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### DYNAMOMETER EVALUATION OF PLASMA-CATALYST FOR DIESEL NOX REDUCTION

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#### ABSTRACT

A three-stage plasma-catalyst system was developed and tested on an engine dynamometer. Previous laboratory testing suggested high NO<sub>x</sub> efficiency could be obtained. With hexene reductant added to the exhaust, over 90% NO<sub>x</sub> reduction was observed. However, with diesel or Fischer-Tropsch reductant the catalyst efficiency rapidly dropped off. Heating the catalyst in air removed brown deposit from the surface and restored conversion efficiency.

Following the engine tests, the used catalysts were evaluated. BET surface area decreased, and TPD revealed significant storage. This storage appears to be partly unburned diesel fuel that can be removed by heating to around 250-300°C, and partly hydrocarbons bonded to the surface that remain in place until 450-500°C.

Laboratory testing with propene reductant demonstrated that the catalyst regains efficiency slowly even when operating temperature does not exceed 300°C. This suggests that control strategies may be able to regenerate the catalyst by occasional moderate heating.

#### INTRODUCTION

The Plasma-Catalyst CRADA program supported by DOE has been running for several years at PNNL, with industry Work-in-Kind from USCAR Low Emission Technologies Research and Development Partnership (LEP: Ford, General Motors, and DaimlerChrysler). Previous reports [1-13] have shown excellent NO<sub>x</sub> conversion on synthetic gas blends intended to simulate diesel conditions. With a cascade system consisting of three stages of plasma-catalyst, over 90% NO<sub>x</sub> conversion was reported [1-3]. A logical extension of this work is to test the system on an engine.

To this end, PNNL constructed a full-scale system and along with the industrial partners tested it in engine exhaust. Following those tests, further examination of the catalysts was performed using synthetic gas benches and analytical equipment. This paper reports the results of those tests and analyses.

#### ENGINE TEST DESCRIPTION

Engine testing was performed using a prototype DaimlerChrysler engine and control system, at FEV Engine Technology Inc. Engine specifications are listed in Table 1.

Table 1 Engine Specifications

<i>Description</i>	<i>Value</i>
Engine Type	4-stroke Diesel
Number of Cylinders	4 inline
Engine Displacement	1943 cm <sup>3</sup>
Bore Diameter	82 mm
Stroke	92 mm
Stroke/Bore Ratio	1.122
Compression Ratio	19:1
Max. Cylinder Pressure	150 bar
Squish Height	0.8 mm
Piston Bowl Volume	20.8 cm <sup>3</sup>
Valves per Cylinder	4
Swirl Level	1.8-1.9
Maximum boost Pressure	2.05 bar
Rated Power	81 kW @ 4200 RPM

The engine was installed in an instrumented engine dynamometer cell. For the data reported here, all data were taken at steady engine speed and load. Figure 1 is a schematic of the test set up. The engine speed was controlled by an electric dynamometer. Coolant and oil temperatures were controlled. The common rail fuel injection system and EGR system were controlled by a flexible and adjustable control system. Inlet air was conditioned and the flow measured. Emission benches (Horiba analyzers for O<sub>2</sub>, NO<sub>x</sub>, HC-FID, CO, and CO<sub>2</sub>) were available for both engine out emissions and post-aftertreatment measurements. Taps allowed measurement before, between, and after each aftertreatment stage. BP Low Sulfur (15 ppm) fuel was used.

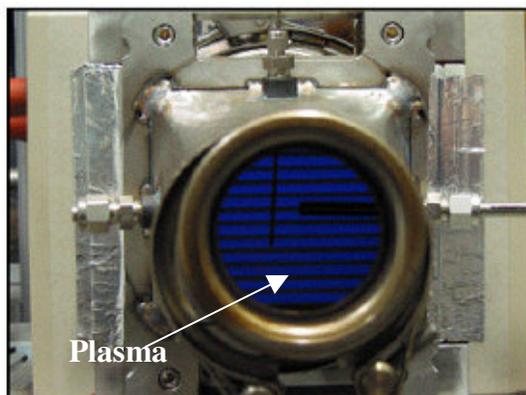


was monitored. Periodically, the DPF was removed and cleaned offline by baking in heated air.

Following the DPF was the plasma-catalyst system, Figure 2. This consisted of three tube array reactor plasma discharge units, each followed by a catalyst. An additional catalyst position was available after the last plasma-catalyst stage to allow space for an oxidation catalyst, although none was used for the data reported here. Each catalyst was provided with a band heater to assist in temperature control. Table 2 lists DPF and catalyst information. The three plasma-catalysts were 400 cells per square inch cordierite monoliths, coated by a vendor to CRADA specifications and then further processed at PNNL to produce barium zeolite-Y (BaY) catalysts. It should be noted that the base coatings were early prototypes and the coating thickness was non-uniform, resulting in poor flow distribution across the bricks. It should be noted that we intentionally designed the system with large bricks (low space velocity) since it is easy to reduce the size later but hard to increase it.

**Table 2 Catalyst Descriptions**

<i>Item</i>	<i>Size</i>	<i>Comment</i>
DPF	5.66" x 6"	Cordierite
Catalysts 1-2-3	5.66" x 6"	BaY



**Figure 3 Plasma unit operating in air**

Figure 3 shows an end view of one of the plasma units with the plasma operating in air.

The discharge power supply consisted of two parts. A low voltage supply created the frequency and waveform, while a transformer stepped up voltage to the required level.

Low voltage power was delivered by a Pacific Power Source model 320-AMX power supply. This is a three-phase unit capable of supplying up to 500W/phase at a common frequency that can be varied between 60-5000 Hz. Power to the three discharge reactors could be varied by changing the output voltages on each phase independently.

The reactors require high voltage ( $\pm 5-12$  KV) to operate. The low-voltage power from the Pacific source was routed to

the dynamometer cell to a bank of three center-tapped high voltage transformers. The transformers were manufactured by Corona Magnetics to our specifications and had a voltage gain of about 147. The transformers were also fitted with voltage and current measurement probes to give an accurate measure of power being dissipated by the discharge. [14] Power was measured at ten second intervals and recorded by the reactor control computer.

A reductant could be injected by syringe pump into the exhaust flow upstream of the DPF. Various reductants were used during the experiments. Previous work with an earlier version of the system had experienced difficulty increasing exhaust temperatures above 150°C. As a result, diesel fuel reductant did not evaporate and caused experimental difficulties. Thus, even with shortened gas path distances in the test cell, in this test series we began by using hexane reductant (Alfa Aesar high purity) since it has a lower boiling point than diesel fuel. Once we established that acceptable temperatures could be controlled, we used first Fischer-Tropsch diesel and then the engine diesel fuel. The reductants and levels will be identified in the following data.

## ENGINE TEST RESULTS

Following various preliminary tests, the system was stabilized at 230°C and 6,000 hr<sup>-1</sup> space velocity (counting the total of all three catalysts). With no added reductant, 43% NO<sub>x</sub> conversion was observed at 15 J/L specific energy deposition. Hexane reductant was added in several steps, and the NO<sub>x</sub> conversion increased. Ultimately, 92% NO<sub>x</sub> conversion was observed over a period of several hours. This set of points is shown on curve A in Figure 4.

Next, the same test was run using Fischer-Tropsch (F-T) reductant. Curve B in Figure 5 shows the data. The NO<sub>x</sub> conversion without added reductant was similar to the previous run. Conversion initially improved as more reductant was added, reaching 75% conversion at 900 ppmC<sub>1</sub>. However, conversion began to drop over time. The effect of changing plasma power from 0 to 30 J/L is shown in curve C on Figure 5; the NO<sub>x</sub> conversion could not be significantly improved by increasing the plasma power.

The following morning, we returned to hexane reductant to determine whether the catalyst had changed or something else happened. Repeating the test with hexane gave the data on curve D, Figure 4. Instead of repeating the >90% conversion from the first day, conversion was only 50-60%.

At this point, the system was disassembled for visual inspection. We determined that the flow was not well distributed across the catalyst; Figure 6 shows a typical view of the catalyst. Significant portions of the catalyst were discolored brown in an uneven pattern. Visual inspection as well as measurement of conversion of NO to NO<sub>2</sub> showed good plasma function.

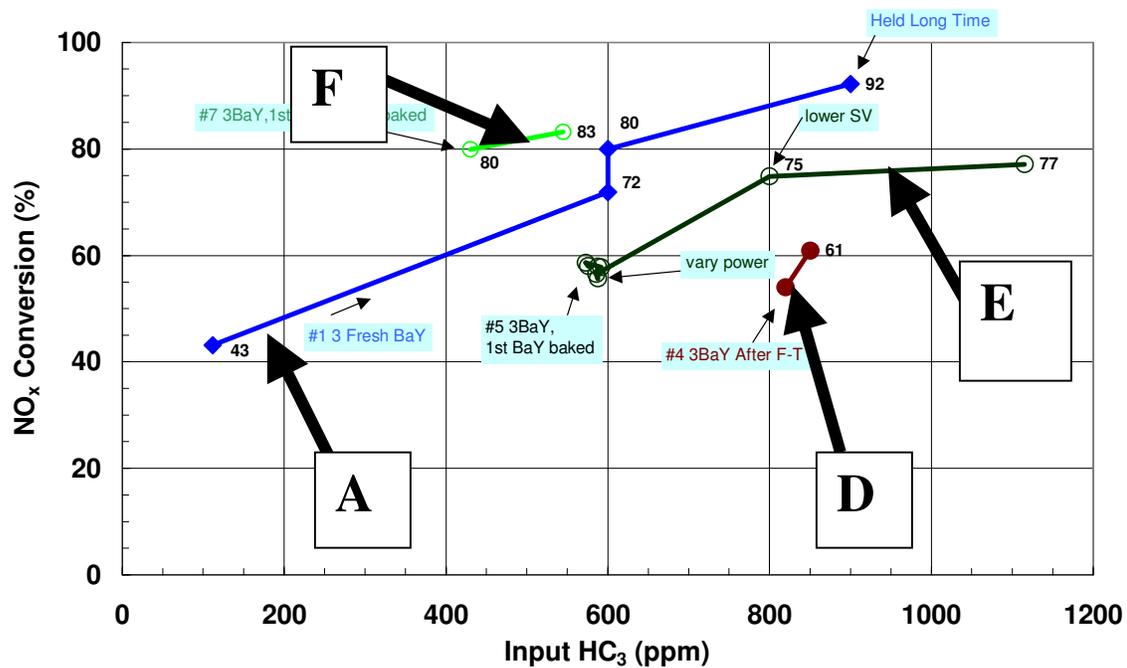


Figure 4 NO<sub>x</sub> conversion results with hexane reductant, for several experiments as described in the text.

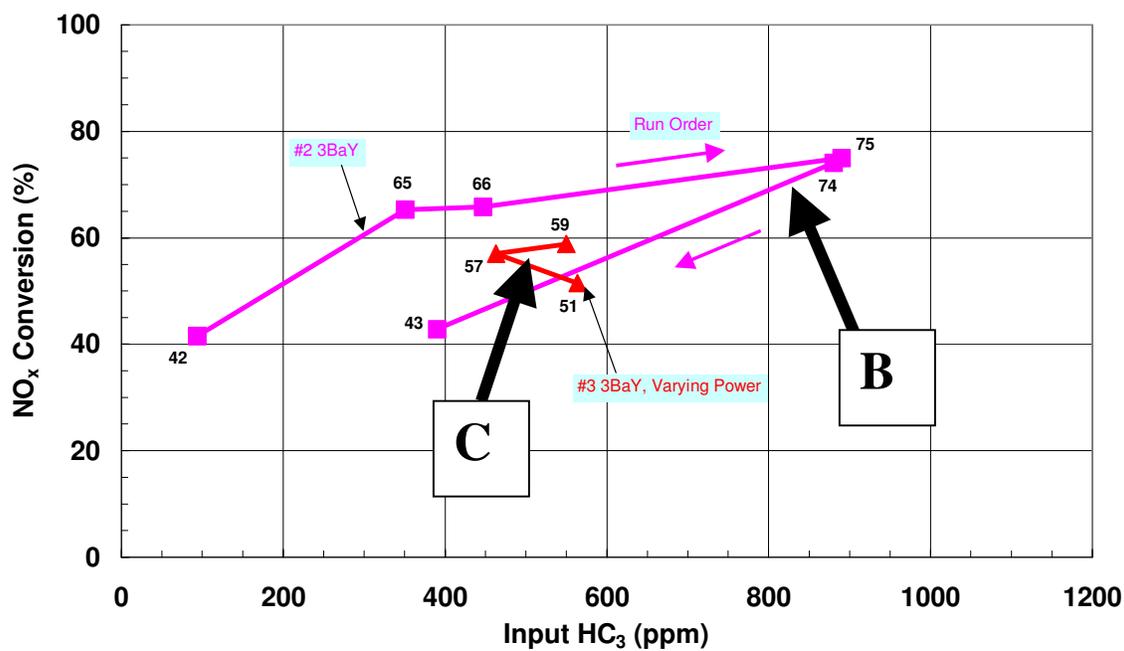


Figure 5 NO<sub>x</sub> conversion with Fischer-Tropsch reductant. See text for conditions.



**Figure 6 View of catalyst face after testing.**

The front catalyst brick was then baked in an oven in air for several hours at 500°C. The catalyst returned to its original white appearance. The system was reassembled and retested with hexane, giving the data on curve E Figure 4. There was a significant recovery of efficiency by cleaning the first catalyst, though not all the way to the original performance.

Following some additional testing (not shown), all three catalysts were removed and baked several hours at 550°C in air and then retested with hexane, giving curve F Figure 4. Efficiency has recovered essentially to the original levels.

Not shown here, some further testing was done with diesel fuel reductant. Like the F-T, catalyst activity dropped over a short time of a few hours, and the catalysts turned brown.

The observations from the engine testing were:

- Good initial conversion approaching the synthetic gas bench test results.
- Over 90% conversion for several hours, using hexane reductant, at 230°C and very low space velocity.
- Catalyst efficiency degraded rapidly with F-T or diesel reductant, and the catalyst turned brown.
- Baking the catalysts in air largely recovers the efficiency.

### LABORATORY POST-MORTEM TESTING

Following the engine tests, cores from the test catalyst were evaluated at PNNL, GM Research, and Ford Research Labs to determine the causes of the degradation and investigate possible corrective strategies.

The data shown here are taken of the Ford Research Plasma-Catalyst Test Stand [1,4]. This stand blends up to 12 bottled gases with water vapor, and tests a single stage plasma-catalyst. A dielectric barrier discharge is followed by a catalyst section. Analysis is by Horiba gas bench (O<sub>2</sub>, HC-FID, NO<sub>x</sub>-CLA, CO, CO<sub>2</sub>) and high resolution FTIR.

Several evaluations were run and results are described below:

- Catalyst as received, at 200°C with propylene reductant
- As above after heating the catalyst in an oxidizing atmosphere
- Catalyst activity versus time for constant gas input flow and composition with a time varying temperature level
- Effect of exposure to diesel fuel reductant in the gas bench
- Catalyst recovery after diesel exposure
- Thermogravimetric analysis of samples under various conditions.

The catalyst core as received was tested in our standard gas blend, Table 3, and at 30 J/L plasma specific energy deposition. NO<sub>x</sub> conversion was very poor, less than 10%. The catalyst was heated in several steps to 500°C in 10% O<sub>2</sub>/N<sub>2</sub>. Large amounts of CO, CO<sub>2</sub>, and various HC compounds were released, and the catalyst turned from dark brown to white. Retesting the catalyst showed the roughly 60% NO<sub>x</sub> conversion expected of a fresh catalyst in this single stage reactor and test condition.

**Table 3 Synthetic gas bench input composition.**

<i>Gas</i>	<i>Concentration</i>
NO	260 ppm
C <sub>3</sub> H <sub>6</sub>	1500 ppmC <sub>1</sub>
C <sub>3</sub> H <sub>8</sub>	500 ppmC <sub>1</sub>
SO <sub>2</sub>	0 ppm
CO <sub>2</sub>	7%
O <sub>2</sub>	7%
CO	1000 ppm
H <sub>2</sub>	333 ppm
Ar	1%
H <sub>2</sub> O	2.8%
N <sub>2</sub>	Balance

Next, we ran an experiment to determine whether operation at a lower temperature might recover the efficiency. Another core sample from the engine test was placed in the reactor. The same gas composition was used, but this time the temperature was controlled over a cycle as shown in Figure 7. This cycle provides temperature levels corresponding to about 80% of the FTP driving cycle for a typical diesel mid-size vehicle, although the rates of change of temperature are much slower than a vehicle experiences. Each cycle was 206 minutes long. The temperature cycle was repeated many times.

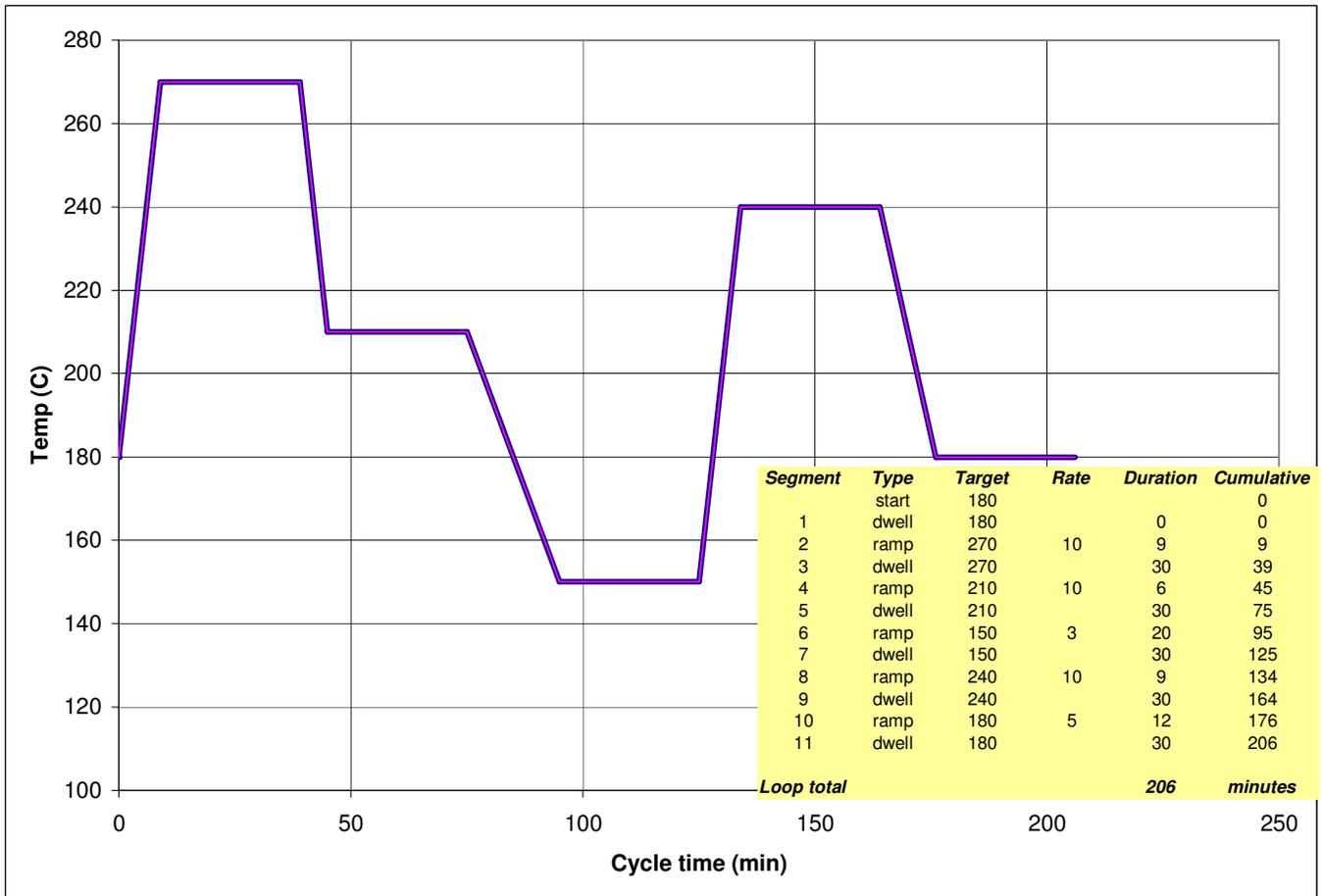


Figure 7 Temperature cycle

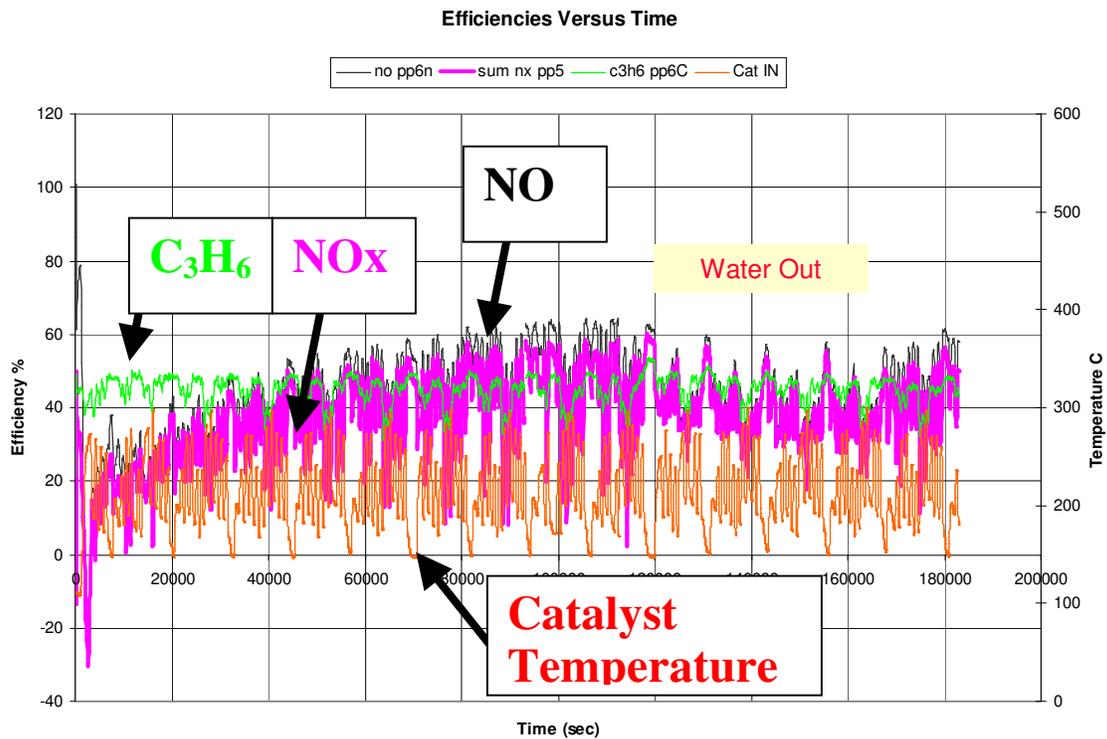


Figure 8 Catalyst conversion efficiency versus time. Total time is 48 hours.

Figure 8 shows test results versus time over 48 hours of continuous operation. NO and NO<sub>x</sub> conversion efficiency gradually recovered while HC conversion stayed constant. Note that the water supply ran out during the second night, and was restored in the morning; this accounts for the dip between 12000 and 17000 seconds. At the end of the test, the catalyst was a light tan color.

This test shows that the conversion will gradually recover even though the temperature never exceeds 300°C. However, a very long time is required for recovery. A practical system for regenerating the catalyst would need to provide a higher temperature.

In an effort to determine what caused the deactivation, and to see if we could duplicate it in the laboratory, the test stand was modified to permit injection of diesel fuel reductant. A syringe pump was used to add diesel fuel. The fuel syringe was passed into the gas tube and placed in contact with a fiberglass wick so that the fuel spreads out on the wick instead of dripping. The wick extends into an oven-heated region held at 150°C. Previous experiments show that this can fully evaporate diesel fuel. All lines following the fuel addition were heated to 120-150°C to minimize wall wetting.

1500 ppmC<sub>1</sub> diesel fuel was added to the gas blend noted above, and the propylene and propane were removed. This setup proved to be rather messy, with very long settling times for HC measurement. However, we were able to run several hours of testing on the same catalyst core used in the thermal cycle tests above. After several hours operation, the NO<sub>x</sub> conversion had dropped from about 60% to about 15-18% at 200°C. This is a similar level to that observed from the engine test sample before further treatment.

We also noted that there were significant gas phase reactions between the diesel fuel and the other gases, causing as much as 50% of the input NO to oxidize to NO<sub>2</sub> independent of the plasma and catalyst. Net HC conversion was only 20%. At this point, the catalyst was once again dark brown in color.

The temperature cycling test was repeated on this sample. As shown in Figure 9, the conversion and rate of recovery were very similar to those for the engine test catalyst. This confirms that laboratory testing with diesel fuel can reveal the deterioration observed in the dynamometer. We should note that in previous CRADA bench testing we had tested a wide range of HC reductants including diesel and F-T, and in those experiments concluded that they were effective. However, in retrospect we realize that those tests were only run a few minutes at a time and thus did not reveal the deterioration observed in these experiments.

From these experiments, we conclude that exposure to diesel fuel has caused a reversible deactivation of the BaY catalyst. This deactivation is rapid. Recovery can be fairly fast at high temperature but takes a very long time at typical FTP cycle temperatures.

## THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric (TG) analysis was performed on two additional cores from the engine test catalyst using a Cahn TG-2131 analyzer. In TG analysis, the sample is heated from room temperature to 800°C at 10 degrees per minute. During this process, the weight of the sample is measured accurately. The output is plotted as percentage weight loss per minute versus time, along with temperature versus time. Thus, a large value indicates rapid weight loss. Loosely, the rate of weight loss is related to the strength of the bond of adsorbates on the surface.

First, one core sample was tested with air surrounding the sample during heating. The result, shown in Figure 10, shows two peaks of weight loss, one around 200°C and the other 350-400°C. The sample was dark brown before the test and white after the test.

Next, another core was heated the same way but in nitrogen rather than in air. Figure 10 shows that the higher temperature peak is much smaller although the lower temperature peak is similar. This suggests that the lower peak is a desorption while the upper peak may involve an oxidation reaction. The sample was brown before the test and dark, sooty black after the test.

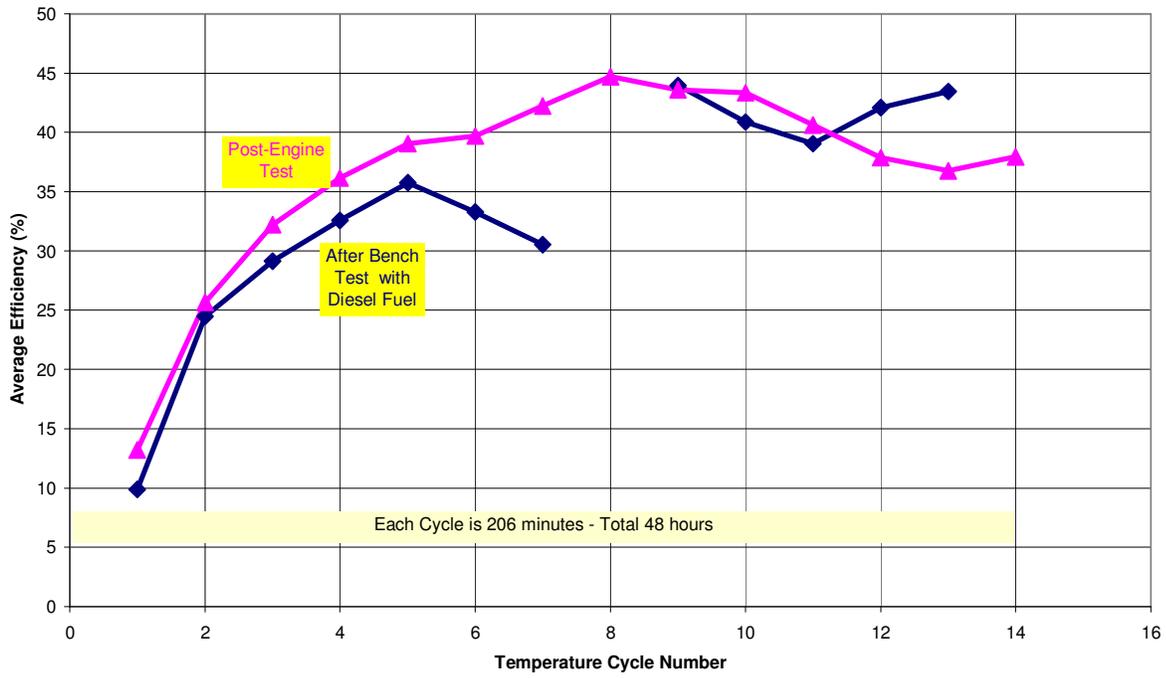
Third, the same sample was retested in air. Figure 11 shows that this sample exhibited the higher temperature peak but not the lower one. At the start of the test the sample was black; after the test it was white. This suggests that the remaining deposits were oxidized.

Finally, the same (now cleaned) sample was dipped in diesel fuel and blown out with compressed air, and then retested. Before the test it was light tan in color, and it returned to white after the test. Figure 12 shows the TG data. The lower temperature peak is present but not the higher temperature one.

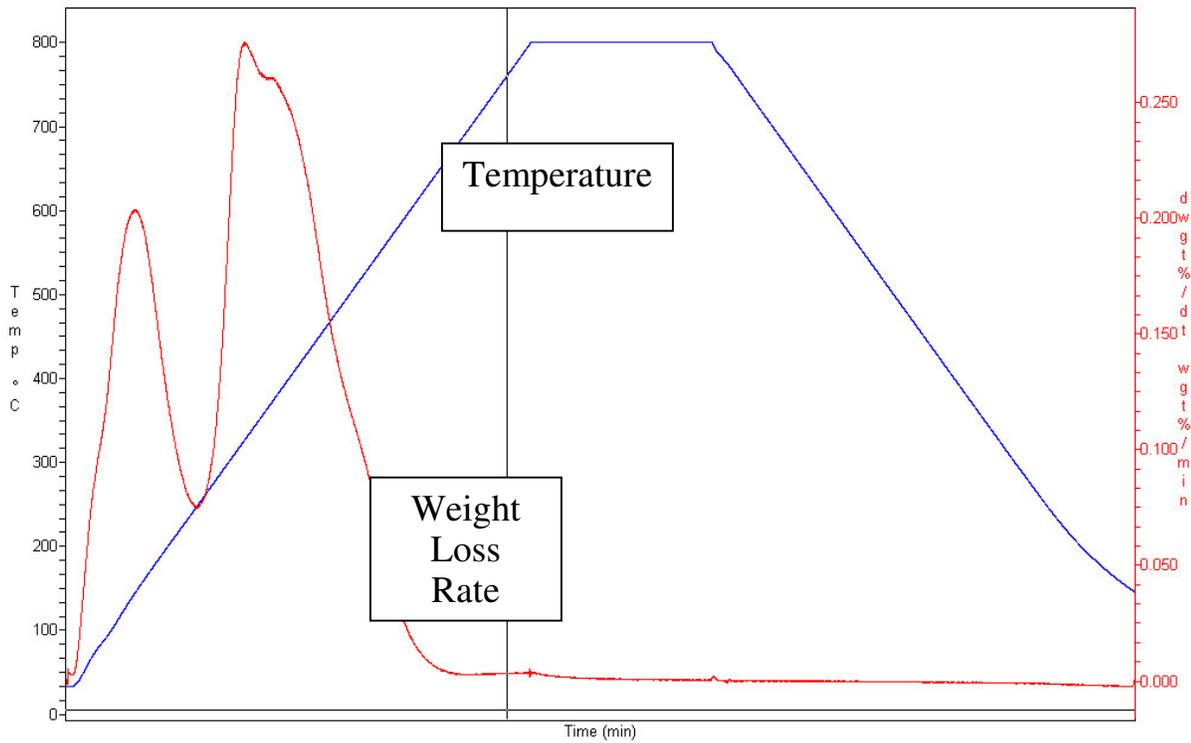
From these data, we recognize that the lower temperature peak is simply diesel fuel condensed on the surface. Since it is lightly bonded, it evaporates off the surface without reacting at temperatures around 200°C. The higher temperature peak, on the other hand, is more strongly bound to the surface. This material remains attached to the surface until the temperature is high enough to oxidize it.

## DISCUSSION

Why does the catalyst deactivate in diesel-like reductant? From the above, we see two types of material being deposited on the catalyst. Fuel condenses on the surface, and HC reacts and bonds to the surface. The former is easily removed above 200°C, while the latter is more firmly bonded. However, the cycling test reported above showed that catalyst performance gradually recovered even when the cycle temperature did not exceed 300°C. At these temperatures, the higher temperature deposit removal is unlikely to have occurred. Thus, we conclude that the "liquid" fuel condensed on the catalyst surface causes the major deactivation.



**Figure 9 NOx conversion efficiency versus cycle number; see text.**



**Figure 10 Engine test core TG results in air.**

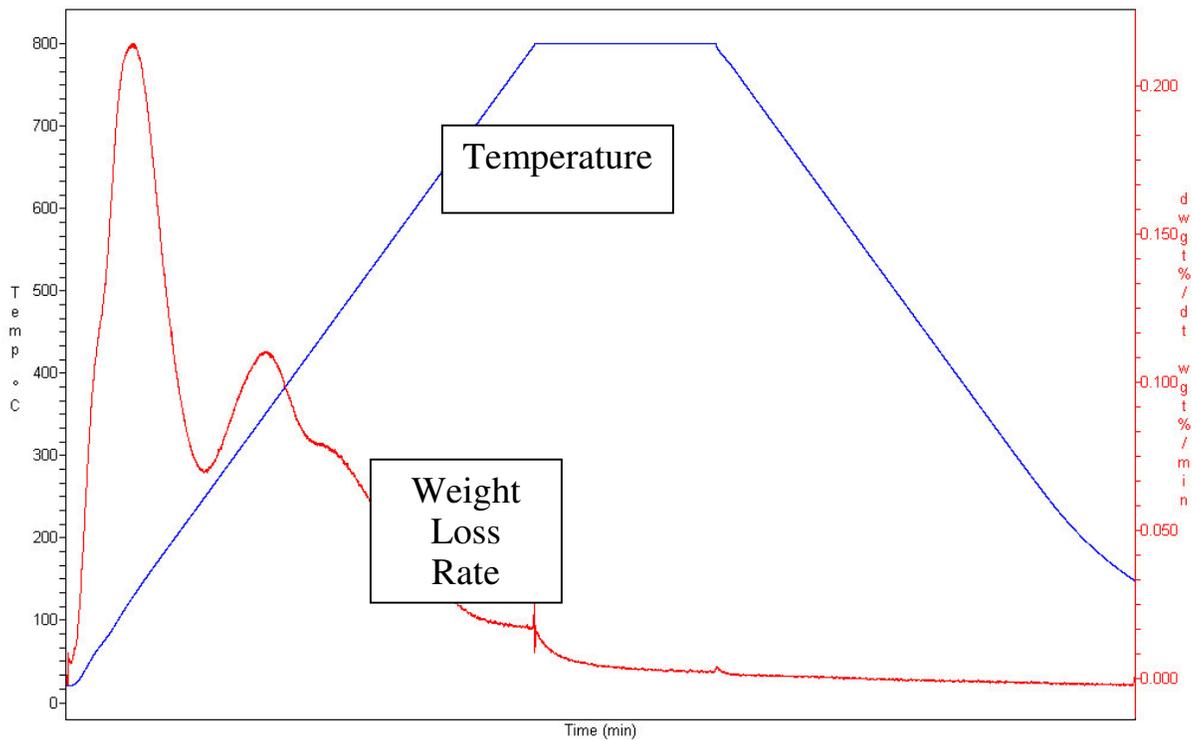


Figure 11 Engine test core TG results in nitrogen.

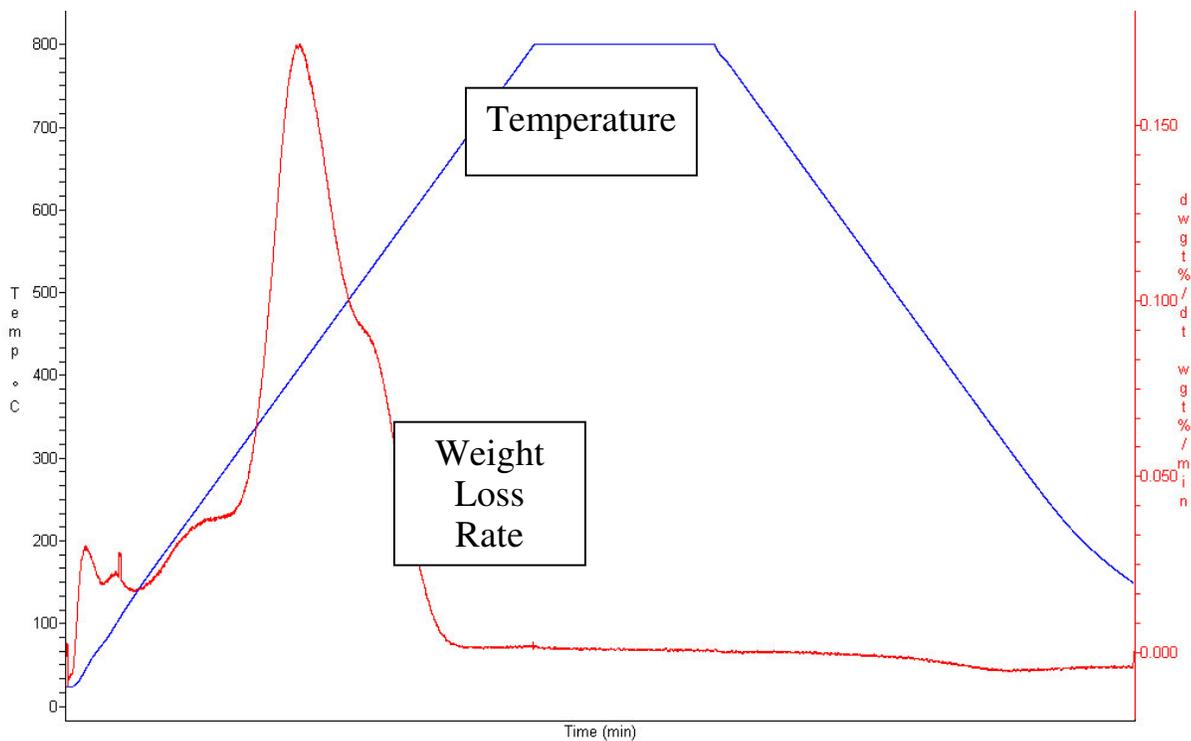
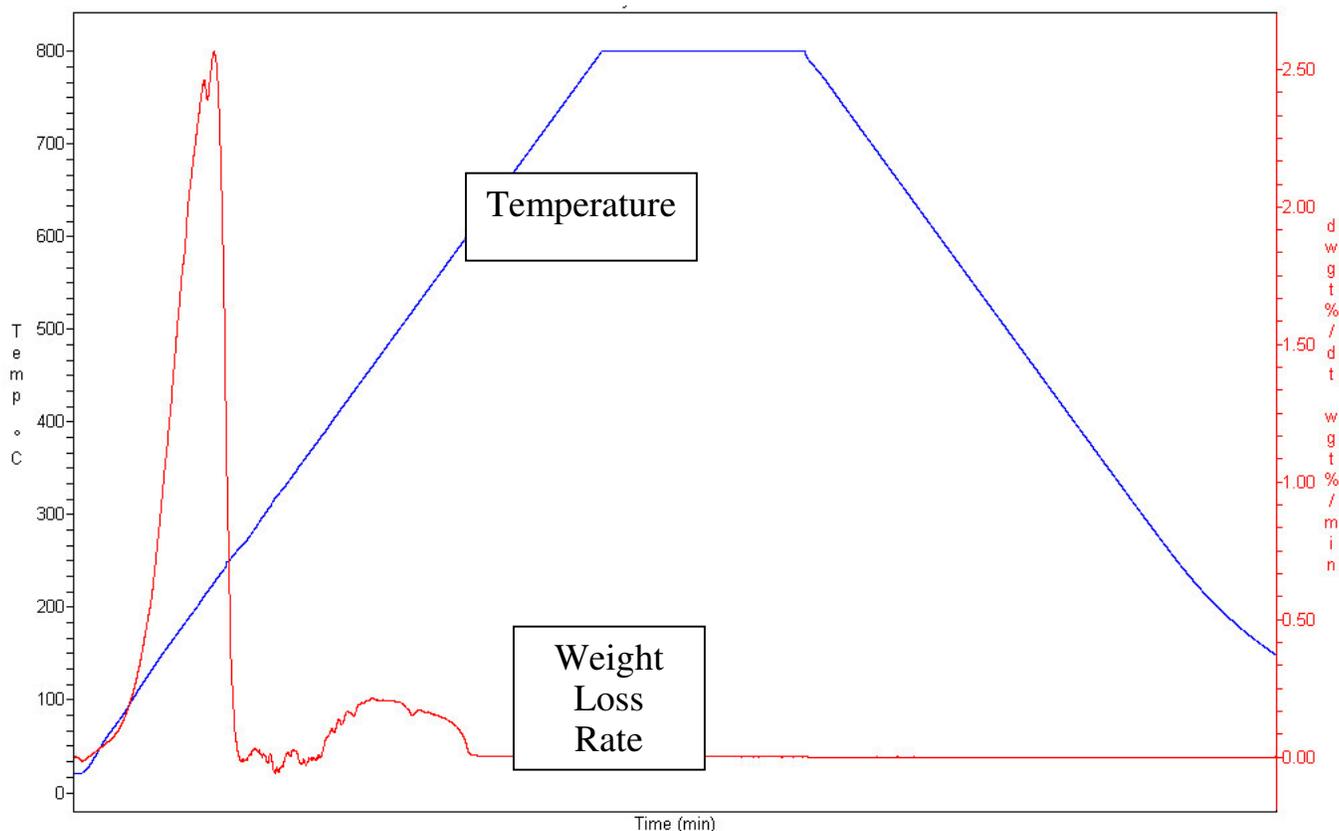


Figure 12 Reheat of sample from Figure 11 in air.



**Figure 13 Sample from Figure 12 retested after soaking in diesel fuel.**

This suggests that regular heating of the catalyst by strategies similar to those used for deSOx heating of diesel lean NOx traps could be used to regenerate the catalyst, and thus maintain activity at some cost to fuel economy. This idea has not been tested, however.

Why does such deactivation not plague other diesel aftertreatment systems? In fact, HC poisoning is an issue for some kinds of urea SCR catalysts. They must be actively heated periodically to maintain high activity. Other catalysts have precious metals such as platinum that improve oxidation capability of the catalyst. High oxidation activity would presumably reduce the temperature of the high-temperature peak in the TG shown above, and keep the catalyst clean. However, such a catalyst would not have high temperature NOx activity since the same oxidation ability will remove the HC reductant needed for NOx reduction. In other words, the deactivation may be inherent in the concept, and only periodic regeneration is likely to permit continuing high activity.

## CONCLUSIONS

High NOx conversion is possible for a plasma-catalyst system in diesel exhaust with fuel reductant. However, rapid deactivation occurs due to deposit of fuel species on the catalyst surface. Thermal regeneration is possible but requires either high temperature or long time.

## ACKNOWLEDGMENTS

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