DIESEL REFORMERS FOR LEAN NOX TRAP REGENERATION AND OTHER ON-BOARD HYDROGEN APPLICATIONS

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ABSTRACT

Many solutions to meeting the 2007 and 2010 diesel emissions requirements have been suggested. On board production of hydrogen for in-cylinder combustion and exhaust after-treatment provide promising opportunities for meeting those requirements. Other benefits may include using syngas to rapidly heat up exhaust after-treatment catalysts during engine startup. HydrogenSource's development of a catalytic partial oxidation reformer for generating hydrogen from ultra-low sulfur diesel fuel is presented. The system can operate on engine exhaust and diesel fuel with no water tank. Test data for hydrogen regeneration of a lean NOx trap is presented showing 90% NOx conversion at temperatures as low as 150 degrees C and 99% conversion at 300 degrees C. Finally, additional efforts required to fully understand the benefits and commercial challenges of this technology are discussed.

I. Introduction

Reforming of transportation fuels to hydrogen-rich gas has been considered for a variety of vehicle applications. The benefits of this conversion are derived from gains in energy efficiency and reduction in undesirable emissions. The product hydrogen and syngas (from *synthesis gas*, a hydrogen and carbon monoxide mixture) can be used in fuel cells to produce electrical energy for power train and accessory loads at high system efficiency. Hydrogen and syngas can reduce emissions from internal combustion (IC) engines through direct use in the combustion chamber, and in the exhaust aftertreatment system.

This paper addresses the benefits of reforming diesel fuel by Catalytic Partial Oxidation (CPOx) to produce syngas for effective regeneration of NOx adsorbers, also known as Lean NOx Traps (LNTs). A discussion is presented of factors important to the successful implementation of CPOx reformers for generating syngas on board production vehicles.

II. CPOx for LNT Regeneration

CPOx is a method for reforming hydrocarbon fuels to hydrogen and carbon monoxide by catalytic reaction with an oxidant. The moderately exothermic process is carried out in a compact, rapid response reactor with minimal requirements for additional inputs such as heat or electrical energy. HydrogenSource, a joint venture of Shell Hydrogen and United Technologies Corporation Fuel Cells (UTC FC), has extensive experience with reforming in general, and CPOx in particular, using a variety of liquid and gaseous hydrocarbon fuels. This process is well suited to efficiently produce syngas in a vehicle. Hydrogen and carbon monoxide are more effective reductants than diesel and lighter hydrocarbons for regenerating LNTs to reduce NOx from diesel engine exhaust [1].

Tests were conducted to demonstrate that syngas produced from a CPOx reformer is effective for regenerating LNTs in a diesel engine aftertreatment system. The benefits of syngas were expected to be most pronounced at low temperatures (<200 °C), where reductant generation from diesel injection into the exhaust is not practical. In these tests, the reformer used was designed for another application and had a maximum throughput considerably less than desired. It was operated on naphtha, a fuel similar to gasoline, air and water. The aftertreatment system installed on the 5.9-liter diesel engine contained a 14-liter LNT. The exhaust configuration simulated one leg of a dual leg LNT system. Valves directed the flow of engine exhaust and syngas to the either the LNT or to a bypass, depending on the cycle, as shown in Figure 1. The reformer and diesel engine were operated at steady state. No attempt was made to optimize the regeneration strategy; fixed trapping and regeneration cycle times were employed. The typical CPOx reformate composition is given in Table 1.

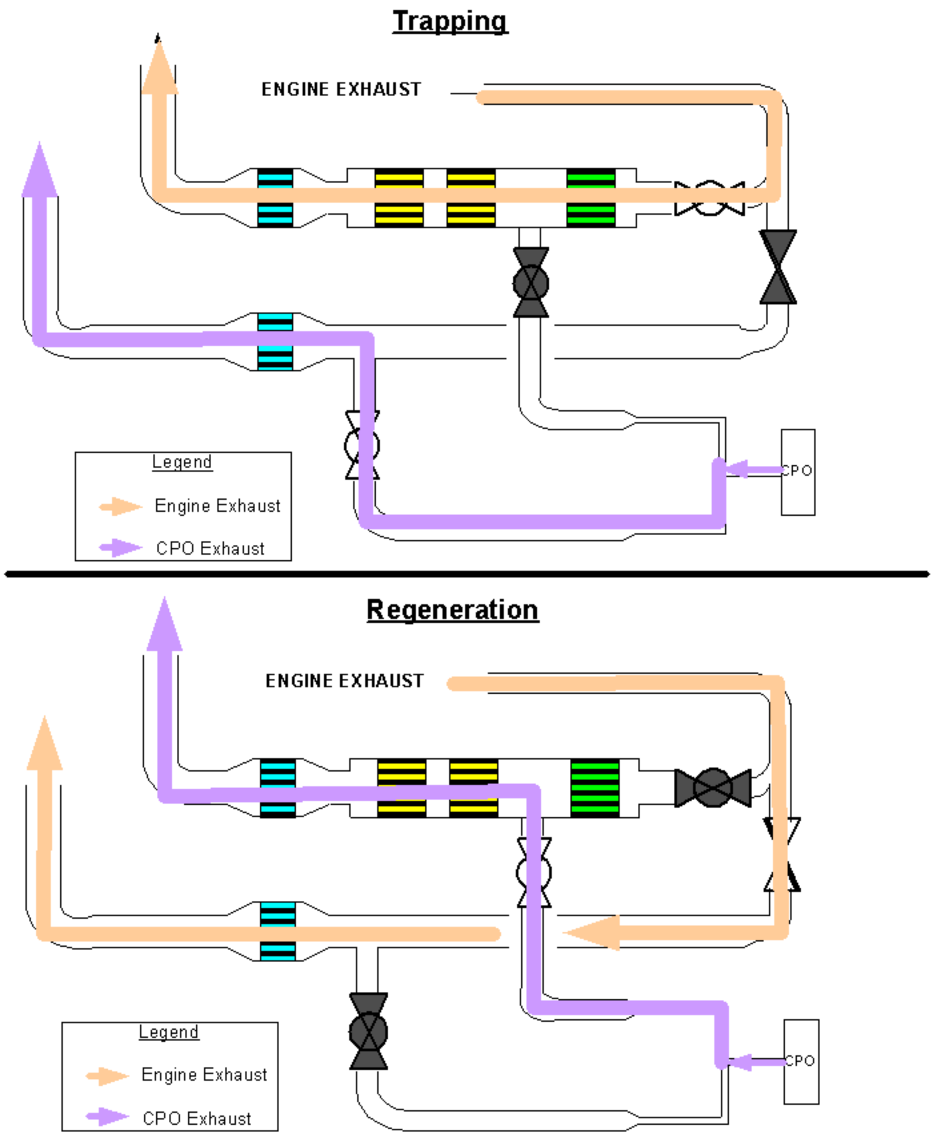

Figure 1. Flow configuration for LNT regeneration testing.

	Composition (volume %)	
	Dry basis	Wet basis
H_2	33	30
CO	18	16
CO_2	6	5
N_2	42	38
H_2O	-	10
Total HC	<1	<1

Table 1. Syngas composition for LNT regeneration testing

Figure 2 shows the NOx slip from the LNT during trapping and regeneration with syngas at an adsorber temperature of 150 °C. The figure also shows that the flow rate of syngas through the adsorber during regeneration was substantially lower than that of engine exhaust during trapping. It is evident that the 83 g/hr engine out NOx emissions during trapping were reduced more than 90% for a period of about one minute at 150 °C. The length of time before NOx emissions increased is a function of adsorber capacity, which is related to its formulation and size.

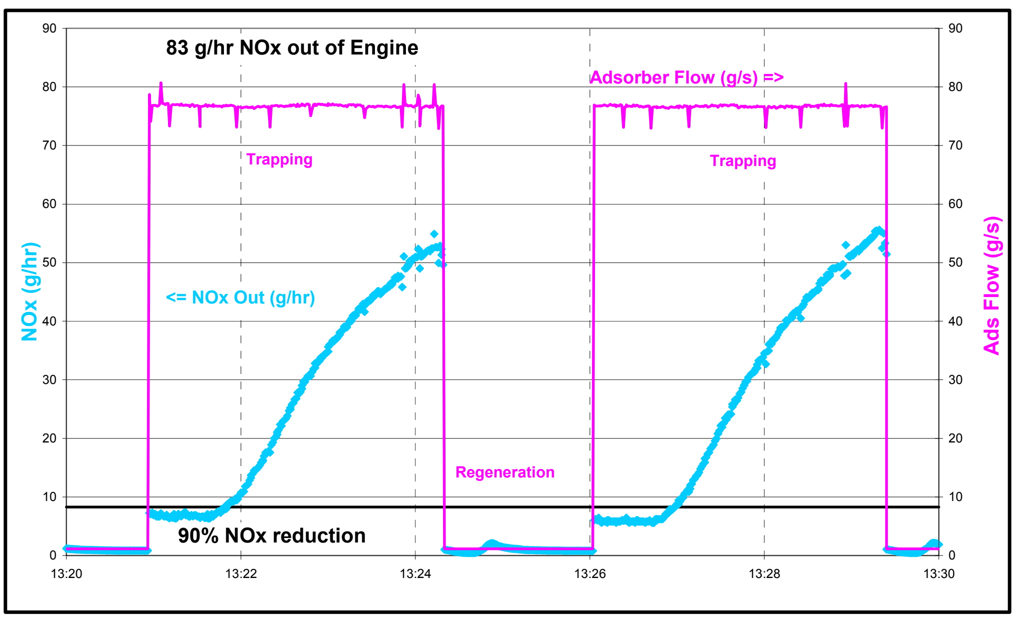

Figure 2. LNT NOx emissions at 150 °C adsorber temperature.

The same variables are displayed in Figure 3 at an adsorber temperature of 300 °C. The results showed >99% reduction from 300 g/hr engine out NOx emissions for a period of about 7 minutes and >90% reduction for about 10 minutes. The calculated fuel penalty to produce syngas at this condition was approximately 1.5%. The overall fuel penalty is affected by factors such as transient response and the need to reduce oxygen in the exhaust, and is therefore a function of the system configuration and operating strategy.

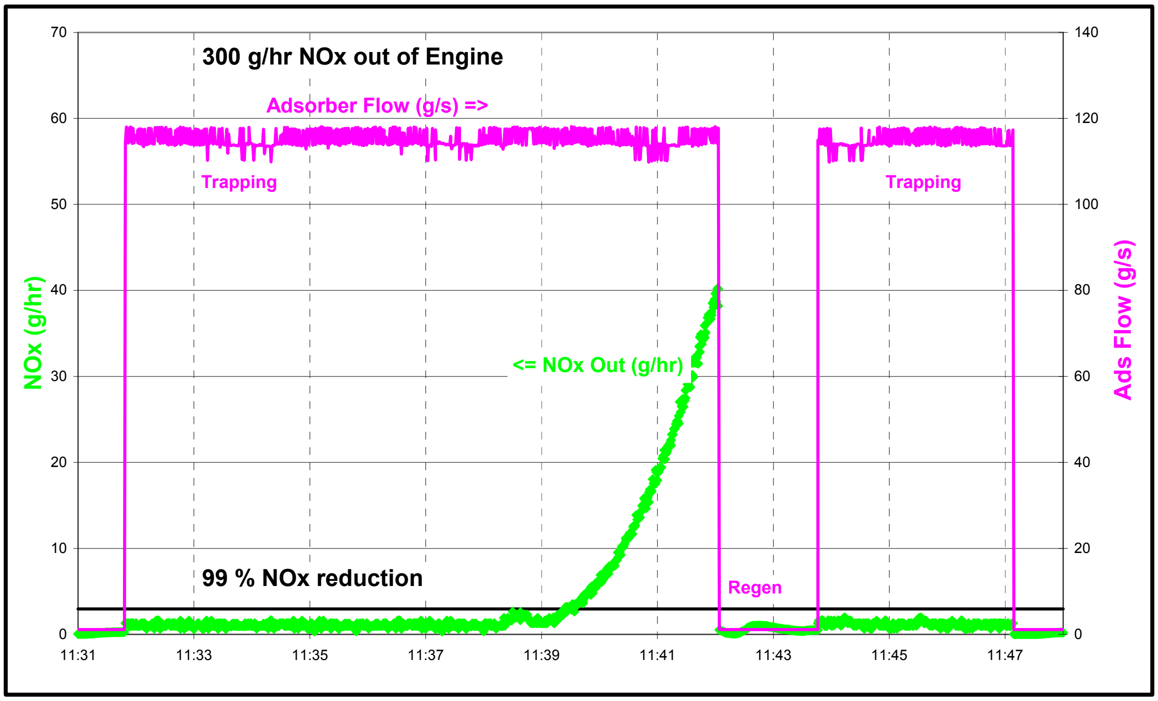

Figure 3. LNT NOx emissions at 300 °C adsorber temperature.

These results demonstrated the feasibility to use syngas as a reductant for LNT regeneration to obtain the high NOx conversion required to meet upcoming stringent emission standards for light and heavy-duty diesel engines. The ability to regenerate at low exhaust temperatures is particularly relevant to light duty vehicles. The potential for generating syngas at low fuel penalty with a CPOx reformer was also shown.

In addition to the benefits demonstrated above, several others are likely to result if CPOx reformers are used. LNTs may have improved desulfation as a consequence of faster or lower temperature processing. Better LNT durability may result due to more effective regeneration and substantially less coking products present in the reductant. Furthermore, platinum in an LNT can light off hydrogen from the reformer in lean engine exhaust at temperatures below 100 °C, providing a means to heat LNTs to higher operating temperatures faster during cold starts. A CPOx reformer may also provide benefits in the thermal control for rapid exhaust catalyst light off and particulate filter regeneration.

III. Diesel CPOx Reformer Development

HydrogenSource is developing a CPOx reformer to operate with ultra low sulfur diesel (ULSD), with a maximum of 15-ppm sulfur as the fuel and lean engine exhaust as the source of oxidant. All diesel sold in the U.S. must meet the ULSD specification beginning in 2006, in advance of the most restrictive light and heavy-duty NOx emission standards presently required. CPOx reformers can be used in conjunction with any LNT system since the reactants will be present in all on-road diesel vehicles.

HydrogenSource is applying its CPOx experience with gasoline to diesel reforming. Figure 4 compares the stability of the baseline catalyst to the improved stability of the current diesel catalyst. These data were obtained with air, water, and ULSD fuel as the reactants. The water (steam) to carbon molar ratio (S/C) in the tests was 1.0. One of the challenges resulting from the use of engine exhaust as the oxidant is its relatively low water content. Although water is not required, it has a beneficial effect on CPOx performance, both in syngas yield and catalyst durability.

Depending on the engine air/fuel ratio (A/F), the resulting S/C for a reformer operating on engine exhaust ranges from approximately 0.2 to 0.7. Figure 5 shows over 500-hour stability data with ULSD and simulated engine exhaust at an engine operating A/F of 34. The syngas yield decreased to slightly more than 80% of its initial value during the test. The figure also displays a logarithmic extrapolation of the data, which is characteristic of certain catalyst performance loss mechanisms. The syngas yield can be extrapolated to be about 70% of its initial value after 10,000 hours. This time period is consistent with the 435,000-mile warranty requirement for heavy-duty diesel engines. The performance loss indicated by the extrapolation can be accommodated in the CPOx reformer design and is considered acceptable.

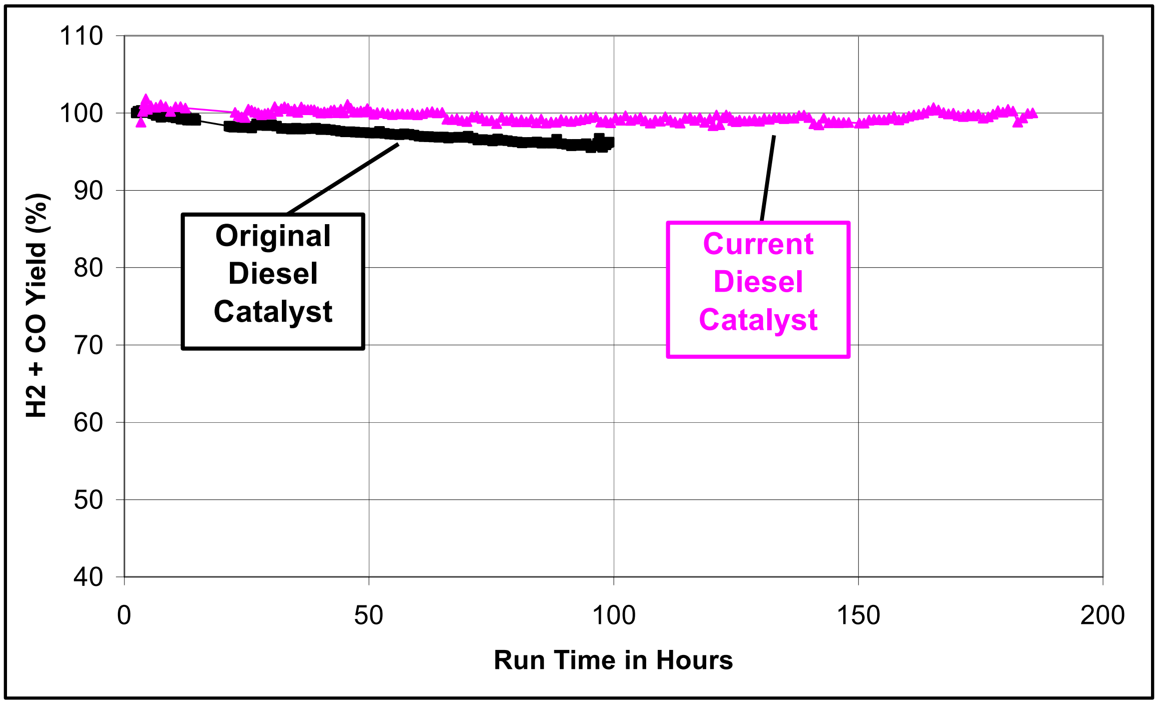

Figure 4. Stability of syngas yield for an improved diesel catalyst configuration.

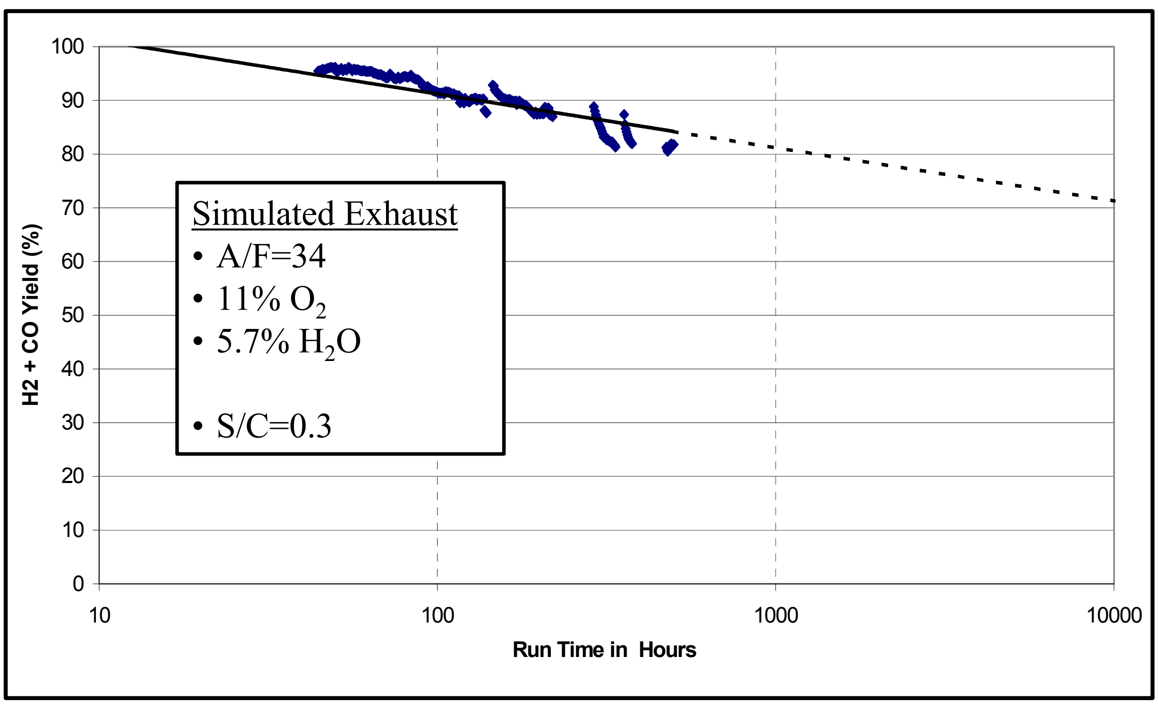

Figure 5. Stability of syngas yield at typical diesel engine operating conditions.

Another imposing aspect of applying CPOx reformers to diesel engine aftertreatment is the requirement to cycle from idle to an operating condition frequently. Depending on the LNT regeneration strategy and useful lifetime of the system, as many as several hundred thousand cycles can be expected. Thermal shock resistance is a requirement since the CPOx process generates internal temperatures in excess of 800 C. HydrogenSource evaluated the effects of up to 1000 thermal cycles of magnitude greater than 800 ^{o}C, resulting from on/off operation, on two types of catalysts. Figure 6 exhibits the stability of syngas yield for a natural gas and a naphtha catalyst configuration. While the natural gas catalyst showed no change in syngas yield, the yield for the naphtha catalyst decreased approximately 6%, an acceptable range for exhaust aftertreatment. Similar tests are planned for the diesel CPOx system.

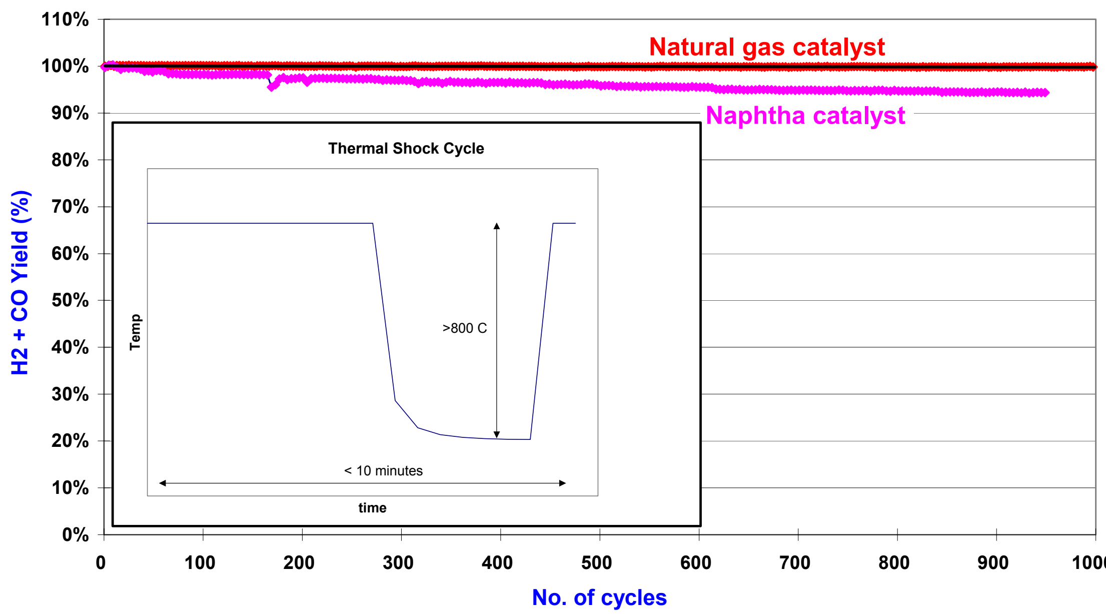

Figure 6. Stability of syngas yield during thermal cycling for natural gas and naphtha catalysts.

It is vital to minimize the cost of an aftertreatment system while ensuring proper function and adequate life. The cost impact of a CPOx reformer on the total aftertreatment system cost is difficult to quantify based on the present development status. Although precious group metals (PGM) are commonly used in the reformer catalyst, the amount is moderate as a consequence of very high space velocities possible with CPOx, typically more than 100,000 hr^{-1}. The effectiveness of regenerating with syngas may allow for smaller LNT volumes and lower PGM loadings, offsetting at least part of the cost of the CPOx reformer. The cost of a fully integrated LNT aftertreatment system with a CPOx reformer must therefore be compared to an alternative approach in order to understand relative costs. While ultimately necessary, this task is beyond the scope of this paper.

IV. Summary and Conclusions

Syngas from a catalytic partial oxidation reformer is highly effective for regenerating NOx adsorbers. NOx conversion efficiencies greater than 90% have been demonstrated at an adsorber temperature of 150 °C. The fuel penalty associated with producing syngas can be as low as 1.5%. The use of syngas may also provide advantages to the desulfation process and improve LNT durability.

A CPOx reformer was designed to operate on ULSD and engine exhaust. A catalyst formulation was developed with improved stability, and may give acceptable syngas yield for the target of 435,000 miles of vehicle operation. Similar CPOx catalysts have been shown to tolerate 1000 thermal shock cycles with minimal degradation.

The cost of an LNT regenerated with syngas from a CPOx reformer may be less than an LNT regenerated in another way due to the effectiveness and benefits of syngas. There is a need to compare the cost of various aftertreatment options on the basis of an integrated system rather than on the cost of individual components, which is beyond the scope of this paper.

V. Future Work

HydrogenSource is integrating a CPOx reformer into an LNT aftertreatment system that will be installed on a light duty diesel pickup truck. The objectives of the project are to demonstrate the feasibility of reforming diesel fuel and engine exhaust to produce syngas in a real world environment and to provide a platform for measuring system performance in various driving cycles. The results will be reported in future papers.

References

1. Poulston, S.; and Rajaram, R. R., 2003, "Regeneration of NOx trap catalysts," Catalysis Today **81**, 603-610.