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Hydrogen generation from plasmatron reformers: A promising technology for NO_x adsorber regeneration and other automotive applications

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HYDROGEN GENERATION FROM PLASMATRON REFORMERS: A PROMISING TECHNOLOGY FOR NO_x ADSORBER REGENERATION AND OTHER AUTOMOTIVE APPLICATIONS

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ABSTRACT

Plasmatron reformers are being developed at MIT and ArvinMeritor [1]. In these reformers a special low power electrical discharge is used to promote partial oxidation conversion of hydrocarbon fuels into hydrogen and CO. The partial oxidation reaction of this very fuel rich mixture is difficult to initiate. The plasmatron provides continuous enhanced volume initiation. To minimize electrode erosion and electrical power requirements, a low current, high voltage discharge with wide area electrodes is used. The reformers operate at or slightly above atmospheric pressure.

Plasmatron reformers provide the advantages of rapid startup and transient response; efficient conversion of the fuel to hydrogen rich gas; compact size; relaxation or elimination of reformer catalyst requirements; and capability to process difficult to reform fuels, such as diesel and bio-oils. These advantages facilitate use of onboard hydrogen-generation technology for diesel exhaust after-treatment. Plasma-enhanced reformer technology can provide substantial conversion even without the use of a catalyst.

Recent progress includes a substantial decrease in electrical power consumption (to about 200 W), increased flow rate (above 1 g/s of diesel fuel corresponding to approximately 40 kW of chemical energy), soot suppression and improvements in other operational features..

Plasmatron reformer technology has been evaluated for regeneration of NO_x adsorber after-treatment systems. At ArvinMeritor tests were performed on a dual-leg NO_x adsorber system using a Cummins 8.3L diesel engine both in a test cell and on a vehicle. A NO_x adsorber system was tested using the

plasmatron reformer as a regenerator and without the reformer (i.e., with straight diesel fuel based regeneration as the baseline case). The plasmatron reformer was shown to improve NO_x regeneration significantly compared to the baseline diesel case. The net result of these initial tests was a significant decrease in fuel penalty, roughly 50% at moderate adsorber temperatures. This fuel penalty improvement is accompanied by a dramatic drop in slipped hydrocarbon emissions, which decreased by 90% or more. Significant advantages are demonstrated across a wide range of engine conditions and temperatures. The study also indicated the potential to regenerate NO_x adsorbers at low temperatures where diesel fuel based regeneration is not effective, such as those typical of idle conditions. Two vehicles, a bus and a light duty truck, have been equipped for plasmatron reformer NO_x adsorber regeneration tests.

INTRODUCTION

In order to meet stringent US emissions regulations for 2007-2010 diesel vehicle model years, after-treatment technology is being developed. Both particulate and NO_x emissions after-treatment technology will be necessary, as it seems that engine in-cylinder techniques alone will be unable to meet the regulations.

The purpose of the present work is to develop hydrogen based technology for addressing after-treatment issues. In this paper recent developments in both the technology for on-board generation of hydrogen as well as applications to NO_x after-treatment issues will be discussed.

Potential on-board generation of hydrogen from renewable energy biofuels for the transportation sector is also discussed.

This application could provide a means to alleviate oil dependency and reduce greenhouse gas emissions.

PLASMATRON TECHNOLOGY

Plasma technology can be used to accelerate chemical reactions. Two modes of operation have been explored for promoting fuel reformation into synthesis gas (hydrogen and carbon monoxide). The first uses thermal plasmas, where electrons, ions and neutral particles are generally in thermal equilibrium, and at high average temperature. This technology has the disadvantages of high current operation (associated with high electrode wear), and high energy consumption. The second mode of operation, using special low current plasmas, has the advantage of low power consumption and long electrode life. However, successful operation of the plasma process is more sensitive to design and operation. In this section, operation of a low current plasmatron as a device for converting hard to reform fuels to synthesis gas is described.

Fuel conversion is accomplished using the process of partial oxidation. In this mode, enough oxygen is supplied in order to capture each carbon atom in the fuel as carbon monoxide, with the hydrogen released as hydrogen molecules. The nitrogen from the air (as air is used as the oxidizer), is inert at the temperatures and pressures of operation, and thus goes unaffected in the reactor.

The use of the plasma allows for a robust reaction initiation for air/fuel mixture. The advantages of this technology include

- fast start up and rapid response,
- relaxation or elimination of catalyst requirements
- effective reforming in compact devices, attractive for onboard applications
- efficient conversion from liquid hydrocarbons to synthesis gas

The technology can be used for a broad range of fuels, from light, low viscosity liquids, such as ethanol, to high viscosity liquids, such as diesel and bio-oils.

The small size enables the use of fuel reformers for multiple applications on vehicles. These applications include:

- Diesel engine exhaust after-treatment
- Use of renewable energy bio-oils
- Fuel supply and ignition control in HCCI (homogeneous charge compression ignition) engines
- Spark ignition engines using hydrogen enhanced ultra-lean turbo-charged operation

For diesel engine exhaust after-treatment, onboard hydrogen production can be used in the regeneration of either NO_x or particulate traps. The NO_x trap regeneration application will be discussed later in this paper. In the HCCI application, the use of fuel reformation to supply a portion of the fuel allows adjustment of engine charge temperature and fuel ignition characteristics providing a means of ignition control. In

the spark ignition engine application, hydrogen rich gas addition allows ultra lean operation and can facilitate the use of high compression ratio and strong boosting. Hydrogen enriched combustion in a turbo-charged high compression ratio engine can provide both increased efficiency and reduced emissions. System optimization studies indicate that a substantial increase in fuel efficiency (up to a 30% increase in net efficiency) and decrease in NO_x emissions are achievable.

Present plasmatron reformers have volumes on the order of 1-2 liters, with an electrical power consumption of about 250 W. Figure 1 shows a photograph of a recently developed plasmatron. The plasmatron is followed by a reaction section which provides time for the development of homogeneous reactions. When high hydrogen yields are desired, a catalyst can be placed downstream from the homogeneous zone.

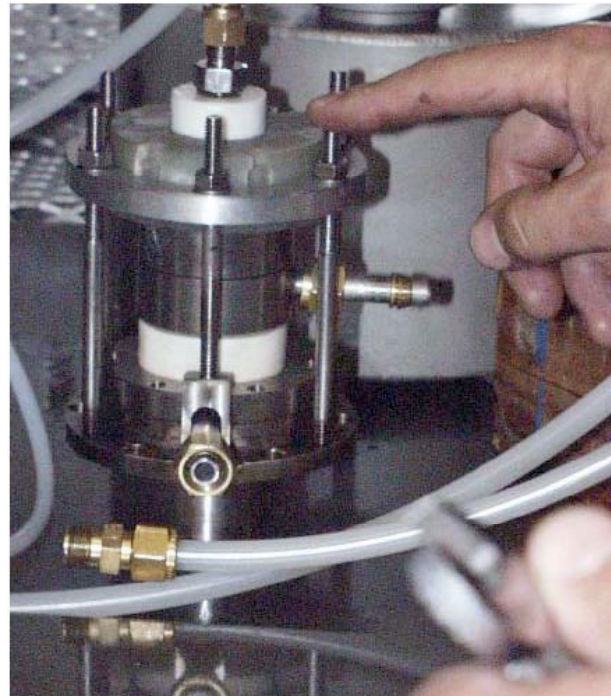


Figure 1. Compact low power plasmatron fuel converter

At present, goals for the diesel plasmatron reformer development includes increased flow rates, operational and configuration optimization and increased simplicity, among other goals.

BIOFUEL REFORMATION

At MIT, plasmatron reforming technology has been used with for a wide range of biofuels. These fuels include corn, canola and soybean oils (both refined and unrefined), and ethanol.

Reformation was achieved with a plasmatron fuel reformer optimized for diesel fuel operation. The device operated at 200 W of electrical power, and at stoichiometry for partial oxidation (O/C ratio ~ 1.1). The available energy from the reformat flow rate was about 20 kW (LHV of the reformat gas, as calculated from the LHV of compounds measured in the gas analysis).

Some of the oxygen required for the reformation is provided by the fuel itself; the O/C ratio includes this oxygen,

Figure 2 shows results from the reformation as a function of the O/C ratio, for corn and soybean oils. The hydrogen yield is defined as the ratio of the flow rate of hydrogen in the reformat to the flow rate of hydrogen in the fuel. A hydrogen yield of 1 thus means that all the hydrogen in the fuel has been released as hydrogen in the reformat. High hydrogen yields are possible (greater than 80%), even at relatively high O/C ratios.

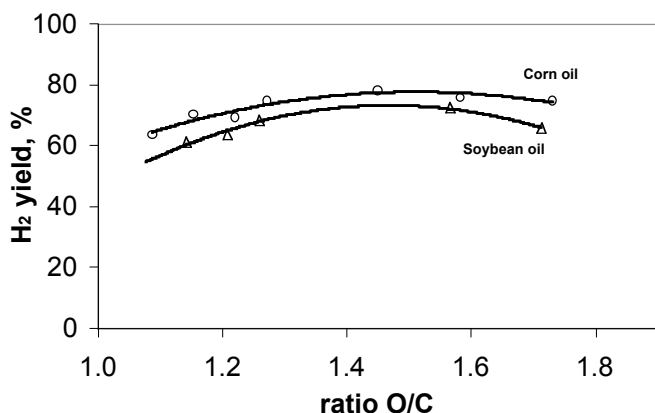


Figure 2. Hydrogen yield as a function of the O/C ratio, for corn and soybean oils

The results in Figure 2 were carried out with a plasmatron reformer that incorporated a nickel catalyst on a crushed alumina substrate. In the absence of a catalyst (for a homogeneous reaction), the hydrogen yields are about 40%, coupled with high concentration of light hydrocarbons (~4-5% C₂H₄)

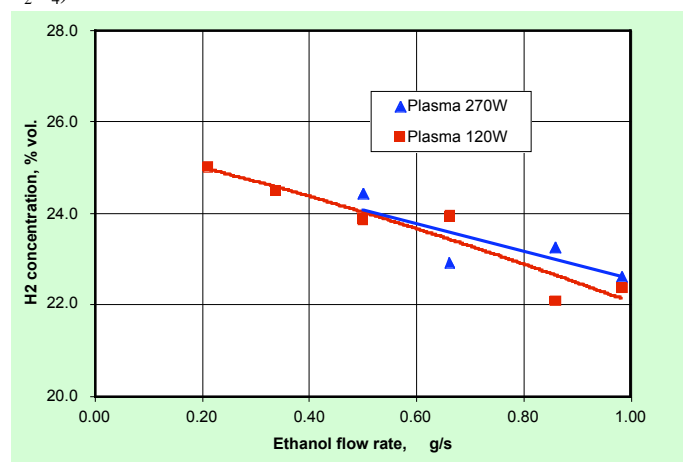


Figure 3. Hydrogen concentration in dry gas for ethanol reforming, as a function of flow rates, for O/C ~ 1.2

The presence of soot was determined using an opacity meter. Virtually no soot was observed in these experiments.

Similar experiments for ethanol are shown in Figure 3, for different powers and varying flow rates. Ethanol conversion is

difficult to perform homogeneously because of the low exothermicity of the partial oxidation reaction. Figure 3 shows the hydrogen concentration of the partial oxidation of ethanol, for O/C ~ 1.2.

DIESEL REFORMATION

The plasmatron fuel converter has been further developed for use with diesel fuel. The goal of reformation of diesel by the plasmatron fuel converter is the conversion of the heavy diesel compounds into hydrogen, carbon monoxide, and light hydrocarbons for use in after-treatment applications. The diesel reformat produced by the plasmatron fuel converter has little residual oxygen and little or no soot. The diesel plasmatron can be cycled on and off quickly (~ 3-5 sec). For diesel after-treatment applications the dynamic performance of the plasmatron fuel reformer is important because of the low duty cycle of operation. For NO_x catalyst regeneration applications, the plasmatron may be turned on for a few seconds every half minute or so. For diesel particulate filter applications, the plasmatron could well be operated for a few minutes every few hours resulting in much smaller duty cycles.

Results for diesel conversion without a catalyst are shown in Table 1. Typical O/C ratios are 1.1, with opacity readings of 0.0% (below the resolution of the device), for flow rates on the order of 1 g/s. The energy conversion efficiency, defined as the lower heating value of the reformat divided by the lower heating value of the fuel, is about 70%. The lower heating value of the reformat is calculated using the measured composition of the reformat.

Table I. Diesel reforming without a catalyst

Electric power	W	250
O/C		1.1
Diesel flow rate	g/s	0.8
Corresponding chemical power	kW	35
Concentration (vol %)		
H ₂		8.2
O ₂		1.4
N ₂		68.7
CH ₄		2.6
CO		14.3
CO ₂		4.7
C ₂ H ₄		2.4
C ₂ H ₂		0.0
Energy efficiency to hydrogen, CO and light HC		70%
Soot (opacity meter)		0

If higher yields of hydrogen are desired, a catalyst can be placed downstream from the homogeneous zone. The absence of oxygen in the reformat due to the partial oxidation process minimizes the occurrence of hot spots within the catalyst. This alleviates one of the catalyst durability issues.

Hydrogen is a powerful reductant, and its use for the regeneration of NO_x traps has been researched in catalyst reactor labs. The goal of the work presented next is to determine the advantages of H₂ assisted NO_x trap regeneration,

using the plasmatron fuel reformer as the source of on-board hydrogen.

PLASMATRON DEVELOPMENT AT ARVINMERITOR

At the ArvinMeritor Columbus Technical Center, the diesel plasmatron fuel reformer has been further developed for after-treatment applications. With a reformer catalyst, the hydrogen concentration in the reformat was about 22% with low soot production of around 20 mg/m³. The plasmatron was enclosed in a metallic housing that minimizes electromagnetic interference (EMI) radiation, which could adversely affect operation and control of the plasmatron. For on-board applications, a 250W power supply with full computer control of the power level, requiring minimal cooling, has been developed, for both 12 and 24 volt vehicle electrical systems. A compact high voltage transformer is utilized in this design. This version of the plasmatron was tested extensively on the bench, prior to installation on vehicles.



Figure 4. Gen H plasmatron developed at ARM.

Figure 4 shows the Gen-H Fuel Reformer which is ArvinMeritor's implementation of the MIT plasmatron .

HYDROGEN ASSISTED NO_x TRAP REGENERATION AT ARVINMERITOR

The objective of this testing was to determine the advantages of H₂ assisted NO_x trap regeneration [2] and to

establish the feasibility and effectiveness of H₂ assisted NO_x traps in a bus and light duty vehicle installation. Initially preliminary experiments were carried out in a test cell using simulated reformat bottled gas. Subsequently due to the promising results, tests using an actual plasmatron fuel reformer have been performed, both in a test cell and on board vehicles. Plasmatron diesel fuel reformer systems have been installed in a Ford F-250 truck to investigate light-duty applications, as well as in a Gillig transit bus, to test heavy-duty applications.

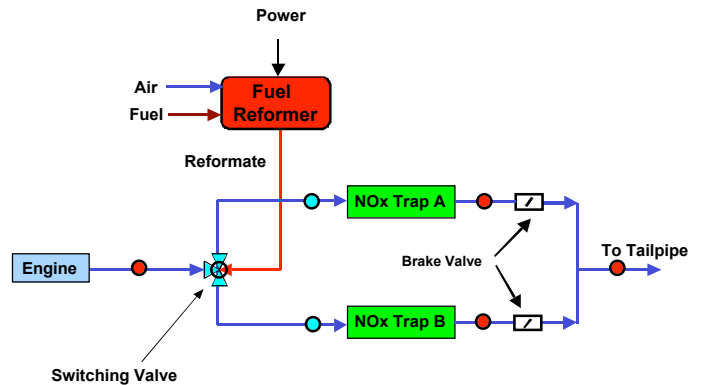


Figure 5. Test set-up for hydrogen assisted NO_x traps

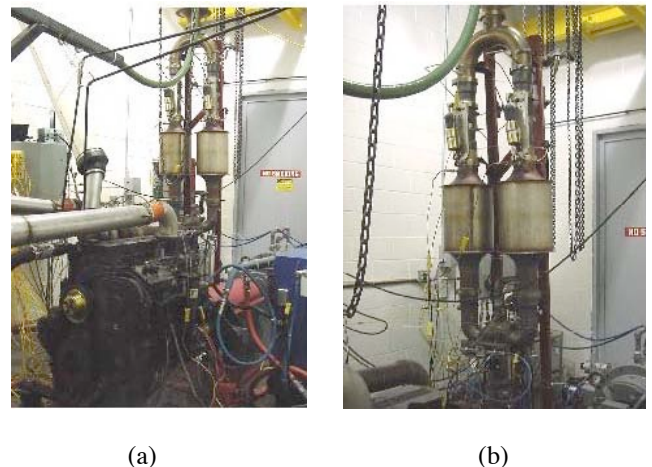


Figure 6. Test cell installation of hydrogen assisted NO_x traps: a) Cummins engine; b) dual leg (14 liter/leg) traps and switching valve

TEST CELL SETUP AND RESULTS

A schematic of the test cell NO_x trap system is shown in Figure 5. The system is a dual leg arrangement of NO_x traps, with a single valve that simultaneously switches the exhaust and reformat flows, so that while one leg is undergoing regeneration off-line, the other leg is adsorbing NO_x. A single plasmatron is used to feed hydrogen rich reformat to both traps. The regeneration of a NO_x adsorber requires a reducing atmosphere (zero oxygen). Due to the free oxygen in diesel exhaust, any leakage past the switching valve increases the required reformat flow since this oxygen must be consumed by reaction with the H₂ and CO in the presence of the precious metals on the NO_x adsorber surface in order to reach a reducing environment. Therefore zero exhaust leakage past the switching

valve is ideal. Flow bench tests of the switching valve and adsorber system indicated a 3% leakage rate. For the Cummins ISC 8.3L engine used in this testing, the available plasmatron reformat flow rate was marginal at a high engine exhaust flows with 3% leakage. An exhaust brake valve was added to each leg as indicated in the schematic. When the brake valve was closed on the regenerating leg the exhaust flow leakage was reduced to an acceptable 1%.

A photograph of the actual test cell setup at Analytical Engineering, Inc. (AEI) is shown in Figure 6. Extensive instrumentation was utilized including a chemi-luminescent NO_x analyzer, NO_x sensors, multiple thermocouples, and a V&F hydrogen analyzer. The fuel reformer, switching valve, and brake valves were all computer controlled. A MY2000 Cummins 8.3L engine was used in these tests. Zero sulfur diesel fuel was used in this testing to avoid sulfur poisoning of the traps. Also the engine oil used was a special low sulfur formulation for the same reason. Even with these measures some minor adsorption degradation was observed over the course of testing.

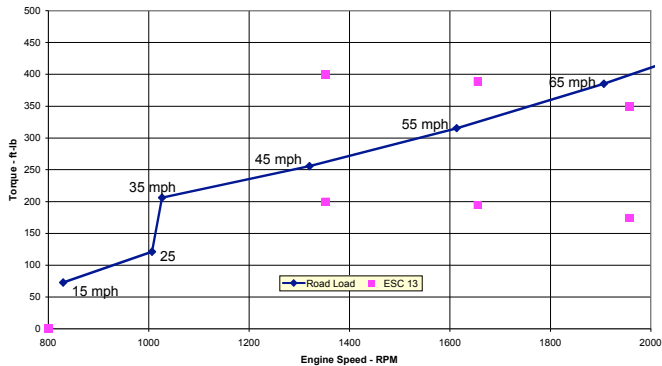


Figure 7. Bus Road Load vs ESC 13 mode

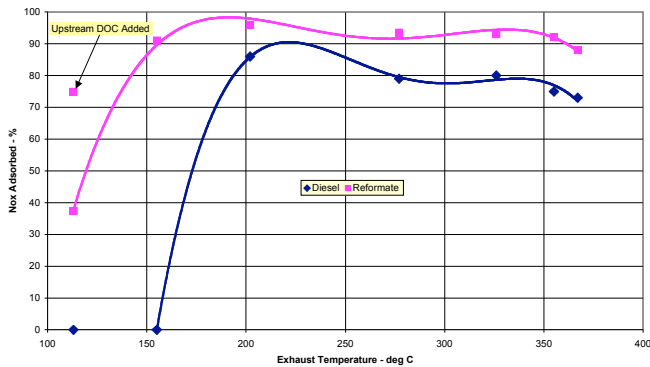


Figure 8. NO_x adsorption comparison. Bus Road Load, at same fuel penalty (reformate vs diesel)

Two sets of engine operating points were used in this testing: the European Stationary Cycle (ESC) 13 modes and a calculated Bus Road Load curve. Figure 7 compares the

operating points. The ESC 13 Mode test is a steady state mode weighted substitute for transient emissions testing. Since the NO_x adsorbers used in these tests were low temperature (barium based) adsorbers [3,4], only the ESC modes below 50% load were tested. The exhaust temperatures at the ESC modes above 50% load were too high (> 450 °C) for these traps to adsorb effectively. Due to the potential low temperature application of H₂ assisted NO_x trap regeneration, a series of calculated bus road load points (37K lb. GVW) were also tested. Below bus speeds of 45 mph, the road load points were at lighter loads with lower exhaust temperatures than the ESC points. All of the operating points were tested for NO_x regeneration using both reformat and diesel fuel injected into the exhaust as reductants for performance comparison.

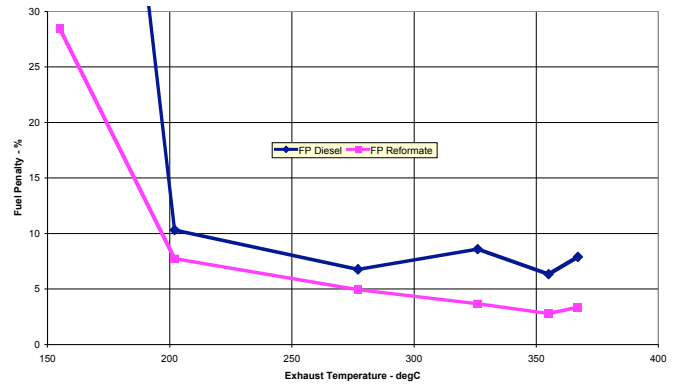


Figure 9. Fuel penalty for Bus Road Load, at same NO_x adsorption

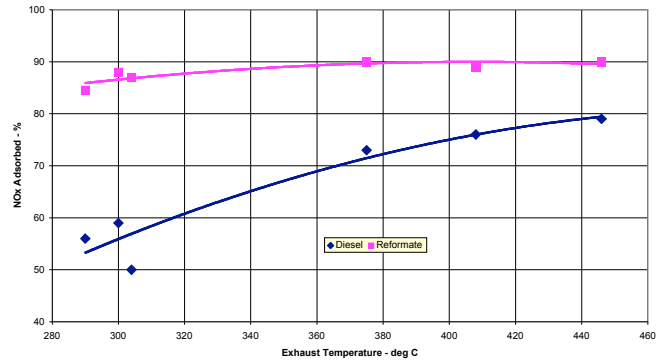


Figure 10. NO_x adsorption comparison. ESC Modes at same fuel penalty (reformate vs diesel)

Two comparisons of performance were tested: (1) %NO_x adsorbed at the same fuel used penalty, and (2) fuel penalty for the same NO_x adsorbed. These two comparisons are made for both the bus road load points and the tested ESC modes. Figures 8 – 11 show these results. All of the reformat regenerations were for a 5 second duration with the fuel reformer processing 0.8 g/s of fuel. The NO_x trap adsorption time was varied with load to keep the minimum instantaneous NO_x adsorption greater than 70%. For the diesel injection

regeneration at constant fuel penalty the total injected fuel quantity was kept at 4 g and the adsorption time was the same as the reformat case. For equivalent NO_x adsorption with diesel injection regeneration the injection rate was constant and the regeneration time varied as well as the adsorption time. Clearly reformat regeneration of NO_x traps is superior at all the operating points tested both in terms of %NO_x adsorbed at the same fuel penalty and the fuel penalty for equal NO_x adsorption.

The reformat regeneration advantage at low exhaust temperatures is especially obvious in the bus road load comparisons. Below 180°C the diesel injection regeneration falls from 70% adsorption to zero at 158°C. Reformat regeneration still achieves 90% NO_x adsorption at 158°C. At idle conditions with adsorber inlet temperature at 113°C reformat regeneration resulted in 38% NO_x adsorption. The addition of an oxidation catalyst upstream of the NO_x trap increased the NO_x adsorption to 75% at 113°C with reformat regeneration. Note that direct injection of diesel fuel into the exhaust for NO_x trap regeneration at these low temperatures is totally ineffective. In addition other testing with different NO_x trap formulations and simulated reformat has shown regenerations at exhaust temperatures as low as 80°C. The ESC modes show a 15 to 50% better NO_x adsorption at the same fuel penalty with reformat versus diesel regeneration. At the same NO_x adsorption the ESC modes show a 40 – 60% fuel penalty advantage of reformat versus diesel regeneration. These fuel penalty comparisons include only the fuel used for regeneration and do not account for required parasitic loads such as electrical and air pumping power. However at most engine operating conditions, these parasitic loads account for a fuel penalty of 0.5%. Only at idle and very light loads are these parasitics significant. Even then the maximum parasitic fuel penalty is about 5%.

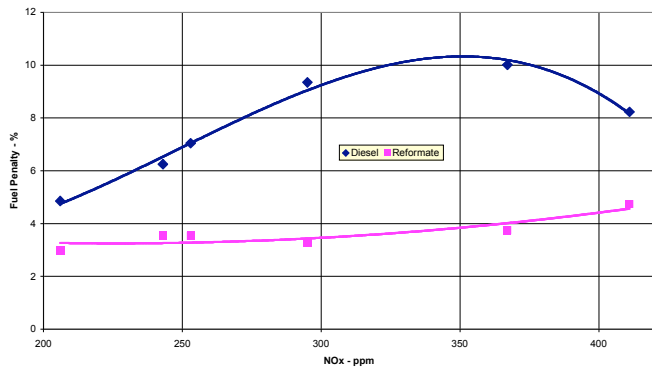


Figure 11. Fuel penalty for ECS Modes, at same NO_x adsorption

In addition to the fuel penalty advantage, reformat regenerations of NO_x traps produce a dramatic reduction in hydrocarbon slip as shown in Figure 12. For equivalent NO_x adsorption, reformat regenerations reduce hydrocarbon slip through the adsorbers by 90–95% at exhaust temperatures of

275°C and above. Below 275°C exhaust temperatures the reduction in HC slip is still 65% or more.

Additional testing completed after this work indicates that by optimizing the regeneration time and reformat flow rates the reformat NO_x trap regeneration fuel penalties reported here can be lowered another 50% from an average of 4% fuel penalty to 2% fuel penalty.

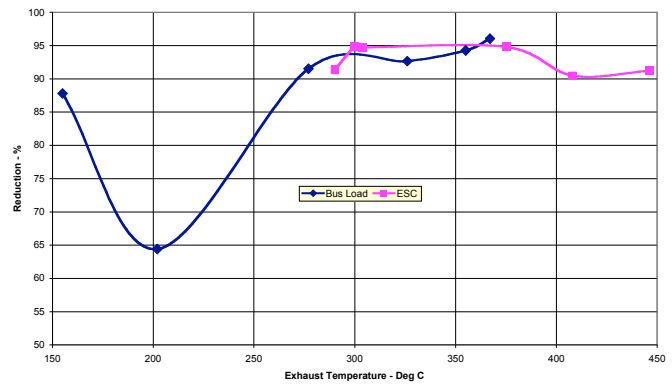


Figure 12. Reduction of hydrocarbon slip when using reformat vs diesel for NO_x trap regeneration.

VEHICLE INSTALLATION AND RESULTS

The H₂ assisted NO_x trap system installed on a Ford F250 pickup truck, with a 7.3L Powerstroke engine, is illustrated in Figure 13. This is a single leg with bypass system using 14 liters of NO_x adsorber with electrically actuated brake valves to switch flow legs. The reformer and brake valves are computer controlled and NO_x concentrations are measured with Horiba NO_x sensors. With reformat regeneration of the NO_x trap, this system is capable of 70% NO_x adsorption.

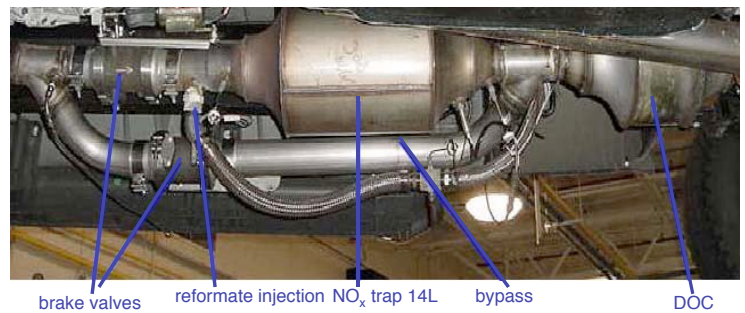


Figure 13. F250 hydrogen assisted NO_x trap installation

The Gillig transit bus installation is shown in Figures 14 and 15. The bus uses a dual leg system with 21 liter of NO_x adsorber per leg. There are separate pneumatically actuated switching valves for the exhaust flow and reformat flow. A single Gen-H plasmatron fuel reformer is used. A PC, utilizing LabView based software, controls the regeneration including the fuel reformer air-fuel ratio and the switching of the exhaust

and reformat flows on a time based cycle. NO_x emissions are measured with NGK NO_x sensors. The engine in this bus is a MY1994 Cummins C8.3L. Due to the high accessory loads, engine out NO_x concentrations as high as 800-900 ppm are observed. This system is capable of NO_x reductions of 80-90% (without optimization).



Figure 14. Hydrogen assisted NO_x trap installation in a bus

fuel reformer box



NO_x trap: 21L/leg

Figure 15 Picture of part of plasmatron diesel reformer system in the back of the bus

RESULTS SUMMARY

- NO_x trap regeneration fuel penalty reductions of roughly 50% versus diesel injection were achieved
- Idle operation NO_x trap regenerations achieved
- Hydrocarbon slip during regeneration reduced by 90%

- Dual leg NO_x trap system installed and operating on a transit bus: 80-90% NO_x reduction
- Single leg bypass NO_x trap system installed and operating on a Ford F250 truck: 70% NO_x reduction

FUTURE EFFORTS

- Investigate potential advantages of reformat desulfation of NO_x traps: Preliminary tests indicate 400°C desulfations are possible.
- Test other NO_x trap formulations: Improve both high and low temperature performance with reformat regeneration
- Develop the ArvinMeritor fuel reformer into a mature product

NOMENCLATURE

Reformat – the gas mixture resulting from the partial oxidation of fuel

O/C – ratio of oxygen atoms to carbon atoms in the reformer air-fuel mixture prior to processing

NO_x – symbol for the variable mixture of NO and NO₂ present in engine exhaust

Fuel Penalty – ratio of fuel used for NO_x trap regeneration to the fuel used by the engine over the full adsorption/regeneration cycle

Hydrocarbon slip – hydrocarbon species that flow through the NO_x adsorber during regeneration without reacting

ACKNOWLEDGMENTS

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