned fuel components are in the SOC fraction of the exhaust. Current methods of SOC analysis include sorption of the compounds on polyurethane foam (PUF)

plugs downstream of the filter and subsequent solvent extraction and analysis, or sorption of the compounds on Tenax™, a solid phase sorbent, followed by thermal desorption -GC-MS. Both of these methods are cost-prohibitive for high throughput sampling. The PUF method uses 2-3 liters of chlorinated solvent for extraction and cleanup, and requires a 12-hour extraction, resulting in high labor and waste disposal costs. The second method uses a special thermal desorption apparatus, which is quite expensive. Also, since no extract is created, the sample is lost if the desorption process or the GC-MS fails.

ORNL has developed a new method for an easier and less costly analysis of these compounds. [10] A special sorbent membrane, Empore™ (3M company) is placed behind the filter in a dual filter holder. The sorbent membrane is a fluorocarbon membrane impregnated with octadecyl silane resin. This allows the dilute exhaust to flow freely through the membrane while it retains hydrocarbons. The membrane is able to retain compounds light as undecane (C₁₁H₂₄) without breakthrough under dilute sampling conditions (T < 52 °C). Figure 13 shows actual exhaust sampling with two sorbent membranes in line after a filter. The second, or backup membrane shows little breakthrough, even for the relatively long sampling time of 15 min.

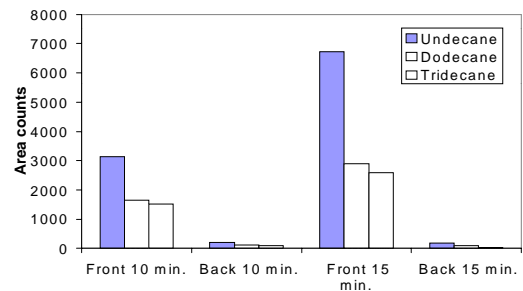


Figure 13. Dilute exhaust from a light-duty diesel sampled through a particulate filter and two sorbent membranes. Dilution ratio was 19:1. Note the lack of breakthrough for all three compounds.

The membranes are used as received and there is a simple, five-minute extraction process, followed by a nitrogen blow down step to reduce the volume of the extract. Detection limits for our GC-MS in scanning mode were on the order of x ng/m³ of exhaust. Selective ion monitoring (SIM) would reduce that even more for specific compounds.

SYSTEM-LEVEL R&D

ZERO REGULATED EMISSIONS ENGINE FEASIBILITY – A research, development and demonstration effort known as the (near) Zero Regulated Emissions (ZRE) powertrain feasibility study is underway at ORNL to show how clean a diesel powertrain can be. The objective is to demonstrate that a modern, low-emission engine utilizing

high quality diesel fuel or alternative fuel, combined with "aggressive" exhaust aftertreatment technology can serve as a near-zero emissions powertrain. One major goal of this effort is to go well beyond characterizing the individual components or sub-systems such as the engine, EGR system, PM filter, SCR catalyst, etc., by exploring the interactions between the components and learning how to control and optimize the entire power system.

Approach – To obtain very low engine-out emissions, it was determined that an advanced diesel engine utilizing special fuel should be employed, therefore, engines designed for low emissions with features such as electronically controlled fuel systems and cooled EGR were seen as top candidates. Any diesel engine and fuel combination will still need a very effective aftertreatment system to bring emissions to very low levels.

A review of advanced diesel particulate filter technologies and NOx removal technologies revealed that multiple promising approaches are being developed as potential products for future diesel engine transportation applications. More than one regenerating particulate trap technology is seen to work relatively well and to be at the verge of commercialization. The aftertreatment technologies for removing NOx appear further from commercialization for vehicle application, but are apparently quite effective under more controlled testing conditions.

Coordinating the control of the engine and aftertreatment components simultaneously to minimize emissions will be a main focus of this work.

The first such system to be studied will feature a Cummins ISB 5.9 L engine (6 cylinder, 24 valve) with an advanced EGR and fueling system utilizing an ultra-low sulfur diesel fuel. The aftertreatment system will include a continuously regenerating particulate trap in combination with a urea-based selective catalytic reduction system (for NOx removal). Consideration will be given to using a low sulfur lubricating oil and other engines and aftertreatment components (such as a NOx absorber system) as the work progresses.

The initial work will involve characterizing the engine out emissions and the capabilities of the aftertreatment components for a set of steady state operating points. These results will point the way to methods for controlling the overall system during transient engine operation. The most challenging aspect is expected to be controlling of NOx to very low levels under transient conditions (due to lack of adequate closed loop control at this time) while avoiding significant NH3 break-through.

It is hoped that levels on the order of <0.5 g/hp-hr NOx and .01-.02 g/hp-hr PM will be achieved.

COOLED EGR SYSTEM CORROSION STUDY – The corrosion risk to a CIDI engine utilizing a cooled EGR system is quite significant. An effort will be undertaken to map the corrosive effects of EGR as a function of engine

operating mode, EGR system operation, fuel sulfur level, and ambient conditions.

Approach – The Cummins engine with a cooled EGR system previously described for the ZRE project will be used for this work. The EGR system and intake manifold will be modified to allow measurement of corrosion potential, gas chemistry, and PM on both sides of the EGR cooler and in the intake air stream. In addition to gas sampling for characterizing gas composition and PM, an electrical resistance corrosion probe and test coupons will be used to measure corrosion and corrosion potential.

HC SPECIATION FOR LEAN NOx REDUCTION CRADA

The objective of this program, a CRADA between Detroit Diesel Corp. and ORNL, is to determine chemical composition of reductant species in the exhaust as a function of post-injection conditions. This information is key to understanding what and how much of certain species are available to the exhaust emissions treatment device. It has application both in passive lean NOx catalyst systems, and NOx adsorber type systems. Experiments were performed on a 1994 Navistar Engine equipped with the capability for post-fuel injection. This allowed an extra amount of fuel to be injected in the cylinder at a user-selectable number of degrees after top dead center. The resultant species were then measured with conventional gas analyzers and gas chromatography-mass spectrometry (GC-MS). Figure 14 shows the CO and NOx for an in-cylinder injection of different amounts of HC. Note the increase in CO and the decrease in NOx. The post injection can then be seen to have two benefits: the first is production of a useful species (CO) for catalytic NOx reduction; and the second is a real reduction in in-cylinder NOx, so engine out emissions are reduced.

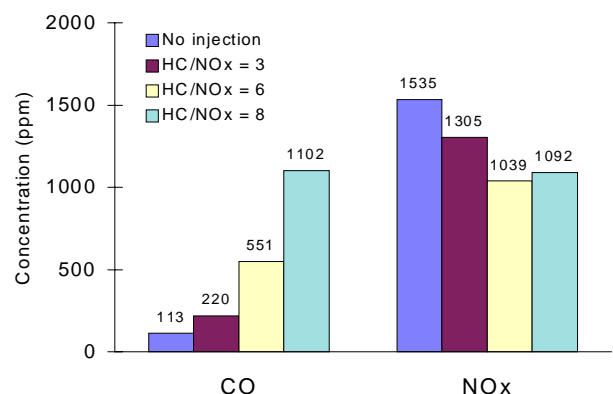


Figure 14. CO and NOx emissions after post-injection of fuel. HC/NOx ratio refers to concentration of HCs in exhaust. Data from 1994 Navistar running onD2 at 1900 rpm, 100% load, which is rated torque.

REFERENCES

1. B.J. Cooper, H.J. Jung, and J.E. Thoss, "Treatment of Diesel Exhaust Gases", US Patent 4,902,487 (February 20, 1990).
2. B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin, M.C. Kung, H.H. Kung, C.Z. Wan and K.E. Voss, "Plasma-Assisted Catalytic Reduction of NO_x", SAE Paper 982508 (1998).
3. *Plasma Exhaust Aftertreatment*, SAE Special Publication SP-1395, eds. J. Hoard and H. Servati. (SAE, Warrendale, PA, 1998).
4. *Non-thermal Plasma for Exhaust Emission Control: NO_x, HC, and Particulates*, SAE Special Publication SP-1483, eds. M. L. Balmer, G. Fisher, and J. Hoard. (SAE, Warrendale, PA, 1999).
5. Rosenthal, L. A. and Davis, D. A., "Corona Discharge for Surface Treatment," *IEEE Trans. Ind. Appl.* **I-5**, 328 (1975).
6. Penetrante, B. M., Brusasco, R. M., Merrit, B. T., Pitz, W. J., Vogtlin, G. E., Kung, M. C., Kung, H. H., Wan, C. Z., and Voss, K. E., "Plasma-Assisted Catalytic Reduction of NO_x," SAE Paper 982508 (1998).
7. Balmer, M. L., Tonkyn, R., Yoon, S., Kolwaite, A., Barlow, S., Maupin, G., and Hoard, J., "NO_x Destruction Behavior of Select Materials when Combined with a Non-Thermal Plasma," SAE Paper 1999-01-3540 (1999).
8. Abdul-Khalek, I. S., Kittelson, D. B., Graskow, B. R., Wei, Q, Brear, F., "Diesel Exhaust Particle Size: Measurement Issues and Trends," SAE Paper 980525 (1998).
9. Luders, Harmut, Kruger, Michael, Strommel, and Luers, Bernhard, "The Role of Sampling Conditions in Particle Size Distribution Measurements," SAE Paper 98137 (1998).
10. Storey, J. M. E., Domingo, N., Lewis, Samuel A., Irick, David K., *Analysis of Semivolatile Organic Compounds in Diesel Exhaust Using a Novel Sorption and Extraction Method*, SAE Paper 1999-01-3534 (1999).